Wet Strength Paper

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Bachelor's thesis

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ABSTRACT

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In this final thesis, the subject is to study the wet strength of paper.

According to the topic, it was started by analyzing the dry strength of fiber networks, and contributes to paper web. Fiber held together mainly by two kinds of forces-van der Waals forces and hydrogen bonds, which give paper strength properties. But when paper gets re-wetted, the strength will lose a lot. In order to get wet strength, wet strength resins are needed to be added to pulp.

The wet strength resins which are most likely used are PAE, UF, MF, DAS and PEI. But if the wet strength of the paper grade is too high, there will be a big problem during re-pulping process. So, it is also essential to study how to de-gradate the paper with high wet strength.

After the study of theory work, experiment was also made to examine the wet strength of certain paper samples. Four types of paper are used in the laboratory works, they are kraft paper, label base paper, tape base paper and wall paper. Basic properties of paper were measured at first, then followed by dry tensile strength and wet tensile strength measurement. The whole experiment was based on ISO Standard.

As the results shows, the wet strength retention of label base paper is the highest. Tape base paper also has a high paper tensile strength and wet strength retention. Although the paper basis weight has a low value in both paper types, the protection and strong connection produced by wet strength resins are rather obvious high.

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Key words: wet strength, PAE, UF, MF, DAS, PEI, degradation of PAE

Contents

ABBREVATION

UF	Urea Formaldehyde
MF	Melamine Formaldehyde
PAE	Polyamino Polyamide Epichlorohydrin
PEI	Polyethyleneimine
DAS	Dialdehyde Starch
HYP	High Yield Pulp Fibers
SBKP	Softwood Bleached Kraft Pulp Fibers
TMM	Trimethylol melamine
MAAC	Maleic anhydride-acylated chitosan
PAM	Polyacrylamides
PVAm	Polyvinylamines

1   INTRODUCTION

In today's paper and paperboard manufacturing, chemicals like fillers, thickeners, sizing agents, defoamers, retention aids and wet and dry strength resins are widely applied.

Wet-strength resins are added to the stock when manufacturing paper or paper board. Paper merely remains 3 to 5% of its dry strength after fully wetted, which is commonly thought to be the help of friction between fibers. But, wet-strength resins impart the paper with a 10 to 50% of its dry strength after wetted. This property is used in many paper and paperboard grades, for example kitchen towel paper, sanitary tissue, coffee filters and some packages.(Herbert H. Espy,1997)

The most important raw material world widely for paper and paper board making is recovered paper. The industry needs to balance the supply of virgin and recycled fiber, which depends on the requirement of fulfill the present economy and environment.

Generally speaking, it is easy to reuse paper and board. But recycling and repulping wet-strength paper is an exception. Its recycling consumes more energy in repulping as well as dedicated chemical conditions or special treatment. (Ulrch Höke and Samuel Schabel, 2010,88）

2   BASICS OF Fiber STRENGTH

2.1 Structure of wood fiber

Wood fiber is a biodegradable natural material from a renewable natural source. The major constituents of wood fibers are cellulose, hemicellulose, lignin and extractives. Each of these components contributes to fiber properties.

As figure 1 shows, the fiber cell wall is made up of layers. The layers are different from one another in formation history, structure and chemical composition. The structure of cell wall can be divided into primary wall, the secondary wall and the middle lamella. The middle lamella can hold neighboring fibers together because of high proportion of amorphous materials. The secondary wall is built of microfibrils embedded in a structure of lignin and hemicellulose. The secondary cell wall consists of three parts, labeled S_1, S_2, S_3 from the outer to the inner layer. (Kaj Henricson, 2004)

Wood fiber structure

W = tubercular core
S_3 = secondary wall inner layer (tertiary wall)

S_2 = secondary wall middle layer

S_1 = secondary wall outer layer

P = primary wall

M = intermediate lamella

FIBER WIDTH ~ 30 μm

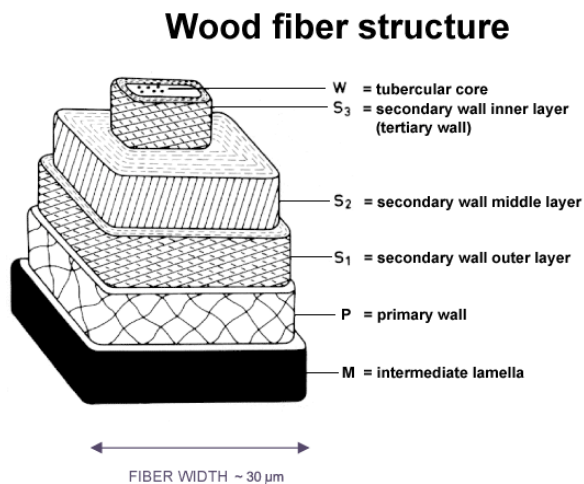Figure 1. Wood fiber structure (knowpap, fiber structure)

The thickness of primary cell wall is approximately 0.03-1.0 μm, and it contains a high percentage of lignin. The secondary cell wall consists of three layers, S_1 and S_3 layers are thin, at 0.1-0.3 μm, while the thickness of S_2 is about 1-5 μm. The fibrils of secondary cell wall layers are wound helically around the fiber axis, while those of the primary

wall are randomly oriented. And the middle layer of secondary cell wall (S2) is responsible for the strength properties of individual fibers. . (Lorraine C. Vander Wielen)

2.2 Cellulose, hemicellulose and lignin

Cellulose $(C_6H_{10}O_5)_n$ is the major component of papermaking fibers, it contributes 40-50% of the wood's dry weight. As figure 2 shows, the chemical structure of cellulose polymers are long linear chains of D-glucose linked by β-1,4-glycosidic bonds of glucose. The degree of polymerization of cellulose ranges from over 10000 to 1000. The highest polymerization is in natural wood, and lowest is in bleached kraft pulp. The hydroxyl groups on linear cellulose chains can form hydrogen bonding networks within and between fibers which give paper strength property. (Lorraine C. Vander Wielen)
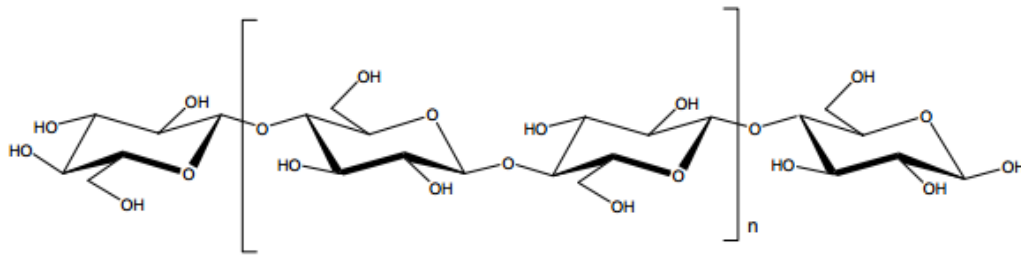

Figure 2. The structure of cellulose (β-1,4-D-glucopyranose) (Gellerstedt, G 1996)

Hemicellulose contributes 20%-30% of the dry weight of wood. Unlike cellulose, hemicellulose has lower polymerization; the degrees of polymerization are approximately 100-200. The side chains of hemicellulose polymers are monosaccharides. The structure of hemicellulose cause it is susceptible to chemical attack. Hemicelluloses are easier to degradation during chemical pulping. In comparison, chemical pulps contain a lower proportion of hemicellulose than mechanical pulps.(Retulainen, E: Niskanen, K; Nilsen, N, 1998)

Lignin is the "glue" that combines the tree together. In pulping process, it is important to remove lignin. The secondary fiber wall contains 70% of the lignin but the concentra-

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tions are lower. It is found that the highest concentration of lignin is in the middle lamella. (Gellerstedt, G 1996)

2.3 Basic mechanism of inter fiber strength

Strength of paper depends on strength of bonds between fibers, individual fiber and distribution of fibers and bonds (formation).

In a paper sheet, individual fibers are held together by two kinds of forces--van der Waals coupling forces and hydrogen bonds, which providing paper with the mechanical and essential structural strength. Normally, the strength of fiber networks are arising from inter-fiber bonding---the strength of individual bonds and all the bonds within the network. The mechanical properties for most of the paper grades are influenced by the area of bonds and the strength of the bonds. Bonding has effect on both the development of structure and the final structure of the paper web, then, affects the structure of paper.

An inter-fiber bond can be defined as the zone where two fibers are so close to each other that molecular entanglement or chemical bonding can occur. Bonds hold fibers together and therefore contribute to the internal cohesion of paper. Inter-fiber bonding is essential to sheet strength. (Vainio, A., Paulapuro, H., 2007)

Inter-fiber bonding strength is especially important when using low-cost high yield pulp fibers (HYP) together with softwood bleached kraft pulp fibers (SBKP) in making traditional wood free paper products.(Dongbo Yan & Kecheng Li,2012)

Except the influence of mechanical properties of paper, fiber bonds can also affect electrical properties, optical properties, and dimensional properties.

2.3.1   The formation of inter-fiber bonds

Inter-fiber bonds formation during the papermaking process. At first, bonding happens through surface tension forces pulling fibers together when water is removed at wire section. The Campbell effect changes gradually to other types of bonding, so inter-fiber bonding happens during solid content increases. An estimate for the start of bonding can be measured by the elastic modulus of paper during drying: wet fibers have higher rigidity than wet bonds, so, the modulus must changes because of bond formation. (Otherwise the fibers would disintegrate into the solution). (Vainio, A., Paulapuro, H., 2007) In kraft pulp, the elastic modulus starts to increase significantly at 50 % solids content (Retulainen, E: Niskanen, K; Nilsen, N, 1998). During drying, pulp fibers shrink laterally, the difference between lateral and longitudinal shrinkage of fibers cause shear stresses in the bond area. The amount of shrinkage is affected by internal fibrillation and chemical composition of the fiber wall, which can influence swelling degree of the wet fiber wall. Shrinkage forces are largest at the outer area of the bond, and bond edges will take the load first when the system is loaded. Shrinkage stresses may cause deformations in bonded fiber segments (microcompressions) and generate axial compressive forces on the crossing fibers in freely dried sheets. The mechanical properties of the bonded segments can be modified by the fiber walls, stresses at bond area and microcompressions, so that the properties of freely dried fibers and bonded fibers will be different. Inter-fiber bonds can also have effect on mechanical properties of fibers.(Retulainen 1997; Retulainen, E: Niskanen, K; Nilsen, N, 1998).

