University of Aveiro Chemistry Department

2021

GUSTAVO APARECIDO BUENO FERREIRA

OPTIMIZATION OF THE WET STRENGTH AGENT LOAD IN THE TISSUE PAPERMAKING

OTIMIZAÇÃO DA DOSAGEM DE AGENTE DE RESISTÊNCIA A HÚMIDO NA FABRICAÇÃO DE PAPEL TISSUE

Universidade de Aveiro Departamento de Química
2021

GUSTAVO APARECIDO BUENO FERREIRA

OPTIMIZATION OF THE WET STRENGTH AGENT LOAD IN THE TISSUE PAPERMAKING

Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Química, realizada sob a orientação científica do Doutor Dmitry Victorovitch Evtyugin, Professor Associado com Agregação do Departamento de Química da Universidade de Aveiro e co-orientação do Doutor Song Won Park, Professor assistente doutor da Universidade de São Paulo

Dedico este trabalho a minha esposa Marina, por me apoiar e estar comigo em toda esta jornada académica, e em memória das minhas amadas avós Anésia e Benedicta; e dos meus tios Sérgio e Aguida.

o júri

presidente

Prof. Doutora Helena Isabel Seguro Nogueira
professora auxiliar do Departamento de Química da Universidade de Aveiro

Prof. Doutor Song Won Park
professor assistente doutor da Universidade de São Paulo

Doutora Ana Margarida Martins Salgueiro Carta
coordenadora de I&D Tecnológica do Instituto de Investigação da Floresta e do Papel (RAIZ)

agradecimentos

Agradeço a minha esposa Marina por todo apoio e motivação para que eu concluísse este trabalho.

Às pessoas que me acolheram em Portugal: Thiago, Adriana, Rafa, Ari, Gabi, Guga, Juliete, Nicole e Thainara.

Ao meu orientador Dmitry, co-orientador Song Won Park e ao pesquisador colaborador da EP-USP Afonso Henrique Teixeira Mendes por toda orientação e ajuda no desenvolvimento deste trabalho.

Aos meus colegas de trabalho da Santher, por toda troca de conhecimento diária, e ao Fábio Ferreira da empresa Solenis, por proporcionar que os ensaios laboratoriais ocorressem.

Agradeço aos meus pais por me proporcionarem acesso à educação e acreditarem no meu potencial.

Agradeço especialmente à Cidinha e ao Tico, por me proporcionarem a calmaria que eu precisava para finalizar este mestrado. A vocês minha eterna gratidão.

palavras-chave

Agente de resistência a húmido, resina de resistência a húmido, papel tissue, controle de carga iônica, controle de carga, resistência a húmido

resumo

Papéis tissue são produtos utilizados para fins higiênicos e sanitários, tais como papel higiênico, papel toalha, guardanapo e lenço facial. Alguns desses papéis possuem a característica de resistência a húmido, que é definida como a resistência do papel após receber uma determinada quantidade de água. Na fabricação de papéis que demandam alto valor de resistência a húmido, o uso de um aditivo para essa finalidade é extremamente importante e deve ser rigorosamente controlado, sempre tentando otimizar a dosagem para reduzir custos. Este trabalho teve como objetivo estudar a carga de resina de resistência a húmido na produção de papel tissue e como o controle da carga iônica em suspensão de fibras pode ajudar a otimizar a dosagem da resina de resistência a húmido. A carga iônica da suspensão de fibras foi mantida entre -10 a -21 µEq / mL, o potencial zeta detetado ficou entre -16,6 a -22,3 mV. Foram comparados os valores das folhas de papel formadas com e sem adição do aditivo de controle de carga iônica. Quando foi controlada a carga iônica da suspensão de fibras, foi possível obter maiores valores de resistência à tração a húmido com menor dosagem de resina.

Keywords

Wet strength agent, wet strength resin, tissue paper, ionic charge control, charge control, wet strength

Abstract

Tissue papers are products used for hygienic and sanitary purposes such as toilet paper, paper towel, napkin and facial tissue. Some of these papers have the characteristic of wet strength, which is defined as the strength of the paper after receiving a certain amount of water. In the manufacture of papers that demand a high wet strength value, the use of an additive for this purpose is extremely important and must be strictly controlled, always seeking to optimize the dosage to reduce costs. This work aimed to study the wet strength resin loading in tissue paper production and how the control of ionic charge in fiber suspension can help to optimize the dosage of wet strength resin. The ionic charge of the pulp suspension was kept between -10 to -21 μEq/mL, the zeta potential obtained was between -16.6 to -22.3 mV. Tensile strength values of paper sheets formed with and without the addition of the ionic charge control additive were compared. When it was controlled the ionic charge of the pulp suspension, it was possible to achieve greater values of wet tensile strength with lower dosage of wet strength resin.

Abbreviations

APAM	Anionic polyacrylamides
ATC	Anionic trash collector
CD	Cross machine direction
CMC	Carboxymethylcellulose
COVID-19	Coronavirus disease 2019
GPAM	Glyoxalated polyacrylamide
HF	Handfeel
ISO	International Organization for Standardization
MD	Machine direction
MF	Melanine-formaldehyde
PAE	Polyaminoamide-epichlorohydrin
PAM	Polyacrylamide
RNA	Ribonucleic acid
TAPPI	Technical Association of the Pulp and Paper Industry
TSA	Tissue Softness Analyzer
TWA	Total Water Absorbency
UF	Urea-formaldehyde
ZD	Perpendicular direction

Index:

List of Figures: VII
List of Tables: IX
1. Introduction 1
2. Tissue paper 4
  2.1. Cellulose fibers in tissue paper 4
    2.1.1. Hardwood pulps 7
    2.1.2. Softwood pulps 7
3. Tissue papermaking process 8
  3.1. Creping Process definition 13
4. Tissue properties 16
  4.1. Grammage 16
  4.2. Thickness 16
  4.3. Specific volume (bulk) 17
  4.4. Softness 17
  4.5. Water absorption capacity 18
  4.6. Dry tensile strength 18
  4.7. Wet tensile strength 18
  4.8. Elongation 19
5. Papermaking chemistry 20
  5.1. Additives for papermaking 24
  5.2. Functional Chemicals 24
    5.2.1. Dry strength 24
    5.2.1.1. Starch 25
    5.2.1.2. Enzymes 26
    5.2.1.3. Polymers for dry strength 27
    5.2.2. Wet Strength 27
    5.2.2.1. Synthesis of Polyaminoamide-epichlorohydrin (PAE) resin 30
    5.2.2.2. Mechanisms of wet strength development of cellulose sheets prepared with PAE 31
    5.2.3. Softeners 32
    5.2.4. Dyes 33
    5.2.5. Optical brighteners 33

- 5.3. Process chemicals 34
  - 5.3.1. Treatment of fabrics 34
  - 5.3.2. Pitch and stickie’s agents 34
  - 5.3.3. Ionic charge control 35
  - 5.3.4. Defoamers 35
  - 5.3.5. Biocides 35
  - 5.3.6. Retention and drainage agents 36
- 6. Optimize wet strength resin dosage 37
- 7. Materials and methods 44
- 7.1. Raw materials 44
  - 7.1.1. Pulp 44
  - 7.1.2. Wet strength resin 45
  - 7.1.3. Ionic charge control 46
- 7.2. Methodologies 46
  - 7.2.1. Stock concentration 46
  - 7.2.2. Specific load of the additives 46
  - 7.2.3. Drainability measurement 47
  - 7.2.4. pH measurement 48
  - 7.2.5. Ionic charge measurement 48
  - 7.2.6. Zeta potential measurement 49
  - 7.2.7. Pulp disaggregation 50
  - 7.2.8. Hand sheet preparation 51
  - 7.2.8.1. Pulp preparation 52
  - 7.2.8.2. Equipment set-up 52
  - 7.2.8.3. Sheet forming 53
  - 7.2.9. Measurement of the paper properties 55
  - 7.2.9.1. Measurement of grammage 55
  - 7.2.9.2. Measurement of dry tensile strength 55
  - 7.2.9.3. Measurement of wet tensile strength 56
  - 7.2.9.4. Measurement of water absorption capacity 58
- 8. Results and discussion 61
- 9. Conclusions 77
- References 79

List of Figures:

Figure 1. Schematic representation of hardwood fibers, including vessels, parenchyma and libriform cells (left image) and the cross section of a hardwood, *Betula spp.* (right image), showing the vessels (V) and rays (F) (Ek et al., 2009b). 6
Figure 2. Schematic representation of softwood fibers, including tracheid and cells (left image) and the cross section of a softwood, *Pinus spp.* (right image), showing the earlywood and latewood tracheid cells (Ek et al., 2009b). 6
Figure 3. Paper sheet directions (Ek et al., 2009a). 8
Figure 4. Block diagram of a general tissue papermaking process. Adapted from (Ferreira, 2019). 9
Figure 5. Disc refiner (a) and Conical refiner (b) (Hergen, 2021; Parason, 2021). 10
Figure 6. Refining stages between stator and rotor bars (Gharehkhani et al., 2015). 10
Figure 7. Cellulosic fibers with and without refining (Campos, 2012). 11
Figure 8. Tissue machine (Valmet, 2020) 12
Figure 9. Yankee cylinder, hood and creping process. Adapted from (Boudreu, 2013). 13
Figure 10. Yankee Cylinder (Hergen, 2020) 13
Figure 11. Microfold and macrofold (de Assis et al., 2018) 14
Figure 12. Creation of microfolds and macrofolds (Boudreau, 2013). 14
Figure 13. Crepe ratio (Ferreira, 2019) 15
Figure 14. Linear structure of cellulose (Thorn & Au, 2009). 20
Figure 15. Intramolecular hydrogen bonds of a cellulose chain (Fengel & Wegener, 1983). 21
Figure 16. Intermolecular hydrogen bonds between cellulose chains (Santos et al., 2001). 21
Figure 17. Electrical potential. Adapted from (Nachtergaele, 1989). 23
Figure 18. Amylose structure (Thorn & Au, 2009). 25
Figure 19. Amylopectin structure (Thorn & Au, 2009) 26
Figure 20. Preparation of polyaminoamide-epichlorohydrin resins (Dunlop-Jones, 1991). 31
Figure 21. The reactivity of PAE resins. I: homo-crosslinking; II: co-crosslinking; III: slow reaction with water (Dunlop-Jones, 1991). 32
Figure 22. Fluorescence phenomenon. Adapted from (Manfredi et al., 2014). 34
Figure 23. Zeta potential measurements for *Eucalyptus* pulp using (A) electrophoretic mobility and (B) streaming potential methods, as a function of the PAE concentration and the mixing time (Siqueira, 2012). 38
Figure 24. Zeta potential measurements of *Eucalyptus* pulp using (A) electrophoretic mobility and (B) streaming potential techniques as a function of PAE concentration and standing time (Siqueira, 2012). 39
Figure 25. Change of concentration of PAE in aqueous cellulosic fiber suspension as a function of contact time (Yoon, 2007). 40