The structure of inter-fiber bonds shows in figure 3 is influenced by beating, pressing and drying. Other important factors affecting bond structure include pulping procedure, fiber morphology, beating equipment and the mode of drying.

The final structure of a fiber-fiber bond of two chemical pulp fibers is a combination of S_1-S_1, S_1-S_2 or S_2-S_2 layers. Flexible fibers can form wrap-around type of bonds and fibrils, and fines form bridges between fibers. On a microscopic scale, fibrils also form

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entanglements (Uesaka 1984). An amorphous bonding layer is formed between the S_1 layer of two beaten fibers by external fibrils, and probably polymer chains as well, this theory was studied by Nanko and Ohsawa (1989). The more beaten the fibers are, the thicker the bonding layer and the better the contact between two fibers will be, partly because of the increased amount of fines.
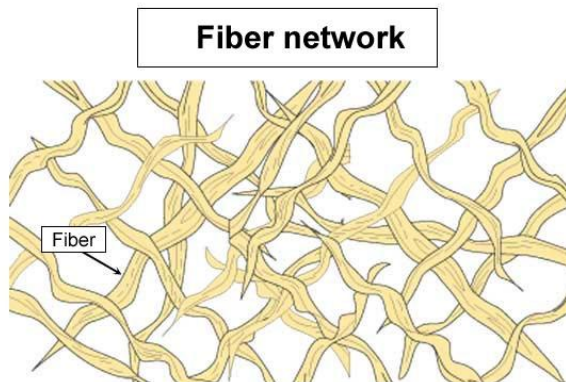

Figure 3. Fiber network (Knowpap, Inter fiber bonds) (Vainio, A., Paulapuro, H., 2007)

2.3.2 Chemical characterizes of bond

The adhesion between fibers is mainly the same as the cohesion within fibers, and hydrogen bonds are the basic link between them. Hydroxyl groups are all are bonded, so there is no free hydroxyl group in paper. And a certain amount of fiber's hydroxyl groups (at least at its surface) are bonded with water molecules.

Fiber adhesion is also affected by other factors except hydrogen bonding. Van Der Waals coupling forces are the most important one. Van Der Waals coupling forces are weaker than hydrogen bonds, but their effect can even be extended further, not like hydrogen bonds which limited in a certain direction. But Van Der Waals forces might have an even greater influence in fiber bonding than above supposed. The reason is that wet web cohesion is primarily caused by Van Der Waals forces.(Knowpap)

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2.4 Fiber Segment Activation

In a network, fibers also have activation as one of the relevant properties. It means that the fiber can be modified into active components of network where originally curly，kinky or other deformed fiber segments, unable to carry load in the network(Fig. 4). Activation of the fiber network occurs during drying. At bonded areas, lateral shrinkage of fibers is transmitted to axial shrinkage in the neighboring area. If this shrinkage is restrained, the free fiber segments will remove their slackness because of drying under stress. Both the segments and bonded areas are capable of bearing load when the segments are activated, and axial elastic modulus of fibers increases. In this way can also leads to further increment of the drying stress. Shrinkage of fibers and inter-fiber bonding are prerequisites for activation. The amount of drying stress needed to activate free segments depends on the fibers (Retulainen 1997).
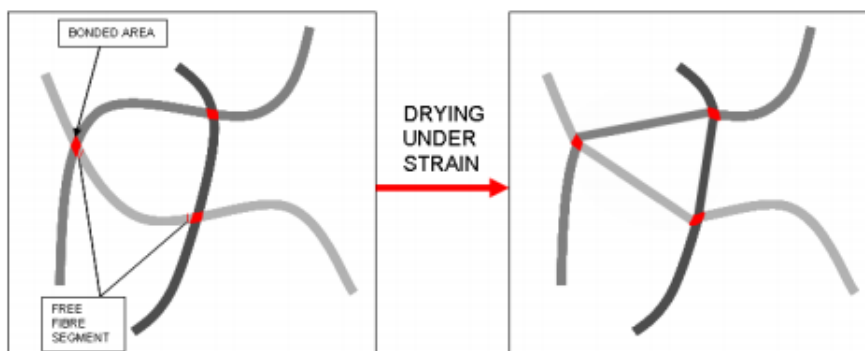
 Figure.4. A schematic illustration of activation. (Vainio, A., Paulapuro, H., 2007)

Activation in bonded segments can rearrange the lamellae and fibrils thus balances larger stress concentrations at the inside the fiber wall and fiber interfaces. The whole fibers have the capability of bearing load more evenly. Activation also may increase the order of cellulose and hemicelluloses and decrease the fibril angle except to make the segment straighter and fibrils more capable of bearing load. (Retulainen 1997).

Activation takes place during drying, and as drying shrinkage is restricted, and the fiber network is unable to contract and shrink, the level of activation becomes higher (Retulainen 1997; Tanaka, A., Hiltunen, E., Kettunen, H., Niskanen, K. 2001). The increase in the elastic modulus of paper can be influenced by straightening of initially slack free fiber segments (Htun 1980). Increasing drying stress will lead to the tensile properties of paper are generally improved. Activation can be improved by total fiber length and maximizing the bonded area.

2.5 The influence to strength of refining

Refining have influence on fiber structures in many different ways. When it comes to the refining effects on fibers, usually means the difference between refined fibers and unrefined fibers. The influence will always vary a lot from one fiber to another. Some fibers have a very severe treatment, but others may almost entirely avoid refining. The basic refining influences on individual fibers are as follows:

2.5.1 Refining effects on fibers

- Primary fiber wall removal

- External fibrillation

- Internal fibrillation

- Fiber cutting

- Creation of new fines and fiber surface

- Dissolution of fiber wall partly and increase fiber conformability

As to the basic effects of refining, the removal of the primary wall will create opportunities for the happening of other refining effects. In order to facilitate contact formation with other fibers, it is important to get more flexible, plastic and swelling fibers from internal fibrillation. As to the build-up of strong fiber bonds at the fiber contact points, external fibrillation and dissolution of fiber component substances are needed. As it is

known that all these basic effects are present in all types of refining processes. (Knowpap)

2.5.2   Refining effects on paper strength properties

In refining process, the fiber bonding area will increase due to fiber surface fibrillation. We can get more flexible fibers when fiber structures open and fibers are compressed. In this way, pulp and fiber bonding can produce paper structure through compress. Due to a better bonding ability, paper tensile strength and burst strength will improve in a same way.

Web wet strength can be probably caused by the compressing effect of refining on the web, refining will also enhance the original web wet strength. Fiber shrinkage tendency can also be influenced by the increasing of refining, thus the web shrinkage tendency during drying. During drying, fibers tend to shrink, also they connected with one and another, which causes micro-compressions. Fiber length will change only 1-2 % while fiber thickness up to 30 % in drying. When individual fibers which in the fiber network are shrinking, the whole fiber network will be shrinking because of this. In the end paper product, shrinkage will be shown as an growing elongation .(Knowpap,web,2014)

3 WET STRENGTH

3.1 Introduction

For the reason that the dry strength of different paper grades alters according to various basis weight, density, and the force between fibers, it is hard to make a definition for wet tensile strength. Thus it is usually indicated by the ratio between wet and dry strength.

Wet strength has two meaning. One is initial wet strength, standing for the strength of undried web on the paper machine. Another is re-wet strength, meaning the strength of finished paper product after fully rewetted by water. In this paper, if not specially pointed out, it means the second one.

The embedded water molecules increase the distance between the individual cellulosic fibers, so that a large part of the strength is lost. The strength of the paper is then only about at most 10% of the dry strength of the paper. This percentage somehow is commonly thought to be the strength of friction caused between the residual celluloses. (Salmen. N.L,1985, 475-483; Bsck E.L, 1973, 505-530)

Special wet strength additives are the only thing that can achieve wet strength to paper. The wet strength agent may be added, usually as suspension, but can also be the surface sizing or coating. By these means, resins can be used widely under cationic, anionic or neutral conditions. A majority of wet strength resins can only take effect after curing the paper therefore linking a complex fibers network, which partially surrounds the fibers and connects them with agents. The rate of this reaction relies largely on the pH and temperature, the reaction is complete after a several days to two weeks. (Vladimir Grigoriev, Chen Lu, Scott Rosencrance, 2012)

3.2　Wet-strength resins

If paper contact with water, hydrogen bonds between fibers will be broken and replaced with bonds to water. In this way, paper will lose the most of its mechanical strength. The strength of a normal paper sheet after rewetted is low, commonly remains 4 - 10% of its dry strength. Wet strength agents may be added to the pulp to protect the fiber-fiber bonds and increase the wet strength. The most commonly used agents are resins. There are two ways to enhance paper wet strength. One is protect mechanism, which means that the resins form a protective network around the fibers and then prevent bonds from break. Another is enhancement mechanism, the wet strength increased because of wet strength agents can react with chemical groups and form covalent bonds which enhance the strength of the fiber network. In addition, wet strength resins can also stabilizing the network because of the resin can penetrate and close the pores in the fibers (Fellers and Norman 1998; Bates et al. 1999).

3.2.1　Category of wet-strength chemicals

UF

1. **General:**

   In the very early time of making wet strength paper is warming paper till a high temperature or saturating paper into diluted sulfuric acid to achieve parchment. Later, in the experiment it was found that paper treated with formaldehyde got a raise of wet strength. However, formaldehyde is toxic for human. What was also found was that the low PH of it would make paper brittle. The product – dime-

thylolurea from reaction of urea and formaldehyde would impart paper wet strength property. Again however, because of its water solubility instead of adhere to fibers. Even if it attached to fibers, fibers got easily swollen due to the sensitivity of hemicellulose, thus it cannot be an ideal wet end additive. Later, the attention altered to the exploit of polymers made of urea and formaldehyde. In this case, in the year of 1935, the initial non-aqueous resin was born from dimethylolurea. However, its non-aqueous property made it only suitable for coating.

The development for UF was the modification using sulfite or amino acid to generate a water-soluble, anionic polymer. Though having a low retention, it can stay on fibers with the help of aluminum ions, also work well with starch. Later on, modifying of UF (figure 5) with diethylenetriamine or other polyamines generated a urea-formaldehyde resin which can adhere on fibers.

Carboxymethyl on the polymer chains reacts with each other forming a three dimensional structure protecting the bonding among fibers.

It has a better effect with a higher molecular weight UF than a lower one.