Figure 26. Formation of a large polymer complex or coacervate (Thorn & Au, 2009). 41
Figure 27. Effect of PAE concentration in wet tensile index (Su et al., 2012). 42
Figure 28. Effect of PAE concentration in dry tensile index (Su et al., 2012). 43
Figure 29. of PAE dosage on the wet and dry strength ratio (Su et al., 2012)...... 43
Figure 30. Schopper-Riegler apparatus with a beaker graduated of 1000 mL with direct read of the °SR. 48
Figure 31. Ionic charge equipment Mutek PCD-04.......... 49
Figure 32. Zeta potential equipment Mutek SZP-10. 50
Figure 33. FDA – Automated Dynamic Handsheet Former produced by Techpap51
Figure 34. Tank with pulp suspension prepared.......... 52
Figure 35. Wire (a), wire installation (b) and wire installed (c). 53
Figure 36. Sheet forming and injector nozzle. 53
Figure 37. FDA – Automated Dynamic Handsheet Former software.......... 54
Figure 38. Sheet pressing. 54
Figure 39. Sheet drying. 55
Figure 40. Dynamometer (a) and dynamometer with the sample (b). 56
Figure 41. Wetting the sample for wet tensile strength analysis. 57
Figure 42. Wetted sample (a) and metal roller (b). 57
Figure 43. Wet tensile strength analysis. 58
Figure 44. Paper sample in the basket for water absorption capacity analysis. ... 59
Figure 45. Paper sample filled with water. 59
Figure 46. Dry tensile strength with and without ionic charge control additive...... 64
Figure 47. Load of wet strength resin *versus* ionic charge and paper dry strength without addition of ionic charge control additive. 65
Figure 48. Load of wet strength resin *versus* ionic charge and paper dry strength with addition of ionic charge control additive. 65
Figure 49. Load of wet strength resin *versus* zeta potential and paper dry strength without addition of ionic charge control additive. 66
Figure 50. Load of wet strength resin *versus* zeta potential and paper dry strength with addition of ionic charge control additive. 67
Figure 51. Wet tensile strength with and without ionic charge control additive..... 68
Figure 52. Load of wet strength resin *versus* ionic demand and paper wet strength without addition of ionic charge control additive. 68
Figure 53. Load of wet strength resin *versus* ionic demand and paper wet strength with addition of ionic charge control additive. 69
Figure 54. Load of wet strength resin *versus* zeta potential and paper wet strength without addition of ionic charge control additive. 69
Figure 55. Load of wet strength resin *versus* zeta potential and paper wet strength with addition of ionic charge control additive. 70
Figure 56. Relation between wet and dry strength with and without charge control. 73
Figure 57. Load of wet strength resin and ionic charge control additive. 74
Figure 58. Water absorption capacity with and without charge control. 76

List of Tables:

Table 1. Characteristics of different tissue papers. Adapted from (Ramires, 2013). 16
Table 2. Comparison of wet strength resins (Dunlop-Jones, 1991). 29
Table 3. Wet strength resins and their pH (Roberts, 1996). 30
Table 4. Bleached Hardwood Kraft Pulp (BHKP) characteristics 45
Table 5. Disaggregated pulp characteristics 50
Table 6. Results of the first part, without ionic charge control. 63
Table 7. Results of the second part, with ionic charge control 63
Table 8. Relation between wet and dry tensile strength 72
Table 9. Cost of chemicals per ton. 75

1. Introduction

The history of paper is an essential part of the human culture and civilization. At first, Egyptians, Greeks and Romans wrote on “papyrus”, a material like paper. In the past, paper was the principal carrier of information and as it was a valuable product; its manufacturing was considered an art, so it was kept in secret because of the outstanding advantages of the product. Papermaking has change from a rare artisan material to a commodity product, it is hard to imagine a world without paper, and it is present in communication, education, packing, hygienic and sanitary, and others applications (Holik, 2006).

As paper is much present in our life, we do not tend to think of it as a particularly complex material. Paper is derived from plant sources and therefore has both morphological complexities, it also has physical and chemical complexity. The papermaking process is highly sophisticated, involving some unit operations. It is in essence a high-speed filtration process yielding a weak wet fibrous network. This wet paper web, despite its weakness, must then be pulled continuously through the pressing and drying sections of the paper machine. At present paper machines achieve more than 2000 m/min, so it requires some of the most advanced control engineering technology available today to avoid frequent breaks, and to obtain good product uniformity (Roberts, 1996).

It is easy to see the presence and importance of paper in our daily life. Packaging papers and boards grades support supermarkets, product presentations and e-commerce packages. In our home sanitary papers made our life easier. Graphic paper such as magazines, books and newspaper accompany us through our life (Holik, 2006).

Paper is a layered mat consisting of a network of cellulose fibers bonded together. The intermolecular forces (Van der Waals, hydrogen bonding and Coulomb or electrostatic forces) act among the fiber-fiber contact to held it together, so the area of molecular contact is the most significant factor regarding the inter-fiber bonding. It is relevant if the distance of molecular contact is closer than ~300 Å is established (Obokata & Isogai, 2007; Dunlop-Jones, 1991). These are sensitive to water, so the extent of bonding decrease as the water content in the paper increase. As there is a need for paper products which retain some strength when subjected to high humidity or when soaked in water, chemical wet strength resins have been developed (Dunlop-Jones, 1991). For tissue papers, paper towel, liquid packaging base paper and others the wet strength is one of the most important properties, which is defined as tensile strength of paper sheets re-wetted with water (Obokata & Isogai, 2007).

The use of chemical additives in the production process is essential to achieve the desired specification, machine stability and productivity. In the manufacture of papers that demand a high wet strength value, the use of an additive for this purpose is extremely important and must be strictly controlled, always seeking to optimize the dosage to reduce costs. In addition, there are other chemicals that are used in this process for various purposes such as: pH control, dry strength, ionic charge control and retention, for example (Roberts, 1996).

Nowadays, due to the competitiveness, in every market process optimization is crucial to keep company growing up and delivering great results to the stakeholders. The market of tissue paper (hygienic and sanitary papers) tend to keep growing in the next years (IMARC, 2020). So, a good knowledge of the papermaking process, which has a lot of unit operations and variables, is essential to achieve great results for the company. The production of paper towels, facial tissue and napkins, products that demand high wet strength values, a good application of wet strength agent may save a lot of money.

In this work, a laboratory study was carried out to understand and optimize the wet strength agent dosage through the control of the ionic charge of the pulp suspension, aiming to obtain a correlation between the dosage of wet strength and ionic charge control additive. This study is important to avoid over dosage of the wet strength resin in the papermaking process, especially in tissue papers like paper towel.

In the first moment, paper sheets were formed in laboratory with a grammage of 45 g/m² and wet strength resin will be added in various specific dosages. At each specific dosage, it was measured the ionic charge of the pulp suspension, the zeta potential of the fibers, dry tensile strength, wet tensile strength and water absorption capacity of the paper sheets. In a second step, it was used an additive to control the ionic charge of the pulp suspension with values which are practiced in the tissue paper industry, around −20 μEq/ml. This control is important because a positive ionic charge of the paper process can cause some problems in the tissue machine like foam generation, forming problems and can affect the Yankee dryer coating. In this step, it was also measured the dry, wet tensile strength, and the water absorption capacity of the formed paper sheets.

2. Tissue paper

Tissue papers are products made from lightweight, dry creped (sometimes wet-creped or non-creped) papers. Their use is for hygienic and sanitary purposes such as: toilet paper, kitchen paper towel, napkin, hand paper towel, facial tissue and diaper paper. These papers have some essential properties such as softness, flexibility, liquid absorption and thickness. They can be produced using cellulose produced from wood sources like bleached short fiber, bleached long fiber, recycled fibers (bleached secondary fiber); it also can be produced with non-wood sources as bamboo, cotton lint, sisal, sugarcane bagasse and others. The grammage of the tissue papers are low, ranging from 10 to 40 g / m² (Campos, 2012; Roberts, 1996).

The market of tissue paper has been growing in the past years, hygiene-consciousness among individuals have escalated the demand for this kind of paper across the world. Nowadays, due to the COVID-19 pandemic tends to grow more. According to Imarc Group (IMARC, 2020) the global market of tissue paper reached US$ 43,5 billion in 2019 and has potential to achieve US$ 60,7 billion by 2025.

The manufacture of tissue papers that are dry creped differs from other types of papers, because after the drying step there is a step called creping. A good knowledge of the creping step is necessary, this process has an impact on the main properties of tissue paper, such as: thickness, softness, elongation and strengths (Ferreira, 2019).

2.1. Cellulose fibers in tissue paper

Tissue papers do not normally contain mineral fillers; they are constituted almost exclusively by cellulose fibers. It is from these fibers that potential properties are expected, such as softness, bulk and high absorption. On the other hand, the achievement of these desired properties should be obtained with a good machine runnability, which is associated with mechanical properties (Ramires et al., 2013).

Nowadays, the main way to obtain cellulose fibers is the Kraft process, it is a chemical process with continuous or batches cooking. The advantages associated to this process are the chemical product recovery system, around 97% of the chemical agents used in the process are recovered; and the ability of the factory generates its own energy through the black liquor (a residual cooking liquor, rich in lignin) which become a biofuel in the cellulose factories (Alves et al., 2015).

Basically, the Kraft process has the function to dissolve lignin, releasing the fibers with the minimum degradation of carbohydrates, cellulose and hemicellulose. This process occurs in the cooking step, where it is used sodium hydroxide (NaOH) and sodium sulfide (Na_2S) as active agents in the reaction with the wood (Alves et al., 2015; Sixta, 2006).