Urea-formaldehyde (UF) resins are the main binders for wood composite boards, such as particleboards, fiber-boards, or hardwood plywood. (A.V.Pocius, 2002, 1039–1104). In the use of UF resins, water solubility, good adhesion, high curing rate, and low cost are the attractive properties. Their shortcomings are low water resistance and emission of formaldehyde because the amino-occurs is not very stable.

(Peep Christjansona, Tnis Pehkb, and Kadri Siimera, 2006, 55, 4, 212–225)
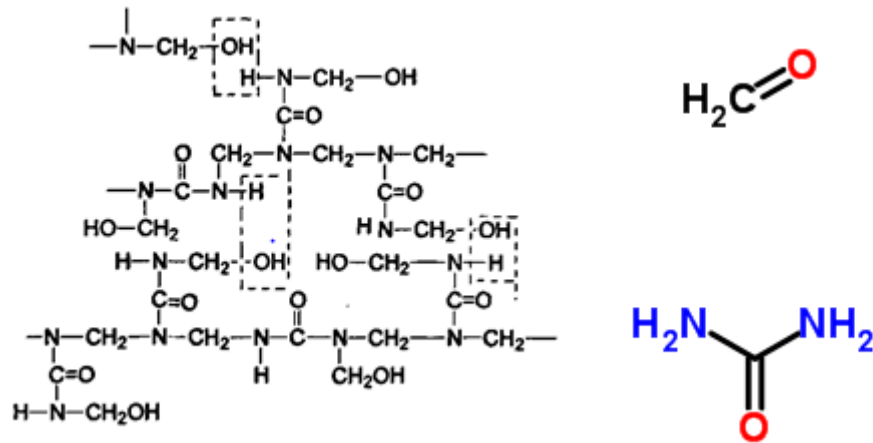

2. **Chemical Structure** :

Figure 5. The structure and crosslinking of UF Molecular Formula: $C_2H_6N_2O_2$

(chemspider,web, 2014, read26.01.2014

3. Properties of UF resins

- It has a very high tensile strength.

- Urea formaldehyde has the property of flexural modulus.

- Has the property of heat distortion temperature.

- Has the capacity of low water absorption.

- It has the property of mould shrinkage.

- Has a property of high surface hardness.

- It can be elongated at break

- It is volume resistance in nature.

  (Oureducation, web, 2014, Read 26.01.2014)

4. Usage of UF resins

Filtrate and dilute UF into around 1% solution before put into use. The amount should be measured as 0.5-3% of the dry wood mass. Make sure the PH stays between 4- 4.5 through the whole paper making process. It is usually added in position of fan pump.

And when using cationic UF, rosin and alum must finish the reaction before adding UF, otherwise UF resin will react with rosin thus generating a compound of foam. When using anionic UF resins, aluminum sulfate should be added to catalyze the solidification. No matter the consistency of UF, when PH is lower than 6, curing gets faster.

5. **Application**

Often used in paper grades as sack paper, liner board, corrugated board, paper made of ground pulp, wrinkled tissue, label paper and paper bag.

MF

1. **General:**

Melamine Resins are hard, thermosetting resin materials made from melamine and formaldehyde by polycondensation. See in Figure 6. It is the second wet strength resin put into production, which was first used in paper industry in 1944.
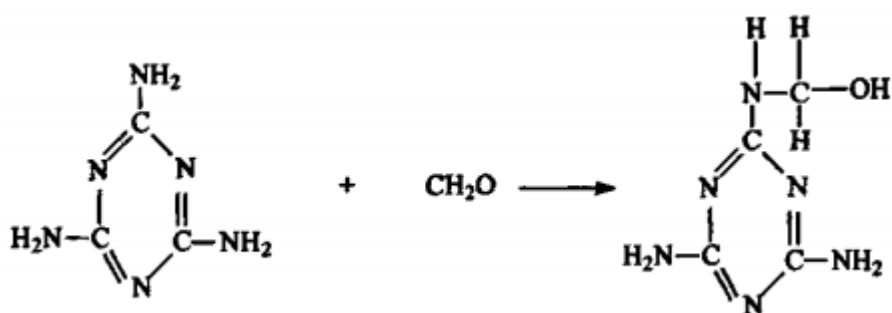

Figure 6. Forming of MF (Yunhong Chang, Research on Modification of PAE Wet-strengthening Agent and its Mechanism of Application，2007, 6)

Altering the proportion of melamine and formaldehyde will result in the product of methylol derivatives from monohydroxy to hexamethylol melamine. At first,

trimethylol melamine (TMM) was considered to be the most effective. However due to the tendency of crystallization of monomer of TMM, it's hard to handle, for a large majority of the commercial wet strength resins are formed by two or more than two monomers to get an easy-handling stock.

In the process of composing the wet strength, there are a number of reactions. Yet, the key reactions are the forming of ether bond and methylene which can be seen in Figure 7.
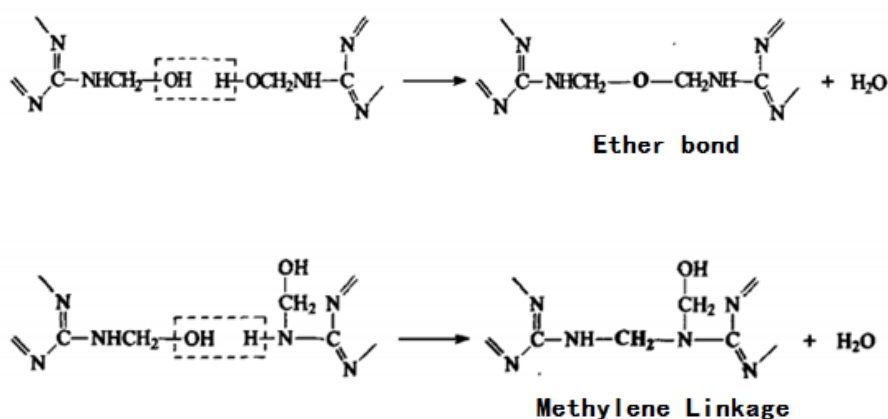

Ether bond

Methylene Linkage

Figure 7. The key reaction of forming bonds (Yunhong Chang, Research on Modification of PAE Wet-strengthening Agent and its Mechanism of Application，2007, 6)

High temperature and low PH will accelerate cross linking reaction. As the initial experiment indicated that water solution of TMM imparted paper with good wet strength, yet costly and hard to slaking thus cannot compete with UM resins. The reaction between TMM aqueous -solution and hydrochloric acid generates water soluble salt which after poly-condensation creates latex particles that can adhere to fibers effortlessly.

Despite the common positive view of trimethylol products, the product via the two steps method by adding excess formaldehyde into the TMM latex got better results. In the later aging period of one step method adopting the easy way to adjust acid amount can get the same product.

The paper having wet strengthened by MF resins will only work after heating and drying. Based on reliable experiments done by Robert Bates, Gary K Robinson, David J Hardman, Harvey J Branton(1996), the mechanism of this wet strengthening is the hydroxymethyl on one polymer chain reacting with the hydrogen of nitrogen on the other polymer chain forming cross linking. This is similar to UF resins mechanism. The dimensional net polymer is also water-insoluble, meaning cross linking creating wet strength. Other evidence of cross linking reaction is MF raised paper dry and wet strength with the same extend. (Marek Gorzynski, Andreas Pingel, 1997) Owing to more cross linkage resulting from more active radicals of MF resins, thus adding the same amount, MF resins works better and longer than UF resins. Nevertheless, UF resins are still cheaper and can be solidified in normal temperature. MF is the same with UF which works better in acid papermaking. They together stayed to be dominant till the 60s.The drawbacks of MF are bad working environment to people, corroding equipment and broke hard to handle.
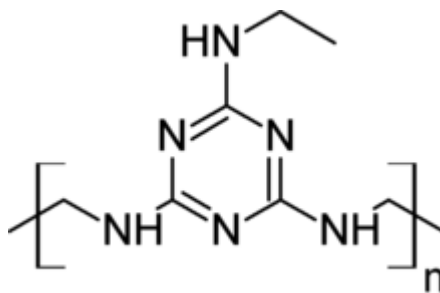
2. **Chemical Structure:**

Figure 8. The structure of MF (Wikipedia, web, 2014)

3. **Properties**

MF is white, tasteless, odorless and has great chemical and heat resistance. Melamine formaldehyde is a thermosetting plastic which cannot be melted. It is stain-resistant and resistant to strong solvents and water.

Melamine formaldehyde is affected by alkalis and concentrated acids--such as sulphuric acid (H_2SO_4) and oxalic acid ($H_2C_2O_4$). Melamine formaldehyde utensils are not microwave safe. They absorb radiation, which causes their polymer bonds to break down and percolate toxins into the food. Melamine formaldehyde ingestion leads to kidney failure.

(Ehow, web, 2014, read 26.01.2014)

4. **Usage:**

MF can only be put into pulp. The amount is 1- 5% of the dry wood mass. It should be added as close to headbox as possible to mix sufficiently. The PH condition should be 5- 6. Normally the curing is fast, however if not slaked enough, the paper product should be going through a solidifying process before storage.

Together with stearic ammonium compound, rosin sizing, oxidized starch can achieve a better wet strength.

PAE (PPE)

1. **General:**

In accordance with modern paper making technology, in1952, an ammonia-based multi-epichlorohydrin wet strength agent (polyethylenepolyamino ammonia epichlorohydrin) was exploited. In 1957, polyaminoamide-epichlorohydrin,

PAE also called PPE was produced and was invented by Alan Bull, David J. Hardman, Brian M. Stubbs, Paul J. Sallis (1960). It is not only a high efficient wet strength resin that can be used in neutral and alkaline condition, but can raise the paper wet strength without losing the flexibility of paper, especially suitable for medical paper. It has low foam in the paper making process, less re-yellowing and better re-pulpability.

2. **The mechanism of PAE:**

Because the attraction between the positive charge of PAE and negative charge in fiber, also the large number of resin adhered to the fiber surface, hydrogen bonding interacts between the hydroxyl on the wet strength resin and hydroxyl in fiber. In the mean time, sooner as the paper sheet is dried, the resin absorbed on fiber takes effect at the dryer surface and forms cross-links of a web structure to prevent or restrict the fiber swelling due to water absorption and protect the hydrogen bonds between fibers and impart paper with superb wet and dry strength.

3. **Properties of PAE:**

Viscosity: 20-70 mpa.s(30℃)

PH value: 3.5-6.5

Charge type: Cation

Dissolubility: Dissolve easily in cold water

4. **Formation process of PAE:**

The similar equipment as produce nylon-66 is used to manufacture polyamide. Dicarboxylic acid together with polyethylenepolyamino ammonia after condensation reaction generate water-borne linear polyamide oligomers. Then they joined together and copolymerized with epichlorohydrin. In this way, a series of products of alkylation of epichlorohydrin of secondary amines on polyamide are created. Among these products, it is extremely critical for the formation of epichlorohydrin-based three amine groups. It self-aminate and generates 3-azetidinol groups and chloride anion, whose structure imparts the resin with high reactivity and cation characteristics. 3-azetidinol groups (as in Figure 9) will have reaction with water, slowly forming a diol and losing reactivity.

$$HO \left[\begin{matrix} O \\ \| \\ C \end{matrix} -(CH_2)_4- \begin{matrix} O \\ \| \\ C \end{matrix} -NHCH_2CH_2NHCH_2CH_2NH \right]_{\overline{n}} H + \begin{matrix} CH_2-CH-CH_2 \\ \diagdown O \diagup \quad | \\ Cl \end{matrix} \xrightarrow[-HCl]{}$$

$$HO \left[\begin{matrix} O \\ \| \\ C \end{matrix} -(CH_2)_4- \begin{matrix} O \\ \| \\ C \end{matrix} -NHCH_2CH_2NCH_2CH_2NH \right]_{\overline{n}} H$$
$$\begin{matrix} | \\ CH_2-CH-CH_2 \\ \diagdown O \diagup \end{matrix}$$
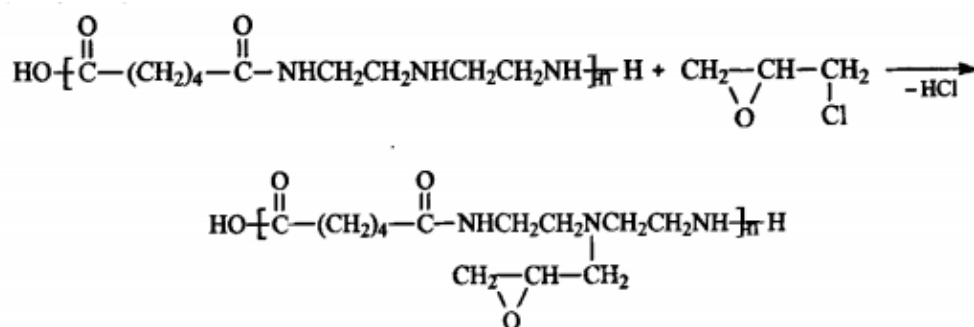
Figure 9. The self-amination and generation of 3-azetidinol groups and chloride anion
(Yunhong Chang, Research on Modification of PAE Wet-strengthening Agent and its Mechanism of Application，2007, 6)

In reaction 1shown in Figure 10, a majority of the amine groups of this precursor are secondary (R_2NH), but a few (<5%) of primary amine (RNH_2) end groups and branches are showed up, as well as carboxyl end groups. Epichlorohydrin reacts with primary and secondary amine groups to create, separately, secondary and tertiary aminochlorohydrins (Reactions 4 and 2). At neutral pH and at temperatures above ambient, the tertiary aminochlorohydrin group cyclize automati-

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cally to form 3-hydroxyazetidinium groups (Reaction 3). Reactivity and perma-
nent (pH independent) positive charge on the resin macromolecule is given by
these strained rings. Some of them, in turn, crosslink the macromolecules simul-
taneously with the alkylation and cyclization reactions during resin produce.
There is no intermediate in the chemically related polyamine–epichlorohydrin
resins, but the epichlorohydrin bridge polyamine units into a long-chain struc-
ture, also alkylating them and cyclizing as in the polyamide resins.

Polyamide formation:

$H_2NCH_2CH_2NHCH_2CH_2NH_2$ + $HOOC\text{-}R\text{-}COOH$ $\xrightarrow{\text{1}}$

H_2O + $H\text{-}[NHCN_2CH_2\text{-}NH\text{-}CH_2CH_2NH\text{-}CO\text{-}R\text{-}CO\text{-}]_n\text{-}OH$

(and $\text{-}NHCH_2CH_2\text{-}N\text{-}CO\text{-}R\text{-}CO\text{-}$ units in minor amount)
$|$
$CH_2CH_2NH_2$

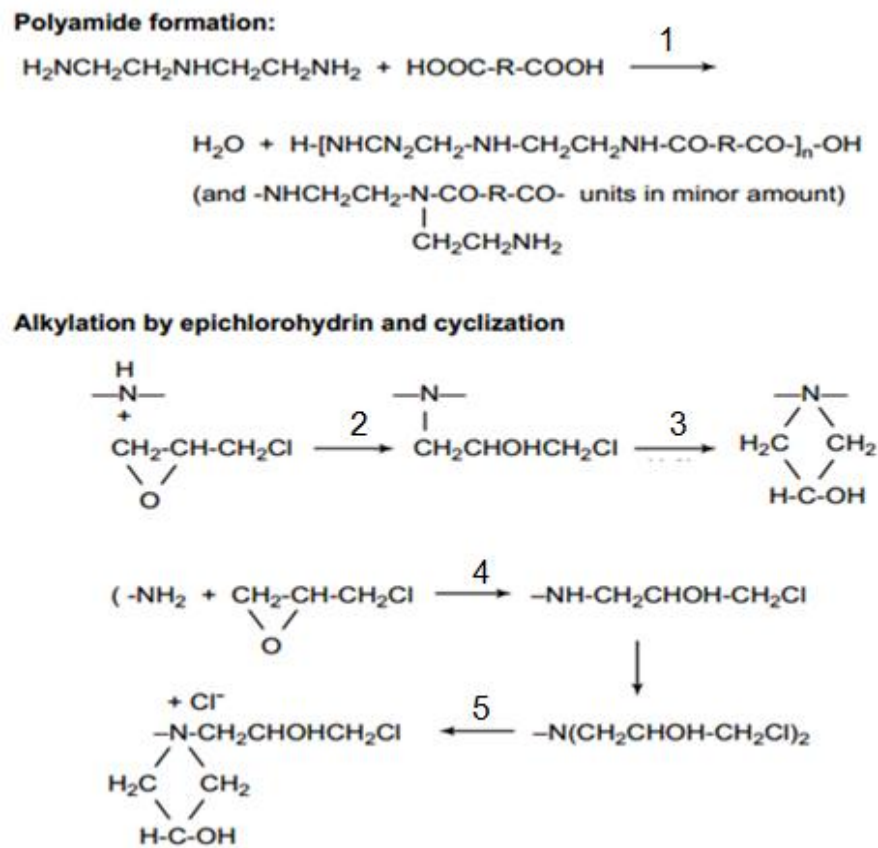**Alkylation by epichlorohydrin and cyclization**

Figure 10. The formation of PAE resins (Herberth Espy, The mechanism of wet
strength development in paper: a review, 1995, 5, read 24.01.2014)

5. **Usage:**

The resins are supplied as dilute aqueous solutions and are injected into the pa-
permaking stock shortly before it reaches the papermaking machine. 0.5-1% sol-

id resin (on dry fiber) can allow wet paper to retain over 30% of its dry strength while without the resin, the strength retention would be 0-2% when wet.

Due to its thermal-setting property, PAE –based paper needed to be heated and dried. And after being made, it should be put into a 105℃ dryer for slaking around 10- 30 minutes.

If the rosin is also needed in the paper making process, PAE should be kept away from the inject point of rosin for the reaction will happen between the anionic rosin and PAE generating foam and precipitation.

(R. Biddle, John Packer, X-Polymers-A-Industrial Resins, 10, read 22.01.2014)

The detailed difference of the three wet strength resins described above is shown in Table 1.

Table 1. Comparison of wet strength resins (John Christopher Roberts, Paper Chemistry, 1996, 111)

Resin	UF	MF	PAE
PH range	3.8-4.5	4-5.5	5.0-9.0
Best oprating PH	4.0	4.5	8.0
On-machine cure(%)	20	50-60	10-30
Time to 100% cure (weeks)	1-4	1-2	1-2
Point of addtition	Thick stock	Thick stock	Thcik or diluted
First pass retention(%)	35	60	80
Major precausution	Low PH	Sulphate level	Chlorine chemicals
Usualdrainage	No effect	Slower	Faster
Absorbency(without rewetters)	Fair	Poor	Good
Sheet brightness	Good	Fair	Fair
Storage(24℃)(weeks)	12-24	1	12
Relative cost	29	53	100

PEI

1. General

   Polyethyleneimine works efficient as a cationic wet strength agent. It is a polymer formed by ethyleneimine in the acidic condition. The forming is shown in Figure 11.
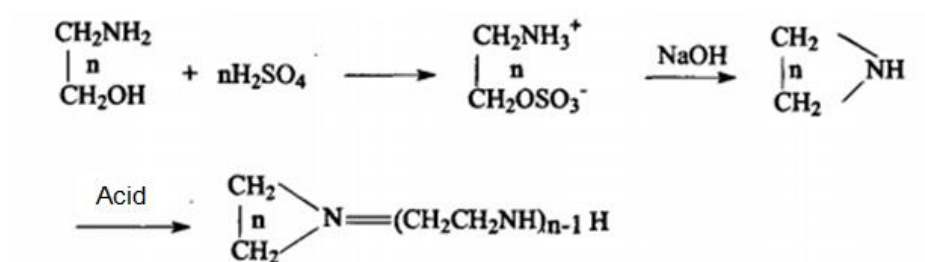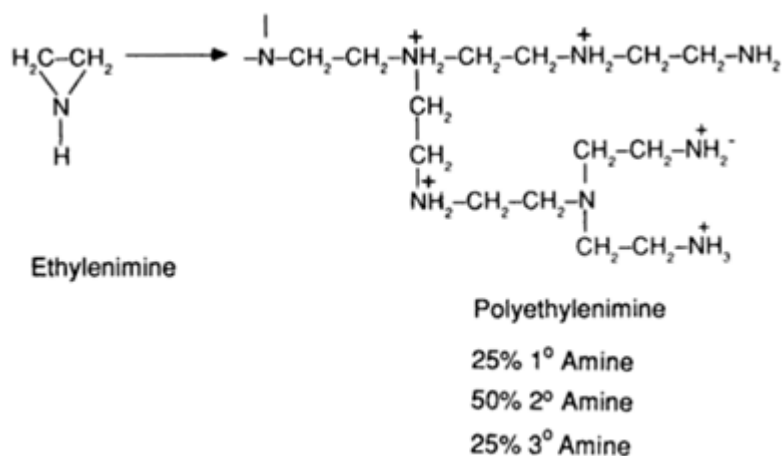
Figure 11. Preparation and chemical structure of polyethyleneimine (PEI)

(John Christopher Roberts, Paper Chemistry, 1996, 110)

2. Mechanism

The inter-atomic and stronger bonding is created without forming a homo or co-cross-linked networks. The ionic bond between cellulose carboxyl radicals and cationic parts in PEI is strong enough to tolerate every chance of the water inference with the polymer.