The cellulose fibers can be obtained from different kind of plants. Plants from the *Angiosperm* group are known as hardwood (deciduous), whereas plants from *Gymnosperm* group are known as softwood (resinous) (Ek et al., 2009b). These two groups of plants are different in fiber morphology and in the chemical composition of basic macromolecular constituents and, for these reasons, are differentiated in the pulp and paper applications.

In the hardwoods, the conductive large cells, vessels, contributes to 20-40% of total cells (Figure 1); the parenchyma and libriform cells contributes to 5-10% and 40-70% of cells, respectively. The most abundant cells, libriform fibers, provides the basic mechanic functions to xylem tissues. The hardwoods contain a moderate amount of lignin (20-24%) and a relatively high cellulose content (45-50%). The hardwood lignin contains essentially syringyl units particularly reactive in kraft delignification.

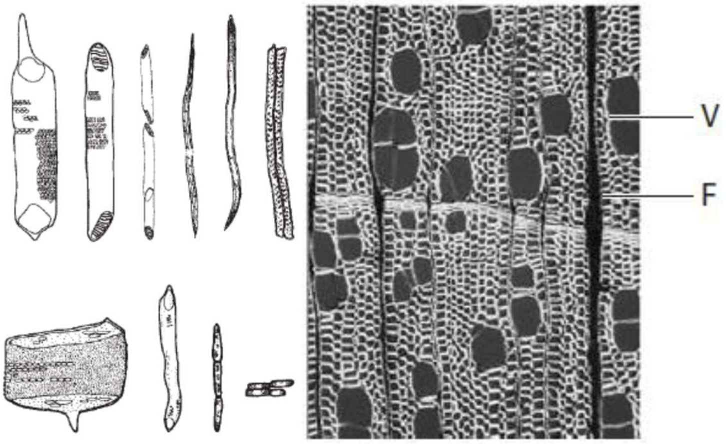


Figure 1. Schematic representation of hardwood fibers, including vessels, parenchyma and libriform cells (left image) and the cross section of a hardwood, *Betula spp.* (right image), showing the vessels (V) and rays (F) (Ek et al., 2009b).

In the softwoods, the tracheid cells possess both conductive and mechanical support functions and contributes to 90-95% of total cells (Figure 2); the parenchyma cells of rays contribute to 5-10% of cells. The softwoods contain a high amount of lignin (26-30%) and a moderate cellulose content (40-48%). The softwood lignin contains essentially guaiacyl units less reactive than the syringyl ones in kraft delignification.

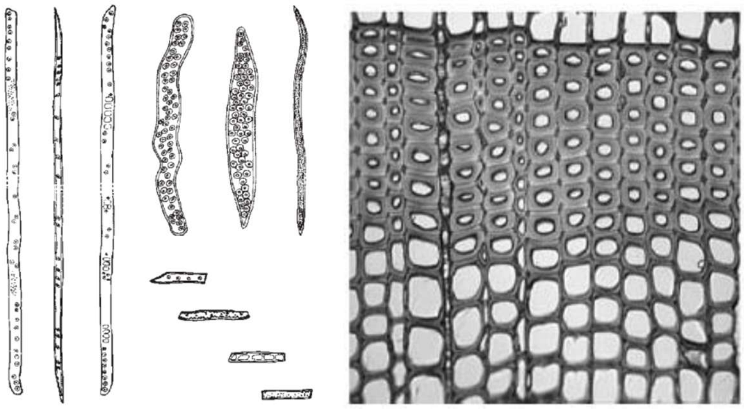


Figure 2. Schematic representation of softwood fibers, including tracheid and cells (left image) and the cross section of a softwood, *Pinus spp.* (right image), showing the earlywood and latewood tracheid cells (Ek et al., 2009b).

2.1.1. Hardwood pulps

Hardwood pulps are obtained by cooking of wood from wild forest trees or the plantation wood (mainly from *Eucalyptus* species). Hardwood fibers have typically length between 0.5 mm to 1.5 mm, so they are called short fibers with the aspect ratio of *ca*. 25-50. These fibers are the most used in tissue paper manufacturing, which are papers that do not require high values of physical-mechanical tensile strength, providing good formation, bulk, softness and absorption (Ek et al., 2009b; Campos, 2012; Milanez & Rost, 2005; Sabino, 2020).

2.1.2. Softwood pulps

Softwood pulps are obtained by cooking of wood species that belongs essentially to the *Pinus* family; they have long fibers with length between 2.5 mm to 5.0 mm with the aspect ratio of *ca.* 100-200. They are used in papers that need higher values of physical-mechanical tensile strength. Besides that, these fibers provide porosity and opacity to the paper, and also contribute to machine runnability, being possible to increase machine speed in papers that a higher tensile strengths are needed (Ek et al., 2009b; Campos, 2012; Milanez & Rost, 2005; Sabino, 2020).

3. Tissue papermaking process

The paper web is a network of layed cellulose fibers randomly distributed in the three directions: machine direction (MD), machine transversal direction or machine cross direction (CD) and the direction along the paper thickness or the perpendicular direction (ZD). Due to this random distribution of fibers, the characteristics have different values depending on the direction analyzed (Lima, 2012). Figure 3 shows the three directions in the paper sheet.

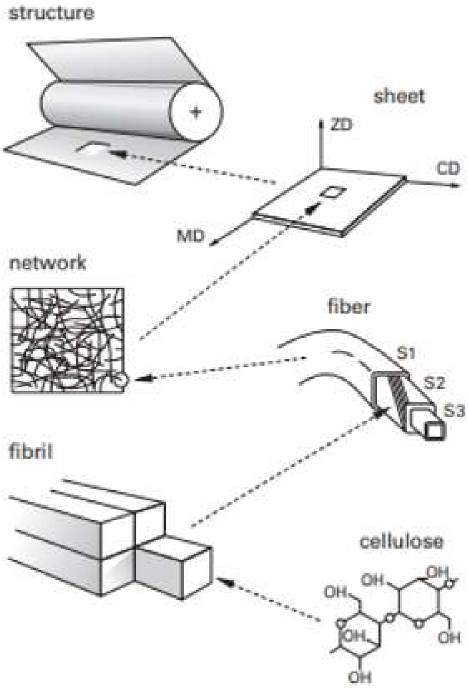


Figure 3. Paper sheet directions (Ek et al., 2009a).

Papermaking consists of several unit operations and the application of physical and chemical principles. These operations can be divided in: stock preparation, forming section, pressing, drying and creping (Lima, 2012; Ferreira, 2019). In the Figure 4 are shown the blocks diagram of a papermaking process.

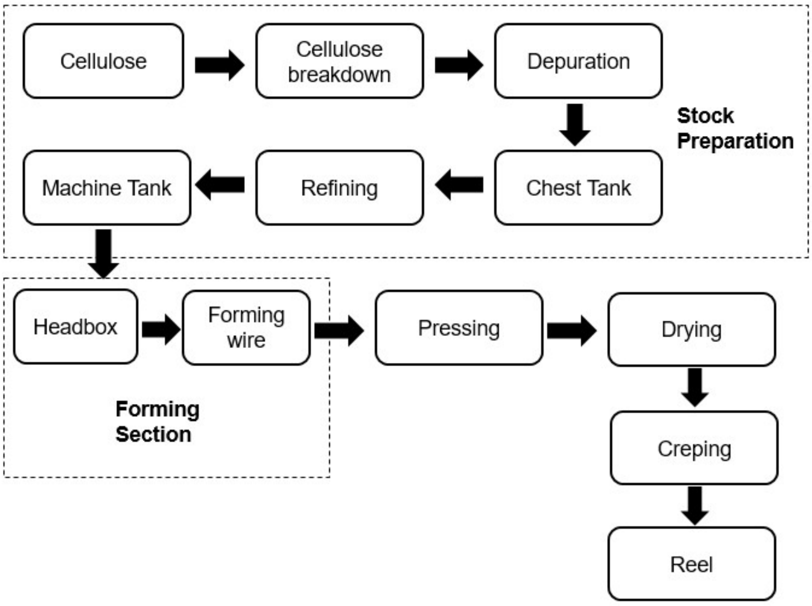


Figure 4. Block diagram of a general tissue papermaking process. Adapted from (Ferreira, 2019).

The first operation is the stock preparation, where the cellulose is breakdown in the hydropulper. In this equipment cellulose fibers are dispersed in water, the amount of water added must be sufficient to make the mass pumpable. After that, there is a depuration step, which the main goal is removing contaminants with the least loss of fibers. These contaminants can be plastics, pieces of metal, wood, among others that can be introduced during the process or transport (Ferreira, 2019).

Subsequently, there is the refining process, which consists of a mechanical treatment that modifies the fiber structures irreversibly, subjecting them to the action of hydration and fibrillation, increasing the bonding forces between the fibers that will compose the paper sheet (Ferreira, 2019). This process occurs in an equipment called refiner. Normally, they are pressurized systems, and they can be of discs or conical (Figure 5).

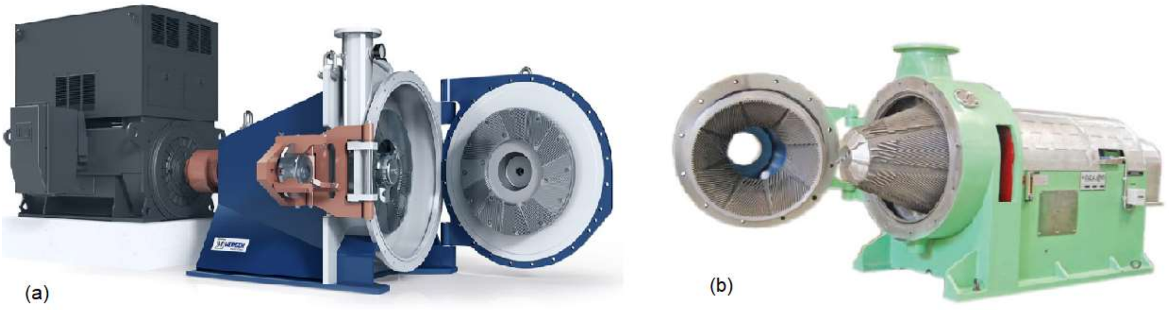


Figure 5. Disc refiner (a) and Conical refiner (b) (Hergen, 2021; Parason, 2021).