(John Christopher Roberts, Paper Chemistry, 1996, 110-112)

3. Usage

Because PEI is cationic in water solution hence it is easily to adhere onto fiber and can be used alone without the need of aluminum sulfate. The PH is range from 6 to 9 which gives better effect and the amount should be 1- 2% of dry wood mass into the head-box.

4. Properties

Different from UF and MF, PEI allows paper products getting a good wet strength after drying section in the paper machine meaning no need to storage for curing. Except for good wet strength effect, PEI can gather the microfibers and raises water drainagability letting paper machine run in a higher speed to around 5- 20%. However, the monomer of acetimidoyl is very active and toxic.

1. **General:**

    Chitosan is tested to have the potential to be used in papermaking, for both internal and surface applications. Several studies focus on the application of chitosan for improving the wet and dry strength of paper, other indicates the compatibility of chitosan with fibers and as a retention and drainage additive, or as dye fixative in producing colored paper. Its antibacterial and the film-forming ability are also studied for further applications in papermaking and paper finishing.

2. **Mechanism of Chitosan**

    Natural chitosan is similar as cellulose. Anhydroglucose units linked by an oxygen bond to form a linear molecular chain comprise the carbohydrate. The structure of chitosan is shown in Figure 12 .makes it possible to have strong bonding with fibers thus giving a dry and wet strength in paper making. (Raluca Nicu, Elena Bobu and Jacques Desbrieres, 2010)
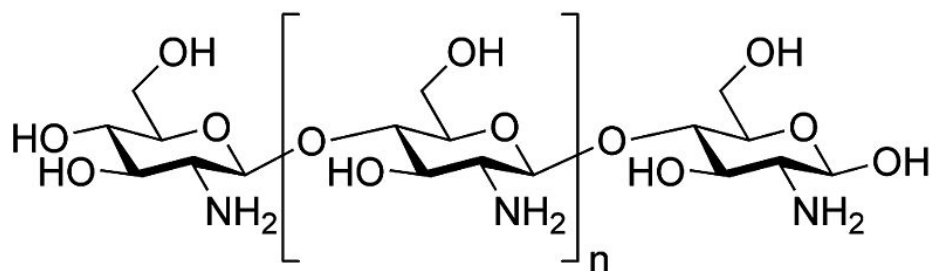
3. **Chemical Structure:**

    Figure 12. The structure of chitosan (Wikipedia, web, 2014)

1. **General**

    Maleic anhydride-acylated chitosan (MAAC) is used to improve the wet strength of paper. In the study of Zicheng Chen, Zhang Hui, Zhanqiang Song, Xueren Qian (2013), the results showed that the wet strength work most effectively at a pretreatment pH of 6 and that the wet strength index and the rate of wet to dry strength rose with higher pretreatment temperature and MAAC dose. A higher curing temperature was advantageous and improved paper with wet strength. MAAC could reach around 80% of the wet strength of PAE and showed its possibility as an alternative to PAE.

2. **The Mechanism of MAAC:**

    The mechanism is basically the same as natural chitosan, but the modified chitosan---MAAC with carboxylic groups has a better water solubility.

3. **Chemical Structure of MAAC:**

    The acylation reaction between chitosan and MA can take place under mild conditions. Nucleophilic substitution with the nucleophilicity of NH_2 is more active than that of the OH in the chitosan molecule. The chemical structure of MAAC is shown in Figure 13.
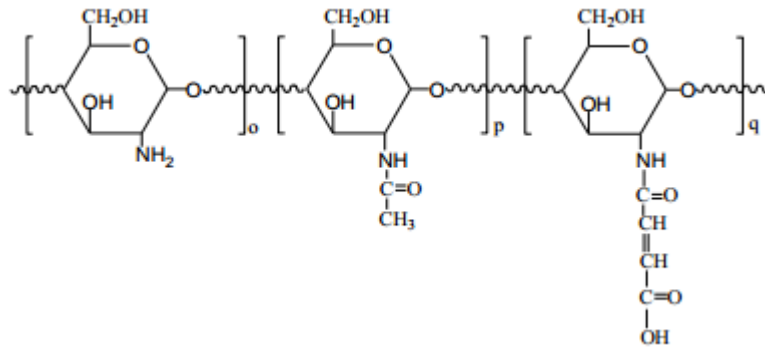
Figure 13.   The chemical structure of MAAC (o, p and q are percentage of the units)

(Zicheng et al., Preparation and application of maleic anhydride-acylated chitosan for wet strength improvement of paper, 2013, 4, read 25.01.2014)

DAS (Dialdehyde starch)

1. Introduction

   Dialdehyde starch is the product of starch having a selective oxidation reaction of vicinal hydroxyl group on 2 and 3 position of glucose group under the condition of periodic acid as in figure 14.
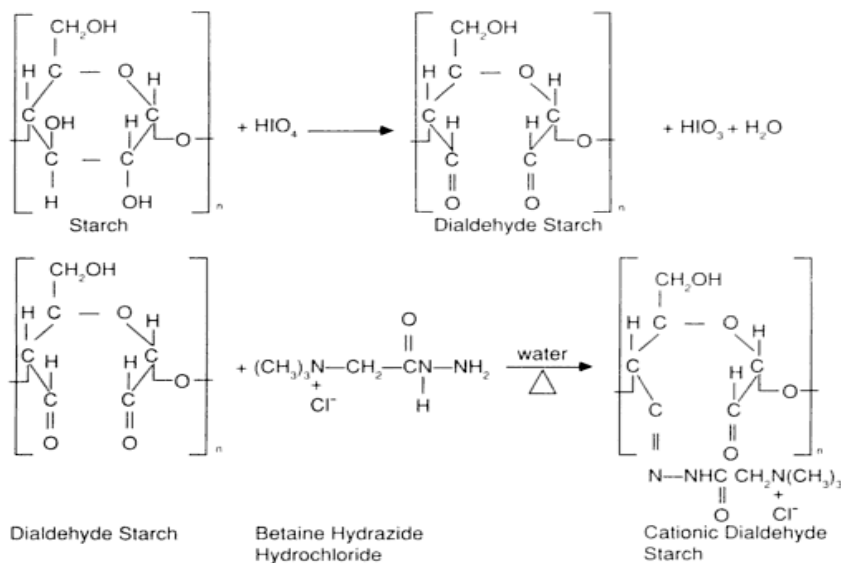
2. Structure:

Figure 14. The preparation of DAS and its modification into cationic product
(John Christopher Roberts, Paper Chemistry, 1996, 113)

3. Mechanism:

When disperse DAS into pulp, the aldehyde group reacts with the hydroxyl group on cellulose producing hemi-acetal group which keeps reacting with other hydroxyl group producing an acetal which combines with fibers.

The reaction between DAS and fibers is a dynamic equilibrium reaction which means once the paper rewetted, reversible reaction happens. Thus this agent is a temporary resin which makes the broke easily to be re-pulped.

4. Usage

Before adding in to pulp, it should be dispersed and emulsified completely. The PH condition should be 4.5- 5.5. 2- 5% of DAS on dry pulp can give satisfying wet strength and at the same time dry strength also get improved.

5. Application

Tissue paper, thin paper, towel paper.

(John Christopher Roberts, Paper Chemistry, 1996,112-114)

3.3   Basics of wet-strength paper

3.3.1   Grades

A wide range of paper materials is wet strengthened- the following is an indicative list:

- Facial tissue

- Consumer and industrial toweling

- Napkins, table cloths, and placemats

- Coffee filters, tea bags, butcher's wrap, and bread wrap

- Carrier board, lettuce boxes, raisin trays, and paper plates

- Industrial filters, laminating paper, and poster board

- Bleached bags, map paper, currency paper, and wallboard tape

(Raimo Alén, 2007, 96)

3.3.2 Problems in recycling

About 20% of the production in paper making is sorted as broke. For the sake of economic reasons, even though it is wet-strengthened paper, it is still needed to recycle and re-pulp. It has been found that under the same pH and temperature which help wet strength additives polymerization also can lead to the opposite – hydrolysis. So, to handle UF and MF resins, acidic PH and higher temperature, for example pH 3.5- 4.5 and 90 °C for 10-20min are needed to re-pulp. PAE resins should be put in alkaline condition (pH 10) with some hypochlorite, while re-pulping PEI in acid pH is easiest way. Temporary wet strength resins as DSS and glyoxal are effortless to re-pulp, whereas some polymer dispersion-based agents remain completely unable to re-pulp.
(Raimo Alén, 2007, 94)

3.4 Contaminants

In paper making, wet-strengthened agents are used in the amount of 0.2-5% based on dry wood mass. In label paper, the amount is often higher to reach the requirement. Except for the effectiveness of those agents on fibers, fines and small fiber parts as so-called contaminants also need to be taken into consideration, for they can work adversely. These anionic fragments attract cationic resins yet benefit nothing to paper structure. Hence, a part of wet strength resin is invalid to the contaminants. Though small quantity of these contaminants won't do much harm to the effect, in higher consistency, interfer-

ence should be take care of. Otherwise, blemishes, holes or deposits will happen in paper product.

Besides, precipitation of other agents can be caused by these contaminants, for instance, by the forming of calcium salts of organic acids, or starch-fat complex. To solve this problem, screening is adopted to separate the coarse dispersed fines before the paper-making or by discharging the circulating water into cleaning process.

Another choice is to fix the main low molecular weight dirt in the paper through most teilhydrophober cationic fixative, after that they can be moved out with the paper from the system. Due to the reduction of concentration of dissolved particles and suspended solids, the water is relieved.

Moreover, impurity is decreased effectively, especially with the existence of other additives. And the flocs with the fixed and suspended impurities get bridged by the electrostatic attraction and hydrogen bond formation. Thus a high charge density but low degree of polymerization fixatives is advantaged. Usually fixatives are cationic polymers, such as polyacrylamides (PAM), polyethyleneimines (PEI) or polyvinylamines (PVAm) , with an average molecular weight of up to 5,000 g / mol and a high charge density of up to 15 meq / g polymer at pH 7 . Typically the charge varies depending on pH.

(Alexander Erdtmann, Method for producing wet-strengthened papers, 2012)

4 DEGRADATION OF WET STRENGTH PAPER

Among the various wet strength agents, polyamideamine epicholrohydrin (PAE) remains to be the most popular additive for its efficiency in alkaline conditions. But, when papermakers are glad with this resin's property, another problem comes – how it can be repulped since the need for recycling. Only a minority of people noticed and concentrated on papers of repulping the wet strength paper.

Espy and Geist (1993) made a study on the comparison of the effect of persulfates ($S_2O_8^{2-}$, HSO_5^-) and sodium hypochlorite. It was showed that for bleached kraft papers, although in a slower speed, persulfates were benefit to the defiberation of PAE-based paper, which can be accelerated by raising the PH (PH=10) and temperature (about 70℃). And from report of the experimental results written by Fischer (1997) about the repulping of many PAE wet strengthened papers with inorganic oxidants (H_2O_2, $Na_2S_4O_8$ or $KHSO_5$). Influential factors like temperature, PH, time and reactant concentration were investigated as well as other parameters. Within all the experiments, a small part of iron (0.15 ppm) and copper (0.30 ppm) were added. Under these conditions, the premise was made by the author that secondary amides may go through an oxidation reaction by free radicals (C-N cleavage) and tertiary amines get oxidized to form amine oxides. For bleach paper, it was improved by the author that repulping with only NaOH at PH =11 was not satisfying. So did the $Na_2S_4O_8$ and $KHSO_5$. Nevertheless, with the help of oxidants (H_2O_2, $NA_2S_4O_8$, $KHSO_5$) of PH=7 at first place and later change into PH=11, repulping process went efficiently. Bhardwaj and Rajan (2004) tried different inorganic chemicals the repulping of bleached wet strength papers, for example NaOH, H_2SO_4, Na_2CO_3, $Al(SO_4)_3$, H_2O_2, $Ca(ClO)_2$. However the details of wet strength chemicals used in the test paper in the experiment were not mentioned. Gigac, J., Fiserrova, M. and Osvaldik, Z.(2005) reported NaClO was the most effective one among NaOH,

$Na_2S_4O_8$ and other products in the market during the repulping of tissue paper. NaOH was effective either under the experimental conditions.

Considering the usual dosage of reagents used for repulping from the work of the above authors, it can be concluded that the amount basically was from 1 to 10% (weight of reagents/weight of paper). And also there is no common standard method to assess the repulpability of wet strength papers.

In the experiment done by Eder, S., Wafa, N., Nathalie, M., Séverine, S.and Evelyne, M. (2013), they used four reagents such as NaOH, $K_2S_2O_8$, H_2SO_4 and H_2O_2. They studied the degradation of PAE-based paper with coating and without. In the study of uncoated paper, potassium persulfate worked most effectively in the condition with sodium hydroxide or without. With just hydrogen peroxide alone, PAE-based paper was partly degradated. Yet a promotion of result happened after the adding of sodium hydroxide creasing the production of radicals. Sulfuric acid didn't affect much of the degradation for close to 90% wet strength is still left. And as for the study of coated paper, persulfate still acted excellent, followed by the combination of sodium hydroxide and hydrogen peroxide. However treatments with sulfuric acid, sodium peroxide or hydrogen peroxide separately were not satisfying. And in the experiment of coated paper, with the same conditions but it got low effect than uncoated one due to the existence of coating layer may having side-reactions with the reagents.

(Eder et al., 2013, 529-540)

5 EXPERIMENT

5.1 Devices

Distance between one surface of a paper or board and the other, measured under an applied static load, using this test method. Measurement of the single sheet thickness or of the bulking thickness, according to the test requirements, by means of a precision micrometer showed in Picture 1.

A test piece of given dimensions is strained to break at a constant rate of elongation using a testing machine that automatically records both the tensile force and the elongation. From the recorded data, the tensile strength, the strain at break, the tensile energy absorption and the tensile stiffness are calculated.

The tensile-strength-testing apparatus shall be in accordance with ISO 1924-2 showed in Picture 2. It is capable of stretching a test piece of tissue paper or tissue product of given dimensions, at a constant rate of elongation of (50 ± 2) mm/min, and recording the tensile force as a function of elongation.

Picture 1. The thickness micrometer (Lorentzen& Wettre 250 989122)

Picture 2. The tensile strength tester

5.2   Process

5.2.1 Preparation

Four grades of paper in this test were prepared: Wall paper, tape base paper, label base paper, kraft paper. These papers were controlled under the condition of 23℃ and 50% RH for 24 hours according to ISO 187 standard.

For the preparation of dry and wet tensile strength test, 15 mm *140 mm paper strips were cut for each grade of 20 pieces of machine direction and 20 pieces of cross machine direction.

For wet strength test, for each paper grade, 10 machine direction strips and 10 cross machine direction strips were put into the two beakers separately with only the central part immersed into tap water and two edges were clipped without wetted(as in Figure 15). Treat under 23℃ for 1 hour.
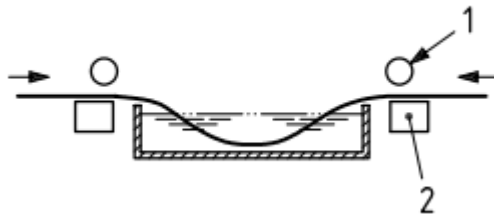

Figure 15. How the test strip is fixed when preparing wet tensile strength test. (ISO 187)

5.2.2 Thickness

Carry out the test in the standard atmospheric conditions in which the samples were conditioned. Place the micrometer on a horizontal vibration-free surface and place the test piece between the open pressure faces of the micrometer at a position at least 20 mm from any edge of the test piece. Permit the test piece to be held by the pressure face, by very carefully allowing the movable pressure face to move steadily and slowly, at a velocity less than 3 mm/s, towards the anvil so that any punching effect is avoided.

Record the micrometer reading at the end of a dwell time of 1 s to 2 s. Avoid imposing any manual stress on the test piece or micrometer while a reading is being made. Make only one measurement on the test piece.

Repeat the above procedure for the remaining test pieces.

5.2.3   Basis Weight

The basis weight of the paper grades according to ISO536 were calculated as the ratio of the weight and the surface area of the sample. The basis weight measurement for each paper grade was performed 10 times.

5.2.4   Dry Tensile Strength

One piece of paper strip was tested on the tensile testing machine (L& W tensile tester) at a time. Test was proceeding under ISO 1924 standard. Ensure that the testing machine is calibrated. Place the test piece in the clamps without straining it and so that any observable slack is eliminated. Avoid touching the test area between the clamps with the fingers. Align and tightly clamp the test piece and perform the test as in Figure 16, 17. 10 test pieces in each direction of machine direction and cross direction for each grade.

Clamping lines parallel to each other within an angle of 1°   Centre-line of test piece perpendicular to clamping line within an angle of 1°   Tensile force parallel to the test piece centre-line within an angle of 1°
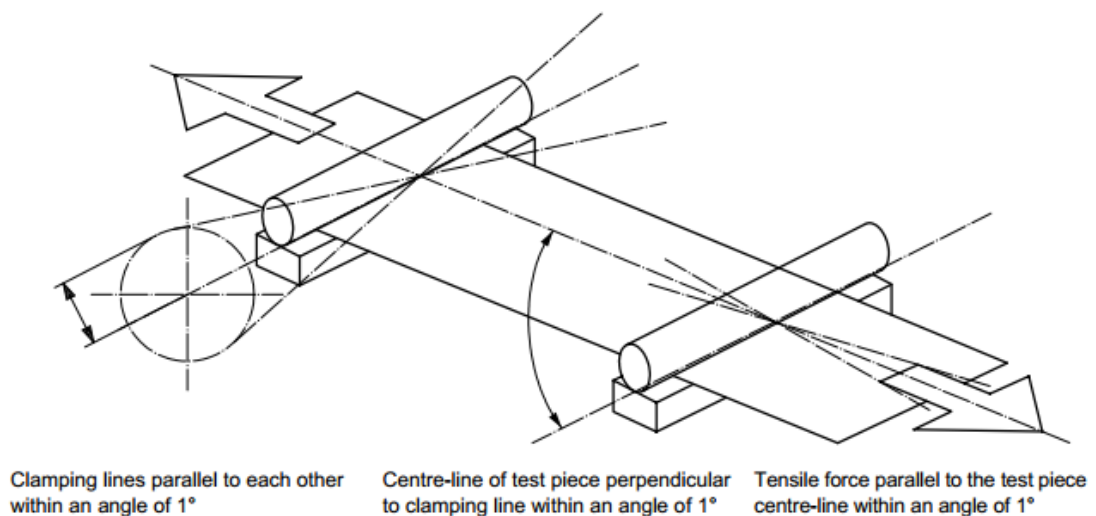
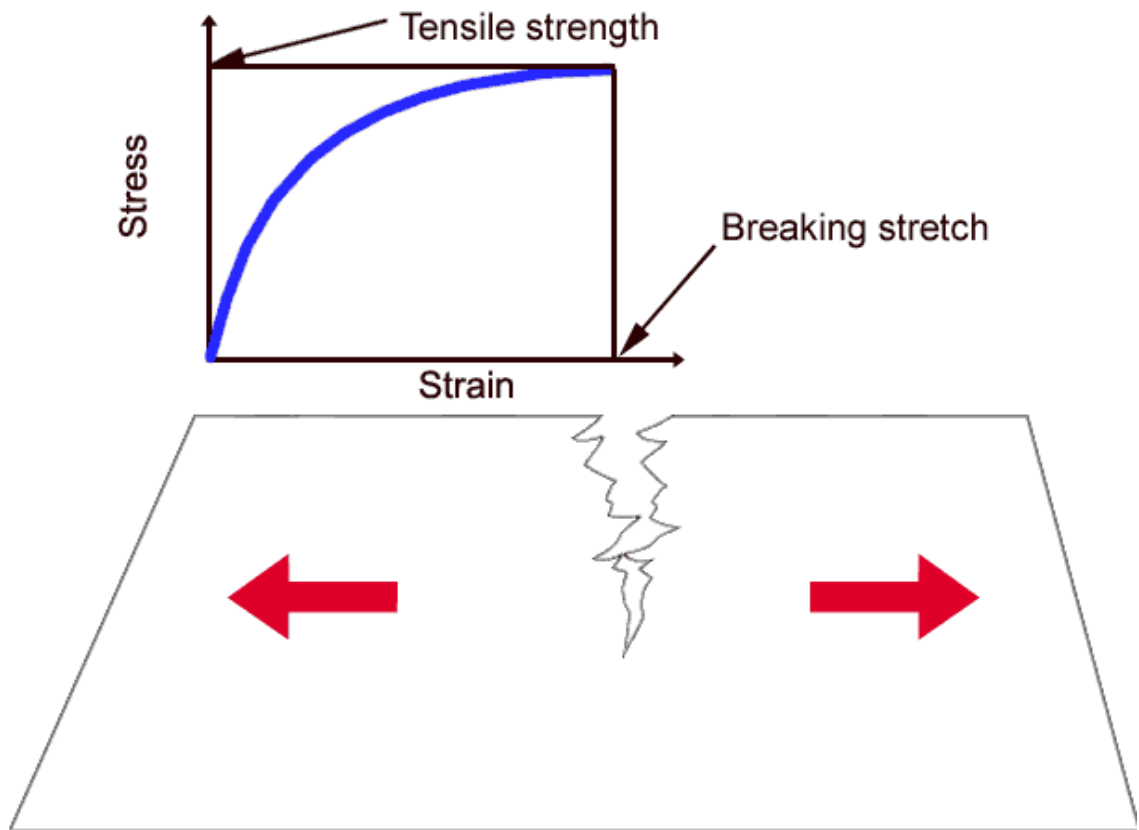Figure 16. The relationship between clamp and test piece (ISO 1924-3, page 3)