In the disc refiner the fibers are treated between two plates, which are parallel, one is the stator and the other is the rotor. Basically, there are three dominant refining stages, they are described below and showed in the Figure 6:

- Stage 1: fibers are trapped and accumulated between the edges of bars.
- Stage 2: the trapped fibers are compressed by the surfaces of the stationary and moving bars.
- Stage 3: fibers are affected by the shear forces, they also hit the bars on the surface to edge and again edge to edge.

Two different forces act on the fibers during the bar crossing, one is due to the contact of the fibers to bars and the other one is between the contact fiber to fiber (Gharehkhani et al., 2015).

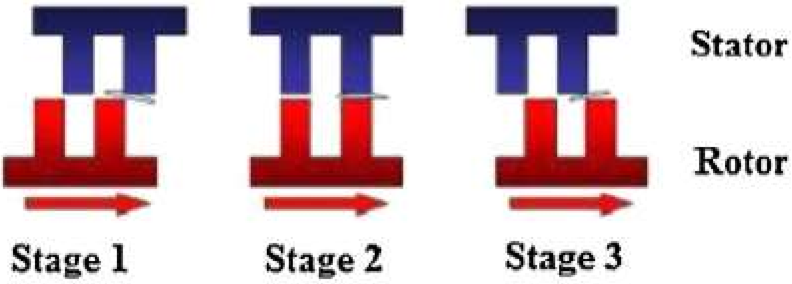
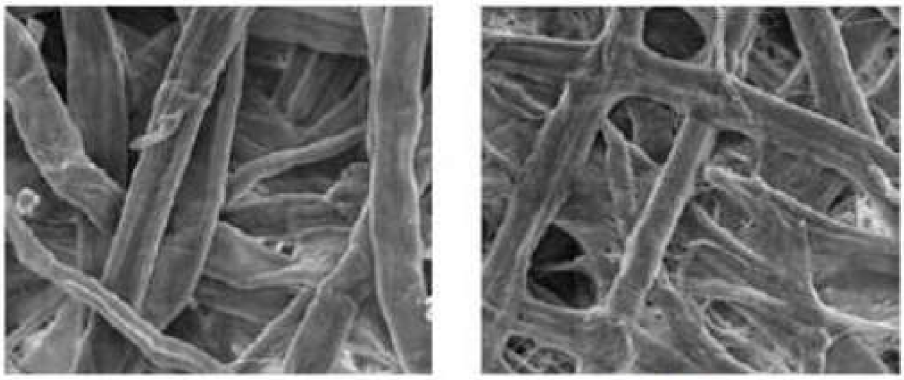


Figure 6. Refining stages between stator and rotor bars (Gharehkhani et al., 2015).

In the Figure 7 is shown cellulose fibers without refining and with refining.



Without refining

With refining

Figure 7. Cellulosic fibers with and without refining (Campos, 2012).

After the refining process, the pulp is stored in the machine tank. In the sequence, this pulp is diluted with white water, forming a fibrous suspension, in a pump called mixing pump or fan pump and it feeds the paper machine.

In the paper machine, the jet of the fibrous suspension is launched over the forming wire, being the jet pressurized and directed through the head box. It is the first section in the paper machine, knowing as forming, where the paper is formed by removing water from the fibrous suspension that come from the previous step, the stock preparation.

After that, there is the pressing process, in this step more water is removed from the paper web; then in the drying section, the paper sheet is dried until a dry content of approximately 95%. In sequence, there is the creping process where the tissue paper acquires specific characteristics as softness, absorption and specific volume. Finally, in the reel the paper web is rolled in jumbo-rolls (Ferreira, 2019; Pires & Cabral, 2011). Figure 8 shows a tissue paper machine, being possible to see each process step.

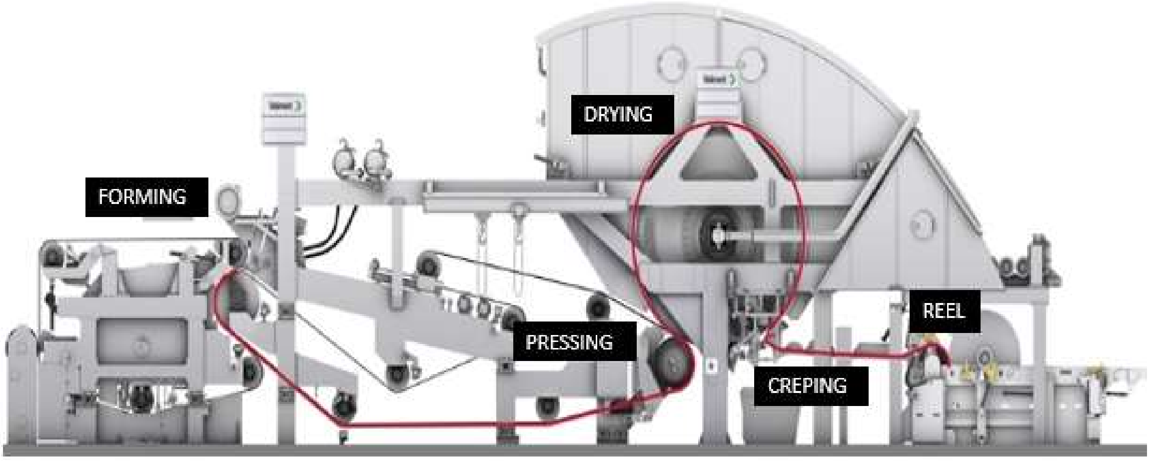


Figure 8. Tissue machine (Valmet, 2020)

Tissue paper manufacturing differs from the others kind of papers in the final of the drying step, where there is the creping process. Moreover, in the drying section there is only one dryer cylinder, with a large diameter that is usually called as Yankee, it could reach around seven meters of diameter. In addition, there is a hood that blows hot air directly to the paper web to help dry the paper (Ferreira, 2019).

The Yankee cylinder is a steam-heated pressure vessel. Besides the function of providing energy for drying, it is also responsible for transporting the sheet of paper, promoting the basis for the creping process (Uner, 2002). It is in the drying and creping process that the main properties and characteristics of the product to be manufactured are defined, such as: softness, tensile strength, thickness, specific volume, elongation and absorption (Silva, 2007).

Figure 9 represents the Yankee cylinder, hood and the creping process and Figure 10 shows the internal of a Yankee cylinder.

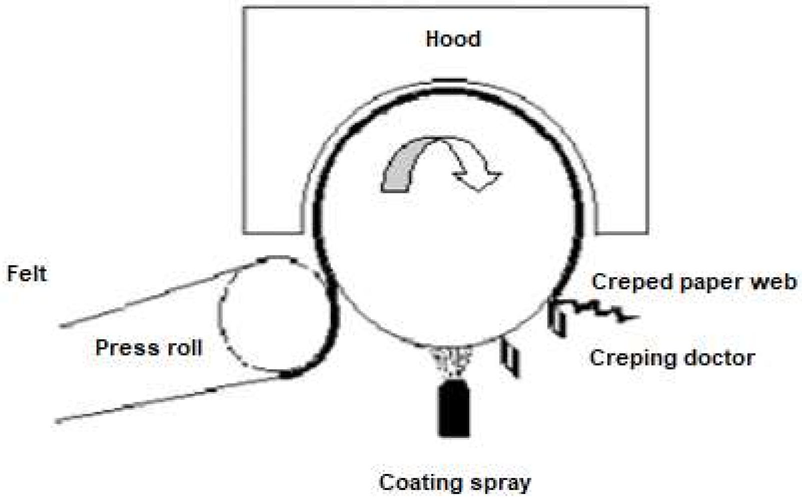


Figure 9. Yankee cylinder, hood and creping process. Adapted from (Boudreu, 2013).

Figure 10. Yankee Cylinder (Hergen, 2020)

3.1. Creping Process definition

The creping process is defined by the manufacturing process that distinguishes tissue paper from other papers. Creping aims to produce a softer, more voluminous and more absorbent paper and, for this reason, is considered one of the most important processes in the tissue papermaking. The creping process starts when the sheet of paper is transferred from the felt to the surface of the

Yankee cylinder through the press roll and is scraped from the surface of the cylinder with the aid of the creping blade (Coelho, 2009).

This process occurs chemically through the coating film, composed generally by adhesive and release agents. These chemicals are sprayed on the Yankee surface promoting and controlling adhesion between the paper sheet and the Yankee dryer. This film also protects this surface and preventing excessive wear of the creping blades (de Assis et al., 2020; Ferreira, 2019). In sequence, the paper sheet is dried to a dry content around 95% and it is scrapped off the Yankee surface through the creping blade; the energy from the blade leads to a wrinkling of the paper, breaking partially the physical structure of the sheet. Thus, microfolds are created and piled up on top of each other on the creping blade. In the moment that the pile of microfolds achieves an enough high, the pile falls into a macrofold. A new pile with microfolds is than started and the process continues (Boudreau, 2013). In the Figure 11 shows the microfold and macrofold of tissue paper and the creation of microfolds and macrofolds during the creping process is shown in the Figure 12.

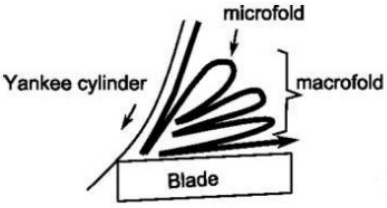


Figure 11. Microfold and macrofold (de Assis et al., 2018)

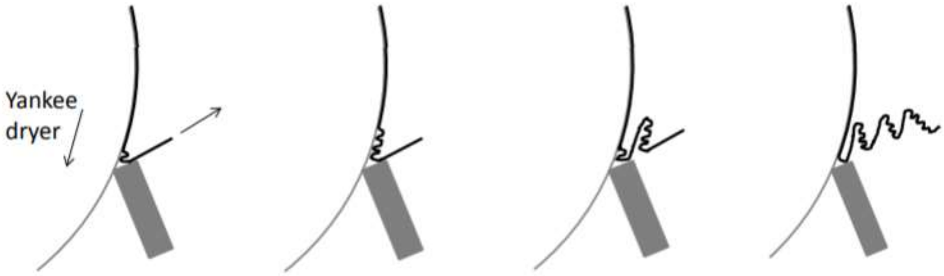


Figure 12. Creation of microfolds and macrofolds (Boudreau, 2013).

After the creping process, the difference in speed between the Yankee drier and the reel defines the crepe ratio. There is a reduction in paper sheet length and the crepe ratio controls the extensibility of the paper web (de Assis et al., 2020).