Figure 17. The tensile strength test mechanism

(Knowpap, web, 16,02,2014)

5.2.5   Wet tensile strength

For tensile-strength testers in which the soaking procedure is accomplished manually, place a test piece in the testing position, as shown. Push the ends of the test piece towards each other so that the middle region of the test piece dips into the water in the soaking vessel as in Figure15. Allow the test piece to soak in the soaking vessel for 1 h. Gently pull the ends of the test piece away from each other, so that the test piece is lifted from the soaking bath. Place the test piece on the tensile testing machine and clamp the test piece. Start the wet-tensile-strength testing. Record the wet tensile force, F, in newtons

(International standard ISO 12625-5:2005(E), 13)

5.3   Results and analysis

Tensile index is used in the comparison of tensile strength in samples with various basis weight. It is calculated by dividing the tensile strength with basis weight multiplied by 1000. The recommended tensile strength unit is the Nm/g.

(Knowpap,web, 2014)

According to different end use of paper grade and the change of tensile strength after wetted, the presence of wet strength can be detected. If immersed into water after between 10 seconds and 2 hours, paper loses a third or even more strength, then it can be told temporary wet strength resins have been added. If less than 20% of tensile strength is lost, then the wet strength additives are permanent wet strength resins.

(Qin Peiyun& Zhao Chuanshan)

It can be indicated via the retention of wet strength:

Wet-tensile-strength retention:

$$\overline{S}_R = \frac{100\% \times \overline{S}}{\overline{S}_D} \qquad\qquad (1)$$

Where

$\overline{S}_R$ is the mean tensile strength retention, as a percentage;

$\overline{S}$ is the mean wet tensile strength, in newtons per meter;

$\overline{S}_D$ is the mean tensile strength of the test piece in the dry conditioned state, in newtons per meter.

(International standard 12625-5,15,2014)

Wall paper

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Wallpaper basis weight is 60-150 g/m^2. The composition is usually from 70-75% me-chanical pulp and 25-30% semi-bleached reinforcing chemical pulp. Also it can be made totally by chemical pulp. (Knowpap, web, 2014)

Machine direction: $\bar{S}_{RWM} = \frac{100\% \times 950}{7610} = 12.4\ \%$

Cross direction: $\bar{S}_{RWC} = \frac{100\% \times 930}{3440} = 12.7\ \%$

From the result of wet strength retention, it can be noticed that the value is almost same which indicates that after been wetted, the paper lost majority of the tensile strength itself. Also from Figure 18, it also shows that at first, the machine direction tensile strength is twice the value of cross machine direction no matter in dry or wet tensile strength. Then after the bonds break in water condition, only the added resins play the important role in holding the paper together.
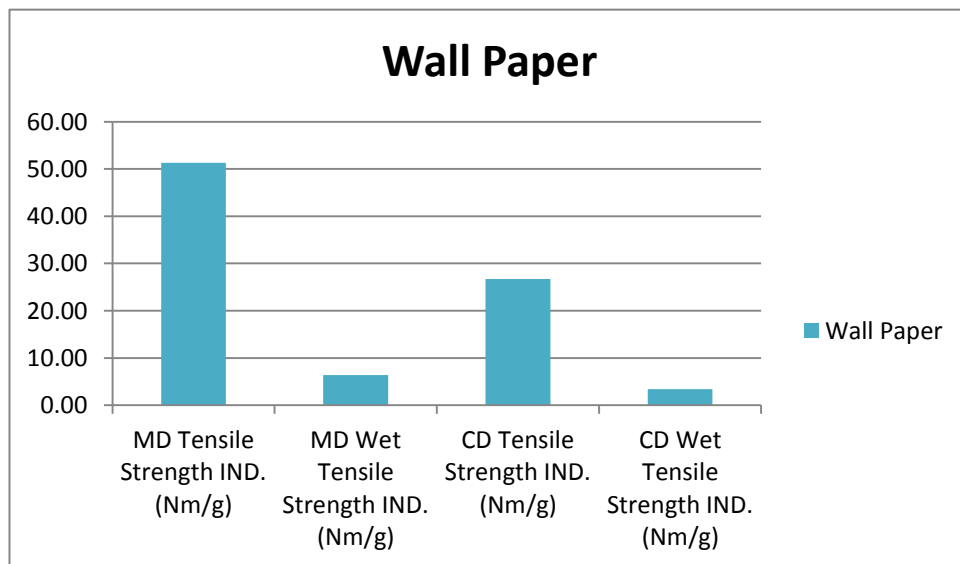

Figure 18. The tensile strength and wet strength development in wall paper in machine direction and cross direction

Kraft paper

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Kraft paper is paper or paperboard (cardboard) produced from wood chips boiled in alkaline condition with sodium sulfate.

Machine direction: $\overline{S}_{RKM} = \frac{100\% \times 909}{7510} = 12.10\ \%$

Cross direction: $S_{RKC} = \frac{100\% \times 377}{3870} = 10\ \%$

It can be seen from Figure 19 that dry tensile strength stays in a rather high level, yet through water immersing, it dropped drastically. The reason can be that strength properties for kraft paper mainly come from its long fibers and refining giving more bonds and also with the help of machine direction orientation.
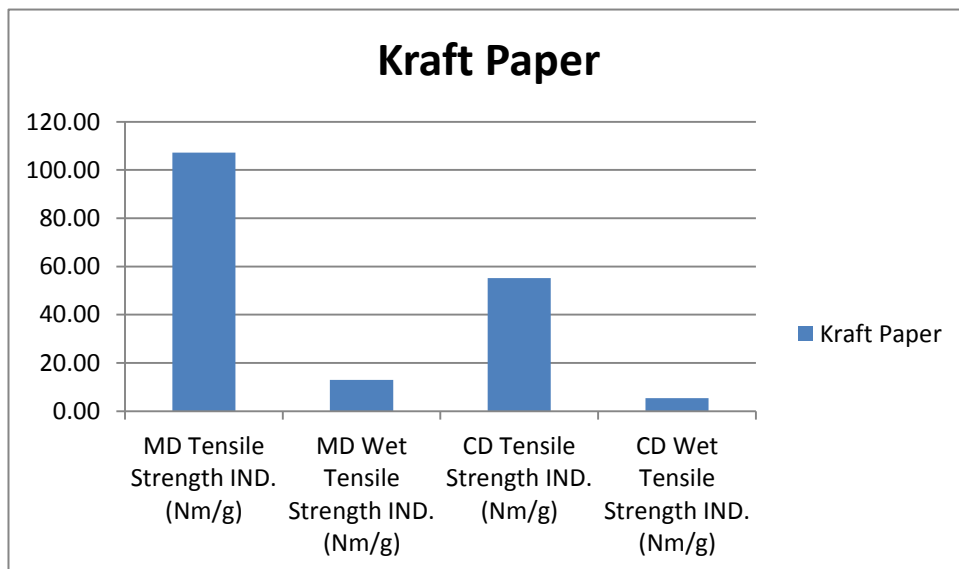

Figure 19. The tensile strength and wet strength development in kraft paper in machine direction and cross direction

Label base paper

Usually two types of base paper are used as label base paper. One is normal paper which is white or yellow with coarse surface and bulky. Another one which is tested in

this experiment is glassine. Glassine is a thin and smooth paper that is air and water resistant. It is translucent unless dyes are added to color it or make it opaque. (Origami-USA, web, 2014)

Machine direction: $\overline{S}_{RLM} = \frac{100\% \times 1380}{5940} = 23\ \%$

Cross direction: $\overline{S}_{RLC} = \frac{100\% \times 930}{3440} = 27\%$

From the retention ratio of wet strength, enough part of wet strength resins has been added into pulp. Due to the chemical pulp and refining process, it gains a tight connection and more bonding areas. As bonding areas and bonding strength increase, paper can get a good strength property. In addition, label base paper is also added wet strength resins for the end use. So, that is the reason why label base paper has a better dry and wet tensile strength (Figure 20).
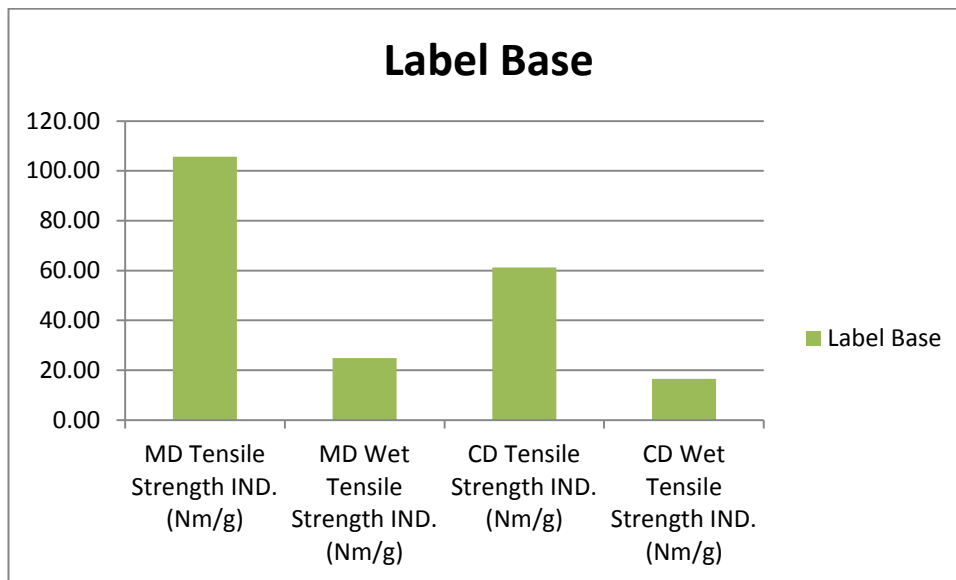

Figure 20. The tensile strength and wet strength development in label base paper in machine direction and cross direction

Tape base paper

Base crepe paper is made of 100% excellent sulfate insulating wood fiber. The basis weight of crepe papers is 25-180 g/m^2 (15 -111 lbs/ream) and the elongation is between 15 to 300%. (WICOR Holding AG,web, 2014)

Machine direction: $\overline{S}_{RTM} = \frac{100\% \times 572}{2550} = 22\ \%$

Cross direction: $\overline{S}_{RTC} = \frac{100\% \times 421}{1140} = 36.9\ \%$

Although from Table's figure, the wet strength of tape base paper is not very high. But the high retention ratio as calculated above indicates that a bit amount of wet strength resins were used. Explanation behind this can be the strong net work of solidified resins preventing the fibers from losing hydrogen bonds and resins themselves forming a non-water soluble system to bear the outside force. And the contribution of good qualified long fibers being used gives the basic structure of a high tensile strength (Figure 21).
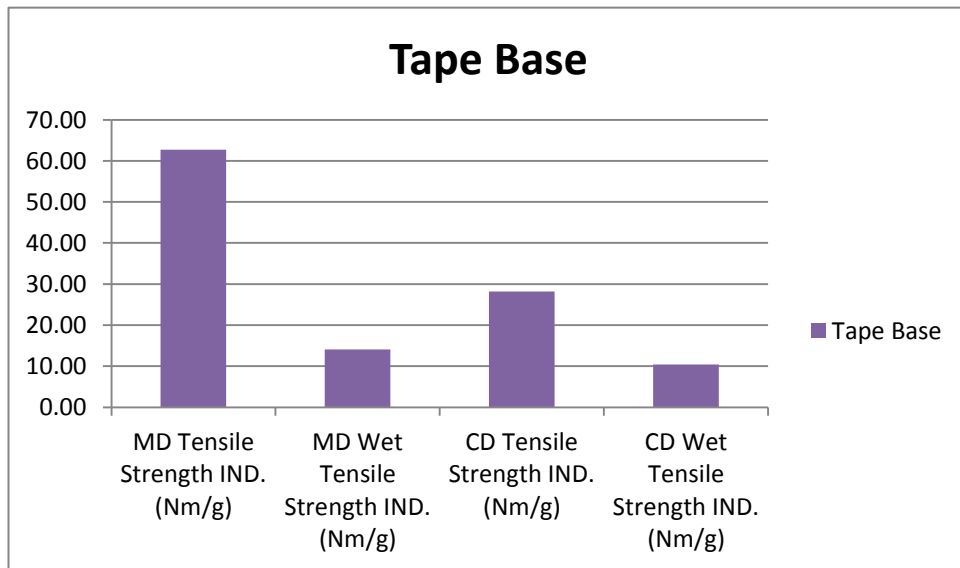

Figure 21. The tensile strength and wet strength development in tape base paper in machine direction and cross direction

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Compared among all the four paper grades, showed in Figure 22, kraft paper and label base paper due to their abundant bonds and long fibers, the dry strength get a big improvement than the other two. But when immersed into water for an hour, the higher wet strength resin level for label base and tape base paper showed their advantages. The wet strength resins as predicted in the theory part of wet strength resins acted effectively to form connections to resist the ions breaking hydrogen bonds and protected the hydrogen bonds between fibers to set apart.

However these samples are just one type of their paper grades. For instance, wall paper contains a large amount of product from high wet strengthened to low wet strengthened depending on the need, and for kraft paper to make packages, the containing of wet strength resins will be much higher than the test piece used in this experiment.
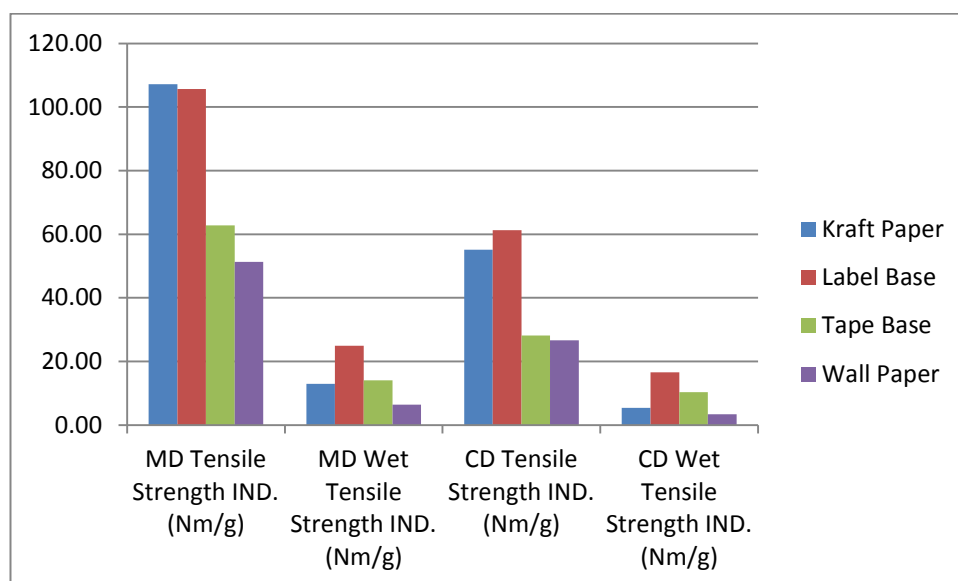

Figure 22. The comparison of four paper grades in dry and wet tensile strength in machine direction and cross direction

6 CONCLUSION

The need for sustainable, environmentally friendly, economic and convenience relies on paper. Improvement for paper products' properties never stop. So after abundant knowledge of paper, the end use properties, for example dry and wet strength, become more and more interesting.

The original strength for paper is affected by the quality of fibers. Thus from the study of plant cell structure to the selection of various wood species relating to which kind of fiber is suitable for a certain product; from the study of how to get cheaper and better fibers to the modification of many types of chemical and mechanical method.

Water plays an important role of paper making and controls the quality of the paper product from the consistency in head box to the reasonable drainage and drying.

However, when paper is wetted, its structure collapses. Thus, with the knowledge of why paper cannot hold together after the contact with water, paper makers with chemical knowledge have been putting up with a lot of effective solutions to solve the problem. From the beginning of sulphuric acid treatment to make the first wet strength paper to the exploit of polymer as UF, MF, PAE, PEI, DAS and the like are produced.

For DAS it works by having a covalent bond with fiber thus enhancing the bonds to have a temporary wet strength. And resins like UF, MF, PAE , they gaining the reputation of economic and a good effect on wet strength. Once used, paper will get a permanent wet strength. However the UF and MF are facing a problem of toxic emission, while PAE with its cationic attraction for fiber and a strong self cross link is getting a wider market in wet strength paper. But, when we talking about wet strength, it basical-

ly means re-wetting of the paper, meaning these resins above don't give the web a wet strength in the paper machine, but the strength after drying and curing to form a three dimensional structure to prevent fiber swelling and protect the paper structure. Specially, PEI works differently as it is a cationic chemical itself as to adhere to the fiber and get ionic bond with fibers. Hence, once dried in the paper machine, there is no need to storage for some time like others.

In fact, wet strength resins do not only give wet strength alone, it imparts the paper with the same promotion of dry strength as well. Beside, because of the non-aqueous of most of the resins, the water drainages faster leading to a high speed running of paper machine.

Due to the economic reasons, waste paper and broke is always recycled. Though the convenience wet strength paper provide, when referring to repulping, these papers are really a problem, as repulping needs higher temperature or bigger stirring rate which consumes extra energy. So chemicals like H_2O_2 with NaOH and $K_2S_2O_8$ was tested effective to degrade those thermal setting resins in order to save time and energy to handle the repulping process.

In the experiment part, the aim is to test the wet strength retention of different paper grades and analyze the reason behind it connecting to its end use. The wet strength index values were applied to calculate and compare for the reason of excluding the influence of basis weight. And to our surprise, wall paper in this test appeared to be the weakest among the others no matter in dry strength or wet strength. But as mentioned before, different end use of this paper grade should be taken into consideration. Kraft paper naturally with its superb chemical long fiber and refining got the highest dry strength. But without the wet strength resin left enough, it still lost a bit of strength after immersed in water. The two thin paper grades, however performed better in this test. This largely depends on the aim use and the protection of solidified resins on the surface

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and in between the fibers resulting in a control of the swelling of hemi-cellulose and cellulose.

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APPENDIX

Table 2. The machine direction dry and wet tensile strength

Paper Grades	Basis Weight (g/m2)	Thick-ness (μm)	Tensile Strength (KN/m)	Tensile Strength IND. (Nm/g)	Wet Tensile Strength (KN/m)	Wet Tensile Strength IND. (Nm/g)
Kraft Paper	70.08	108.30	7.51	107.21	0.909	12.97
Label Base	56.24	73.50	5.94	105.71	1.380	24.95
Tape Base	40.56	96.80	2.55	62.75	0.572	14.11
Wall Paper	148.30	222.70	7.61	51.31	0.950	6.40

Table 3. The cross machine direction dry and wet tensile strength

Paper Grades	Basis Weight (g/m2)	Thick-ness (μm)	Tensile Strength (KN/m)	Tensile Strength IND. (Nm/g)	Wet Tensile Strength (KN/m)	Wet Tensile Strength IND. (Nm/g)
Kraft Paper	70.08	108.30	3.87	55.15	0.377	5.38
Label Base	56.24	73.50	3.44	61.23	0.930	16.55
Tape Base	40.56	96.80	1.14	28.18	0.421	10.38
Wall Paper	148.30	222.70	3.96	26.70	0.504	3.40