The crepe ratio (Figure 13) is defined by equation 1 and 2.

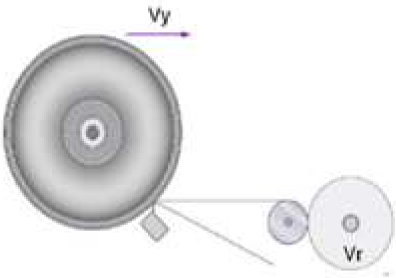


Figure 13. Crepe ratio (Ferreira, 2019)

$$Crepe\ ratio = \frac{Yankee\ speed}{Reel\ speed} \qquad (1)$$

The crepe ratio can be adjusted according to the desired characteristics of the paper; in this case the values are always greater than 1. These values vary from 1.05 to 1.60, but the most common values in the industry are between 1.10 to 1.35. If the crepe ratio is closer to one, the paper is very stretched, it will have a smaller elongation; on the other hand, higher crepe ratio will provide a paper web with greater elongation (de Assis et al., 2020; Pan et al., 2016).

The crepe ratio also can be expressed in percentage, as show in the equation 2.

$$Crepe\ ratio = \frac{Yankee\ speed - Ree\ \ speed}{Yankee\ speed}.100 \qquad (2)$$

In this case the values are always less than 100%, generally between 5% to 38%. Both equations are used in the tissue paper industries to calculate the crepe ratio.

4. Tissue properties

Tissue papers have important properties as dry tensile strength, wet tensile strength, water absorbency capacity and softness. As there are different grades of tissue paper, each one has its priority of properties and consumer ranks them differently. For example, facial tissue has softness as the most desirable property; on the other hand, water absorbency capacity and wet tensile strength are the most important characteristic for paper towels (Liu, 2004).

Ramires (2013) summarized in Table 1 the main desired characteristics for different tissue papers.

Table 1. Characteristics of different tissue papers. Adapted from (Ramires, 2013).

Type of paper	Desired characteristics
Hygienic	Softness, bulk, absorption, strength
Paper towel	Absorption, wet strength, bulk, dry strength, softness
Napkin	Softness, bulk, dry strength, texture, absorption
Facial tissue	Softness, wet strength, dry strength, absorption

4.1. Grammage

This property measures the paper weight per area of the paper sheet, the common unit used is g/m². In tissue paper grammage is low, ranging from 10 to 40 g/m², varying according to the type of tissue paper (Campos, 2012; Holik, 2006; Roberts, 1996). The grammage is measured according to the standard ISO 12625-6.

4.2. Thickness

Thickness is important because this property determine the roll diameter of rolled products or the stack height of folded products. Usually, it is measured on a multiple plies using a deadweight micrometer and quoted in µm. The standard used for this measurement is ISO 12625-3.

4.3. Specific volume (bulk)

The specific volume or bulk of the paper web, usually measured in cm^3/g, is the volume that a certain known mass of fibers occupies in space when the sheet of paper is produced. This characteristic is widely associated with structural softness, a paper with greater bulk may be more pleasant to the sensations that generate the perception of softness (Ramires, 2013). It is calculated through the thickness divided by grammage. The measure of the specific volume is not usual in tissue paper mill.

4.4. Softness

Softness is the one of the most desired properties in tissue paper, especially for toilet paper, napkins and facial tissue.

This property is related to the human feeling when the paper is touched. It is not easy to determine because it involves a high level of subjectivity. It has two principal components: structural and superficial softness. The structural softness is generally correlated to the elasticity module of the paper web, while the superficial softness is correlated with its surface texture (Ramires, 2013).

Structural softness is defined as the perception of softness obtained when the sample is pressed by hand. The superficial softness is the feeling obtained when the fingertips are lightly rubbed over the surface of the material (Milanez & Rost, 2005).

The human panel is the most widely accepted method to measure the softness. There are two methods of human panel: scoring and ranking methods. In the scoring method, trained people should grade the softness of sample tissues on a certain scale, according to references with fixed scores; so the participants grade the samples against the references provided. In the ranking method the participants should rank the samples from least to softest by a pair-wise comparison, in this case, there is not necessary reference samples. Other method used to measure paper softness is using an equipment, which was created to mimic the perception of softness of the human hand. This equipment is the Tissue Softness Analyzer (TSA), produced by Emtec. The measure of the softness in this equipment is by spinning a lamellar fan on the surface of the sample. When the lamellas of the fan touch the free fibers of the sample, the roughness of the surface and the overall stiffness of the sample are measured. In this equipment an algorithm made the calculus using the panel test results, and with the values of grammage and thickness a value of handfeel (HF) is given; a higher HF value corresponding to a higher softness (Wang et al., 2019).

4.5. Water absorption capacity

This characteristic is important for tissue papers because it measures the amount of water that can be absorbed per gram of paper. All kind of tissue papers should have this desired characteristic (Ramires, 2013). The standard ISO 12625-8 shows the methodology to analyze the paper water absorption.

4.6. Dry tensile strength

Dry tensile strength is defined as the amount of force, in a given direction, that a sheet of paper can withstand without breaking. This property is very important to the machine runnability; low dry strength can generate paper web breaks. It is also a characteristic that is important to some tissue papers, like kitchen towels and napkins (Ramires, 2013). In order to achieve the desired dry tensile strength for the end product, some additives can be used or a percentage of long fibers (softwood) in the fibrous mixture can be added. This property is analyzed by the standard ISO 12625-4.

4.7. Wet tensile strength

Wet tensile strength is crucial to many applications, specially to paper towels; this property is defined as the strength of the paper after receiving a certain amount of water (Ramires, 2013). This property implies that the paper sheet will maintain a high level of its strength, usually between 20% to 40%, even when it is saturated with water. The additives used for wet strength work by forming covalent bonds between fibers through an adhesive or by forming their own cross-linked network of covalent bonds (Bajpai, 2018). It is very common to use additives based on polyaminoamide-epichlorohydrin (PAE) to optimize this property (Ramires, 2013).

The methodology to measure wet strength is according to the standards ISO 12625-5.

4.8. Elongation

This property is the maximum elongation of a strip in a tensile test at rupture and is a measure of elasticity expressed as a percentage increase compared with the original length between the clamping jaws. It is an important property for tissue papers that it is generated in the creping process. Paper with more crepe waves has higher elongation. As the crepe is formed in the machine direction the MD elongation is higher than CD elongation (papers that are not creped the CD elongation is higher than MD) (Kirwan, 2013). Elongation is measured by the standard ISO 12625-4.

5. Papermaking chemistry

The raw material of paper is cellulose that is obtained usually from wood, although it is possible to use fibers from bamboo, cotton, sugar cane bagasse, linen, sisal and others (Santos et al., 2001). Cellulose was named by the French botanist Anselm Payen. In 1842, he isolated it from plant material as a solid residue after extensive alkali extractions. The word comes from cellulosus – Latin for “rich in small cells”. This name is indeed appropriate for the most important constituent in plant cell walls (Ek et al., 2009b). It is the most abundant renewable polymer resource in worldwide, its structure is a strictly linear homopolymer consisting of β-1,4-glycosidic linked D-glucopyranose units. The cellulose molecular formula is $(C_6H_{10}O_5)n$, where n = 10,000 to 20,000, and it depends on the cellulose material (Sixta, 2006). In the Figure 14 are presented these bonds.

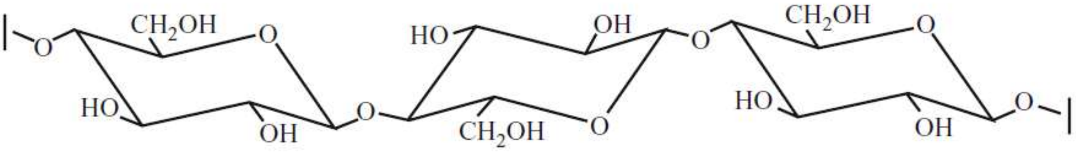


Figure 14. Linear structure of cellulose (Thorn & Au, 2009).

From a chemical point of view, fibers are formed by the interactions between cellulose molecules, provided by hydrogen bonds between the hydroxyl groups of glucose monomers. The hydroxyl groups of cellulose molecules can form two types of hydrogen bonds. Intramolecular bonds that occur between hydroxyl groups of adjacent glucose units in the same cellulose chain, these are the bonds that give them the same rigidity (Figure 15). On the other side, the intermolecular bonds occur between hydroxyl groups of adjacent chains and are responsible for the formation of the supramolecular structure, as shown in the Figure 16 (Santos et al., 2001; Fengel & Wegener, 1983).

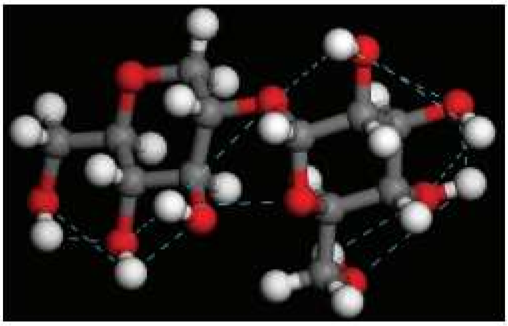


Figure 15. Intramolecular hydrogen bonds of a cellulose chain (Fengel & Wegener, 1983).

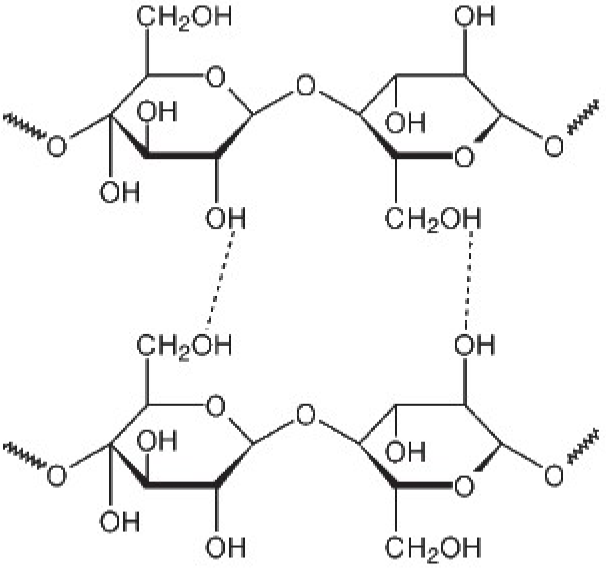


Figure 16. Intermolecular hydrogen bonds between cellulose chains (Santos et al., 2001).

The formation of hydrogen bonds between fibers allows the formation of paper sheet. Besides that, there are other types of fiber-fiber bond that occur in the paper: mechanical interlocking, capillary forces, Coulomb forces and Van der Waals forces. These bonds are also important for the interaction between the chemical additives and the fibers. It is important to guarantee the paper strength and other characteristics for various types of paper (Santos et al., 2001; Hirn & Schennach, 2015).

The paper properties are largely dependent on the bonds between the fibers. Particularly, those strength properties are directly related to the number of hydrogen bonds in the paper. The correct choice of a fiber material and the correct refining of the pulp are the normal way of affecting the number of bonds in the paper. There are still many limitations which ones can be achieved by refining and other process tools, so in the practical papermaker is continuously looking for ways to expand property and also process space to be able to manufacture new products or increase paper machine productivity (Lindström et al., 2005).

Cellulose fibers in aqueous solution normally carry negative charge due to the presence of ionisable acid groups in hemicelluloses and lignin. So, the carboxyl groups are primarily responsible for the negative charge character of most cellulosic materials (Cadena et al., 2009; Marques, 2013; Hubbe et al., 2007). The dissociation of the hemi-acetal hydroxyl groups of the cellulose fibers can also contribute to the negative charge on its surface (Nachtergaele, 1989).

Depending on the charge of the particle surface and ions in solution, attraction or repulsion phenomena will be observed. Since the fiber surface is negatively charged, the first ion layer formed around is of opposite charge, that is, positive. In the solid liquid interface, a two-part electrical layer is formed, as shown in the (Figure 17). The first layer is known as Stern layer, it is a thin layer of ions adjacent to the surface of the solid and of opposite charge. The other part is a diffuse layer, composed, principally, of ions of opposite charge of the solid (Gauy-Chapman layer). The Stern layer is absorbed, strongly, on the fiber surface and is not disturbed by the application of shear to the system. The zeta potential of the cellulose fiber is the existing potential between these two layers, the Stern layer and the diffuse Gauy-Chapman layer (Marques, 2013; Nachtergaele, 1989). In the sheet formation the zeta potential of each species to be retained should be within ±10 mV of zero to give maximum retention, although this value can change when it is used high molecular weight charged polymer for retention (Bajpai, 2018).

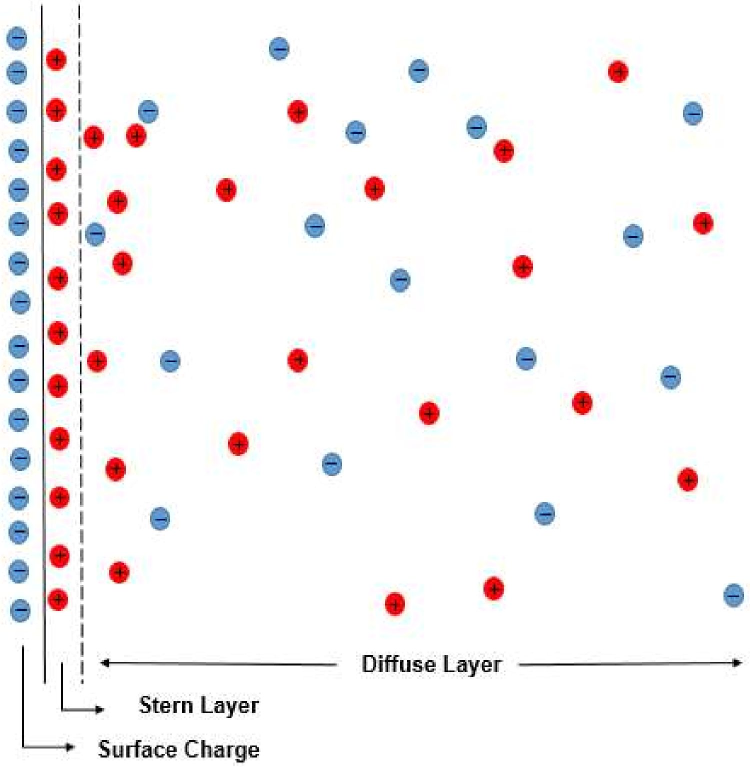


Figure 17. Electrical potential. Adapted from (Nachtergaele, 1989).

In addition to the zeta potential, it is possible to determine the ionic demand of a suspension. This parameter can be defined as the amount of polymer that needs to be added to a given sample to cancel the surface charge of the colloidal matter in it. Since the suspensions found in paper mills are mostly negatively charged, the polymer used for neutralization is usually cationic (Marques, 2013).

Refining process produces some effects in the fibers, resulting changes in fiber structure, such as fibrillation, which can be divided in external fibrillation (increasing the specific surface area of fibers) and internal fibrillation (breakage of inner bonds and fiber swelling), fines formation, fiber shortening and fiber straightening. In the refining process, some changes happen to the electrokinetic properties of fibers take place. When suspended in water, fibers develop a negative surface charge, it is widely known that charge groups affect the fiber swelling, fiber conformability and flexibility, wet-end chemistry, retention of cationic papermaking additives, flocculation and paper web mechanical properties, like dry and wet tensile strength (Gharehkhani et al., 2015). Therefore, a detailed knowledge of these interactions is important to improve paper properties, machine runnability and whole process optimization.

5.1. Additives for papermaking

Chemicals used in papermaking can be divided into two groups: functional and process chemicals.

Functional chemical additives add value to the end product, introducing properties superior to those of untreated paper (Haettich & Vazquez, 2018). These additives are substances that provide specific quantifiable properties in the paper sheet. The most relevant additives are used for dry strength, wet strength, softness and shade/color control (González, 2017).

Process chemicals are added to avoid and/or compensate operational disturbances that may occur in papermaking process. They are used to improve production, efficiency, reduce the number of paper breaks and machine stoppages. They are chemicals for treatment of fabrics, pitch and stickie's agents, defoamers, biocides, retention agents and drainage agents (González, 2017; Haettich & Vazquez, 2018).

Wet strength resins and softeners agents are the two most frequently chemical additives used in tissue production. The addition of the first one is necessary for many tissue products, since it can render enough strength to remain the paper integrated and applicable under wet conditions. The softeners agents are used to improve tissue softness, usually it is added in the wet end of the tissue machine (Liu, 2004).

5.2. Functional Chemicals

5.2.1. Dry strength

Currently it is used some additives for this purpose, starches are widely used as dry strength agent; polymers are become more common in the paper mills.

Enzymes used as auxiliary of refining are also used aiming to reduce refining energy or dry strength additives.

5.2.1.1. Starch

Starch is a polymer of glucose, composed of two different types of macromolecules called amylose and amylopectin. The proportion between these molecules are directly related to the functionality of the starch. Amylose is a practically linear structure and is formed by glucose monomers, with a degree of polymerization from 1000 to 5000 units, where the monomers are linked by α-1,4-glycosidic bonds, which may also contain 0,1% of α-1,6-glycosidic bonds (Figure 18) (Ramires, 2013).

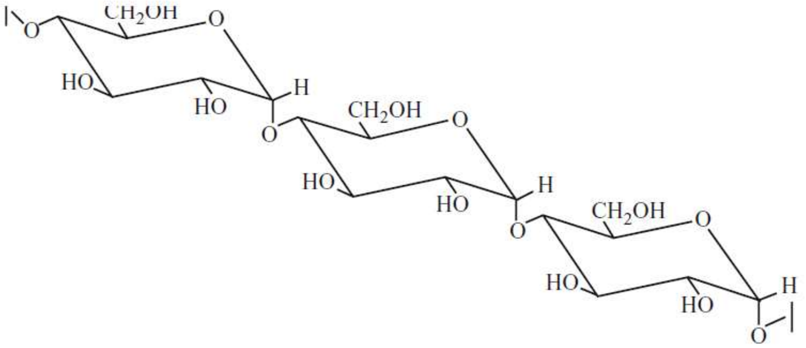


Figure 18. Amylose structure (Thorn & Au, 2009).

Amylopectin, unlike amylose, is a highly branched and high molecular weight molecule, composed of α-1,4-glycans, arranged in groups and interspersed with α-1,6-glycans (Ramires, 2013). The amylopectin structure is shown in the Figure 19.

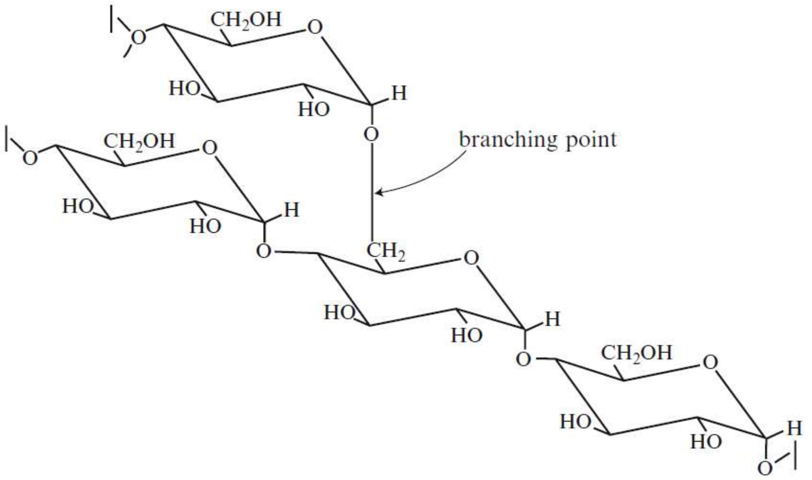


Figure 19. Amylopectin structure (Thorn & Au, 2009)

Practically all plants produce the starch. During the photosynthesis, the green leaves of plants, which contain chlorophyll, are able to absorb sunlight and utilize the energy catalyzing the formation of glucose and oxygen from carbon dioxide and water. This glucose is polymerized into starch, a food reserve, or cellulose (Thorn & Au, 2009).

In its natural form, starch has almost non-ionic state. Normally, starches are modified so positive and amphoteric ionic charges are introduced into their chains (Ramires, 2013). Considering the wet end chemistry, ionized starch is added to increase the paper dry strength, improving inter-fibers bonds. Starch in its cationic form also improves particle retention and can neutralize the anionic waste by controlling cationic demand (Silva, 2010).

5.2.1.2. Enzymes

Enzymes are groups of organic substances, normally from protein nature (there are also enzymes made up of RNA, ribozymes). They can have intra or extracellular activity, with catalytic functions, catalyzing chemical reactions that, without their presence, would hardly happen. This is achieved by decreasing the activation energy necessary for a chemical reaction to occur, resulting in a faster reaction. This catalytic capacity of enzymes makes them suitable for industrial applications (Domis, 2010).

Different microorganisms in order to degrade the cellulose produce the cellulase enzyme, which deconstructs the cellulosic structure and allows the release of nutrients (glucooligosaccharides and glucose) from the plant cell. There are four classes of cellulolytic enzymes, which differs by the hydrolytic mechanisms: endo-glucanases or endo-cellulase, cellobiohydrolases cellobiose, glucosidases or celobiase and exo-glucanases or exo-cellulase (Domis, 2010).

In papermaking, enzymes can reduce energy in refining process or reduce the use of dry strength agents, because cellulase enzymes (mainly endo-cellulases) cause partial depolymerization of cellulose, assists in fibrillation, promotes the fiber swelling (they also become more flexibles) and reduces the production of fines (Venditti, 2020).

5.2.1.3. Polymers for dry strength

The use of synthetic dry strength agents has been growth in the recent years. Polymers like glyoxylated polyacrylamides and polyvinylamine are common additives for this purpose. In some cases, these polymers can be used with natural products such as starch, in order to increase the strength beyond the level normally seen with these materials. Polyacrylamide is the most used polymer although polyvinylamine are growing in popularity. This is because of the relatively low cost, and the ability to readily put an ionic charge onto these polymers (Thorn & Au, 2009).

As the use of hardwood and recycled fibers increases and there is a tendency for the further lowering of the paper basis weight the use of dry strength additives become important to keep paper properties and quality. The conventional application of dry strength agents are in the aqueous solution to the paper stock before sheet forming (Mihara et al., 2008).

5.2.2. Wet Strength

Wet strength is a measure of paper's ability to maintain its dry strength when it is wet. Paper has wet strength when it retains at least 10% of its original dry strength after it has been fully soaked in water (Thorn & Au, 2009). Certain types of paper can only fulfil their purpose if they have adequate wet strength, such as filter papers, tissue papers, papers for bags, label papers, wallpapers, laminate base papers and all papers which, in the course of further processing and use, risk breaking when rewetted. The required wet strength is obtained with the aid of wet strength resins (Holik, 2006).

One of the first chemicals used as wet strength additive was formaldehyde, which rose the paper wet strength, but the offensive odor and the brittleness of the paper resulting from its low pH were drawbacks. After that, dimethylolurea, an urea-formaldehyde reaction product, produced wet strength in the paper web, but it was not effective due to it is readily soluble in water and not substantive to pulp fiber. Then, these products were improved and later supplemented by urea-formaldehyde (UF) resins which were modified with diethylenetriamine or other polyfunctional amines to give a cationic resin which was substantive to pulp (Dunlop-Jones, 1991).

In 1944, the first patented product was developed, melamine-formaldehyde (MF) resin. Comparing to UF resin the MF has relatively large number of reactive groups, the paper produced with MF resin has higher wet strength per unit of resin and also greater permanence during ageing. Both require, for best performance, acidic papermaking conditions. As it was needed a resin which could be used in a papermaking process that was neutral or alkaline, it was developed the polyaminoamide-epichlorohydrin (PAE) resins. In the production of the PAE resin it is formed an azetidinium group (Figure 20) which are responsible for the reactivity and the cationic character of this wet strength resin. As PAE resin is a polymer with highly cationic charge, it is rapidly absorbed by the fibers, which are negatively charged, in the pulp suspension. Nowadays, PAE resins are used extensively in practically all types of paper with wet strength as tissue papers, liquid packing, coffee filters, among others (Dunlop-Jones, 1991).

The glyoxalated polyacrylamide (GPAM), was introduced in the paper and board industry in the late of 1960s, becoming widely accepted. This resin gives temporary wet strength to paper and also behaves as a dry strength additive. This resin is prepared by crosslinking a low molecular weight polyacrylamide (PAM) with glyoxal, resulting in a cationic polymer which is substantive to pulp fiber. The cationic backbone is then crosslinked with sufficient glyoxal to react with most, but not all, of the PAM backbone amide groups (Dunlop-Jones, 1991).

A comparison among these four types of wet strength resins is shown in the Table 2.

Table 2. Comparison of wet strength resins (Dunlop-Jones, 1991).

Resin	**MF**	**UF**	**Glyoxal/PAM**	**PAE**
Principal advantages	Permanence Low cost	Low cost Easier repulping	Neutral sheet Dry strength Repulping temporary	Neutral or alkaline Retention Performance
On-machine cure (%)	50 - 60	20	60 - 95	10 - 30
Time to 100% cure (weeks)	1 - 2	1 - 4	1 - 2	1 - 2
Solids content (%)	12	25 - 40	6 - 10	12 – 33
Point of addition	Usually thick stock	Thick stock	Thick or dilute	Thick or dilute
First pass retention (%)	60	35	40	80
Broke handling	High temperature Low pH	Easier than MF	Easiest Helped by high temperature and high pH	Hypochlorite or high pH and temperature
Absorbency (without rewetters)	Poor	Fair	Best	Good
Sheet brightness	Fair	Good	Best	Fair
Usual drainage	Slower	No effect	Slightly faster	Faster
Storage (24°C) (weeks)	1	12 – 24 at lower solids	1 (10%) 4 (7,5%)	12
Relative cost	53	29	100	100

All wet strength agents are bi or multi-functional molecules with the capability to crosslink with each other or with cellulose. The correct choice of chemistry will depend on the pH of the papermaking process. Urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins have better performance in acidic systems; on the other hand, polyaminoamide-epichlorohydrin (PAE) resins are more effective in neutral and alkaline systems (Roberts, 1996). In the Table 3, the wet strength resins and their curing pH are summarized.

Table 3. Wet strength resins and their pH (Roberts, 1996).

Wet strength resin	**pH**
Urea-formaldehyde	3,8 – 4,5 (best at 4,0)
Melamine-formaldehyde	4,0 – 5,5 (best at 4,5)
Polyaminoamide-epichlorohydrin	5,0 – 9,0 (best at 8,0)
Glyoxylated polyacrylamide	4,5 – 7,5 (best at 6,0 – 7,0)

5.2.2.1. Synthesis of Polyaminoamide-epichlorohydrin (PAE) resin

PAE resin are the most commonly used wet-strength additives for wet strength. It is synthesized from polyamideamine chains by reacting with epichlorohydrin. First, a dibasic acid is condensed with diethylene triamine, resulting in a water-soluble polyamide. This polyamide has a secondary amine moiety which is alkylated with epichlorohydrin. Therefore, a number of reactions take place. It is formed, predominantly, tertiary aminochlorohydrin groups. Then it is self-alkylate to form 3-hydroxyazetidinium groups which are responsible for the reactivity and the cationic character of this wet strength resin (Obokata & Isogai, 2007; Dunlop-Jones, 1991). The Figure 20 shows the steps of the preparation of polyaminoamide-epichlorohydrin resins.

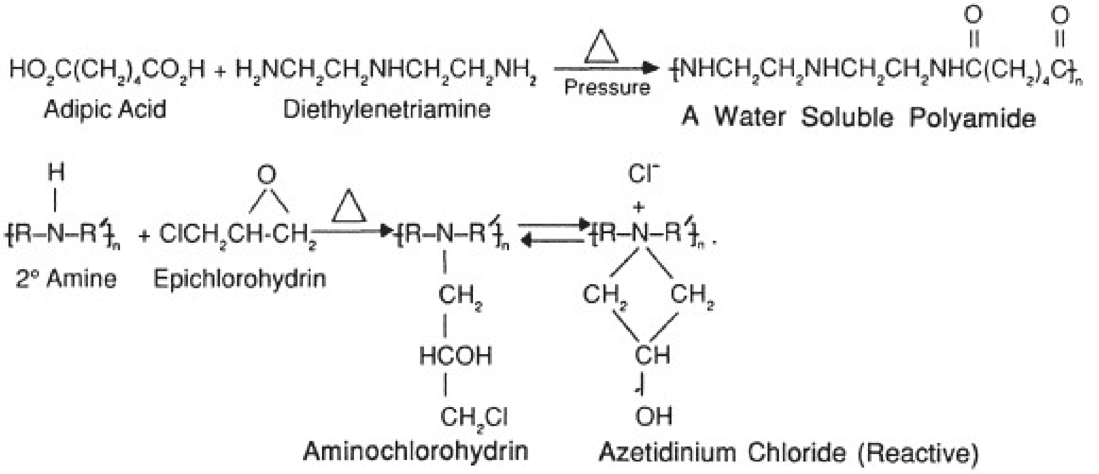


Figure 20. Preparation of polyaminoamide-epichlorohydrin resins (Dunlop-Jones, 1991).

5.2.2.2. Mechanisms of wet strength development of cellulose sheets prepared with PAE

According to Dunlop-Jones (1991) it is necessary one of four things described below to produce paper with wet strength:

1. add to or strengthen existing bonds;
2. protect existing bonds;
3. form bonds that are insensitive to water;
4. produce a network of material that physically entangles with the fibers.

Chemical additives were developed to achieve this characteristic, like polyaminoamide-epichlorohydrin (PAE) resins. In general, they are water soluble polymers and chemically reactive. The reactions can occur in two ways: homo-crosslinking, the polymers react with themselves; and co-crosslinking, the polymers react with cellulose or the materials on its interface (Obokata & Isogai, 2007; Dunlop-Jones, 1991). When the resin is dried in the paper sheet, there are two possibilities for reaction. In one, the groups hydroxyazetidinium can react through the amine groups of other molecules of resin, giving a homo-crosslinked network. The other one is the reaction of the groups hydroxyazetidinium with the available carboxyl groups in the paper. There is also a slow reaction between PAE resin and water (Dunlop-Jones, 1991). It is possible to see in the Figure 21 the reactivity of the PAE resin.

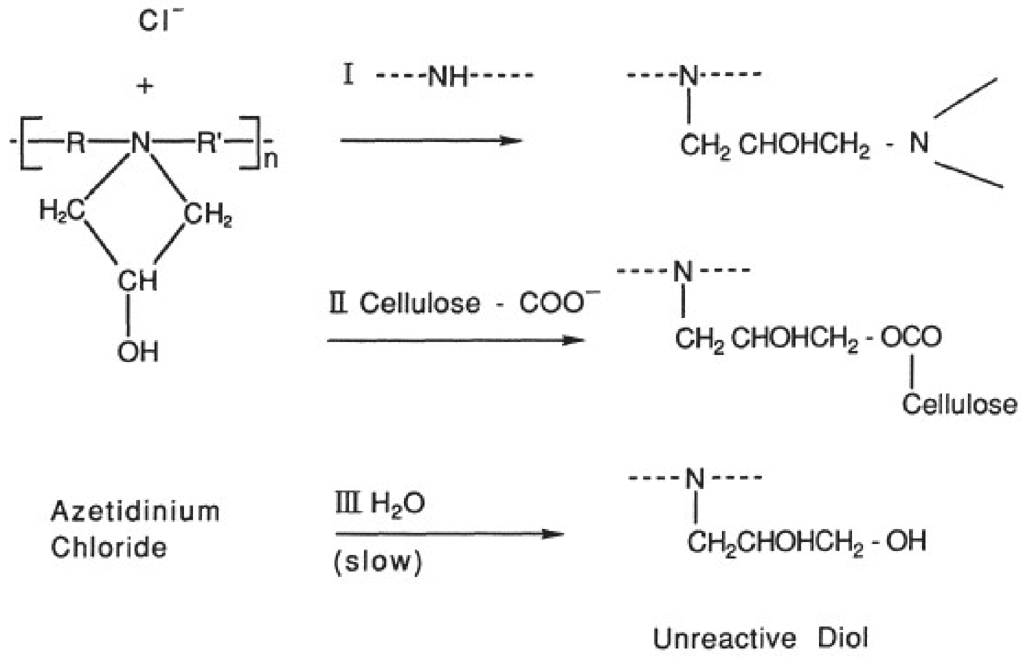


Figure 21. The reactivity of PAE resins. I: homo-crosslinking; II: co-crosslinking; III: slow reaction with water (Dunlop-Jones, 1991).

There is some evidence suggesting that PAE resins are predominantly involved in homo-crosslinking rather than being cellulose-reactive (Dunlop-Jones, 1991).

5.2.3. Softeners

Softeners are additives used to improve the softness sensation. They are compounds of quaternary dimethyl dialkyl ammonium. They act as disconnecting agents, interrupting connection between the fibers, improving the softness. These agents have some negative effects in the mechanical properties of the paper web and also it may decrease the hydrophilicity of the added papers and, therefore, their absorption capacity (Sabino, 2020). Paper with low dry strength tend to have a higher superficial softness sensation.

5.2.4. Dyes

They are additives that add color to the paper, changing the visual state of the fiber. Some insoluble dyes called pigments are also used in colored papers. Dyes can be divided into two main groups: inorganic dyes (natural and synthetic) and synthetic organic dyes. The most used is the water-soluble synthetic organic dyes. (Campos, 2012). The water-soluble dyes have very similar chemical constitution, there are little differences in structure, such as, by exchanging substituent groups ($–NH_2$, $–OH$, $–SO_3H$, and $–COOH$) can result in different properties like shade, light fastness or solubility. Knowledge of the chemical structure of the single components in the coloration of the paper helps the understanding of the electrostatic interactions between cellulose and dye (Holik, 2006).

5.2.5. Optical brighteners

Optical brightener is a fluorescent dye that absorbs part of the incident ultraviolet radiation, increases its wavelength by fluorescence and reflects it in the visible light range, actually in the blue light wavelength. Such a phenomenon increases the amount of visible light emitted by the paper. The blue fluorescent light compensates the natural yellow hue of the cellulose, resulting in a higher level of clarity than the original color. These compounds are di-sulfonated, tetra-sulfonated and hexa-sulfonated and they differ chemically from each other by the number of sulfonic groups of each molecule. The optical brighteners have in their molecular structure electrons in the fundamental state (S_0) that pass to an excited state (S_1) after the absorption of the UV energy of a photon. For the electron to return to its natural state, it is necessary to release the absorbed energy, it is carried out releasing a photon with less energy than the absorbed one (Figure 22). That is, the optical brightener increases the wavelength of the incident UV radiation, reflecting it as visible radiation (Manfredi et al., 2014).

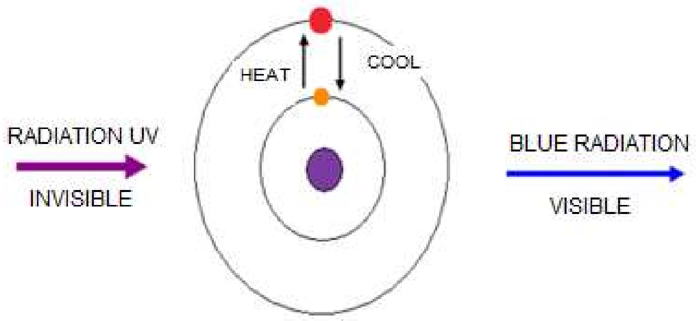


Figure 22. Fluorescence phenomenon. Adapted from (Manfredi et al., 2014).

5.3. Process chemicals

5.3.1. Treatment of fabrics

It is necessary use chemicals to cleaning fabrics in order to remove the contaminants maintaining their dewatering capacity. In addition, many chemicals act as surfactants and reduce the resistance to the flow of water in the felt, causing inconveniences such as picks on paper sheet during the passage through the press nip and difficulty of dewatering in the suction box (Oliveira, 2002). These chemicals can be acidic or alkaline, the origin of the contaminant will determine the choice of the product (Campos, 2012).

5.3.2. Pitch and stickie’s agents

These additives are dispersing agents, usually they consist of a mixture of synthetic surfactants. The action of dispersants can occur through two mechanisms, that is, stabilization of dispersed stickie’s and stabilization-dispersion of existing deposits (Soares, 2007). The pitch control and other hydrophobic substances in the stock water system can be done using adsorbents, like bentonites, micro crystalline talc or mica, which are pigments with a high specific surface area in water. It is also used a classical way to solve pitch problems on paper machine, by dosing aluminum sulfate (alum) in an acid environment (pH 4.5 – 5.5); at a higher pH (5.5 – 7.0) the alum can be replaced by poly-aluminum chloride (Holik, 2006).

5.3.3. Ionic charge control

Ionic charge is also known as ionic demand or chemical charge. This measure represents the amount of negative or positive groups that are present on the surface of the fibers, fines and colloidal particles in the suspension. It indicates how much cationic or anionic additive is necessary dosing to neutralize the charge of the fibrous suspension (Bonicenha et al., 2020). These additives are also called fixatives and there is a variety of fixatives to adjust the charge. Basically, these chemicals have two functions: the first one as a cationic fixative, which adsorbs colloidal anionic trash onto the fibers, avoiding agglomeration and deposits; and the second one as fixative with anionic/cationic charge, which impacts a lot the overall charges of the process that greatly influence the performance of other strategic additives such as wet strength resin, starches and retention aids. That is why the charge control measurements in white water or flotation water are so important to avoid over dosage and loss of performance of paper additives and process chemicals (Thorn & Au, 2009).

5.3.4. Defoamers

Defoamers are fatty surfactant substances that prevent foaming and associated sedimentation. It is added in the form of a solution, in a certain concentration to keep the formation of foam controlled. Typically, defoamers are used in tissue papers that use wet strength agents (in this case foam problems are more serious), in papers that use starch or secondary fiber with fibrous material. The use of these products must be controlled, as they usually can produce a release effect in the paper web on the Yankee dryer. This product requires constant monitoring of its application and may generate more foam if applied improperly (Campos, 2012).

5.3.5. Biocides

This additives control microorganisms present in the process, it makes the machine with a low level of fungal and bacterial contamination, increasing the interval between chemical cleaning, known as boil out (Campos, 2012). The attack of microorganisms can be controlled by physical or chemical processes.

- Physical: washing equipment with hot water, pressure, detergents, dispersants and scraping the surface with powerful brushes.
- Chemical: consists of incorporating preservatives into the system. The most used products are organosulfur, organohalogen and phenolic compounds (Robusti et al., 2014).

5.3.6. Retention and drainage agents

These chemicals are added in the paper manufacturing in order to do not lose cellulose fines and mineral charges by dragging water on the forming wire, compounds that increase retention are often added, which are called retention agents. The use of these compounds has become very common in papermaking, the most used compounds are polyacrylamides (Holik, 2006).

6. Optimize wet strength resin dosage

The use of wet strength resin mainly in the manufacturing of paper towel and napkins demand a good knowledge of the paper machine wet end. The application point, retention time and interaction among chemicals are some examples of features what happen in this part of the machine.

The optimization of the use of wet strength resin is difficult and large dosages can cause a cationic charge reversal in the circuit of the paper machine. In this case the operators must find a compromise between the action of the wet strength resin and charge reversal. The charge control along the stock preparation is essential for optimizing the use of wet strength resin. A method that is widely used in the paper factories is the charge measurement, which can be done through ionic demand and zeta potential analysis. The values of these analysis can help to investigate the impact of the wet strength resin (Stumm & , R. Grenz, 2009).

Stumm & Grenz (2009) showed that a strategy for optimization can be derived from charge balance in the paper manufacturing. They studied the charge balance, especially for the application of wet strength resin. It showed that if the additive adsorbs weakly, adsorption can be improved by changing the dosage point or increasing the reaction time. If the fibrous material used has a low surface charge, it will result in a low adsorption. The adsorption can be improved by choosing an additive with a lower charge density. Alternatively, the surface charge of the fibrous material can be increased by refining or by adding hydrocolloids, e.g. carboxymethyl cellulose.

Another variable that can influence in the paper wet strength and the adsorption of the wet strength resin is the retention time. Siqueira (2012) studied the adsorption of PAE resin at different dosages (0.1%, 0.6% and 1%) into the *Eucalyptus* pulp suspension. The adsorption was indirectly followed by measuring the zeta potential (microelectrophoresis and streaming potential methods). The results of different potential measurements obtained as a function of mixing and standing times of the PAE addition levels indicate that the adsorption, reconformation and/or penetration phenomena reach an apparent equilibrium for the tested concentrations after 10 min for electrophoretic mobility and streaming potential method (Figure 23 and Figure 24).

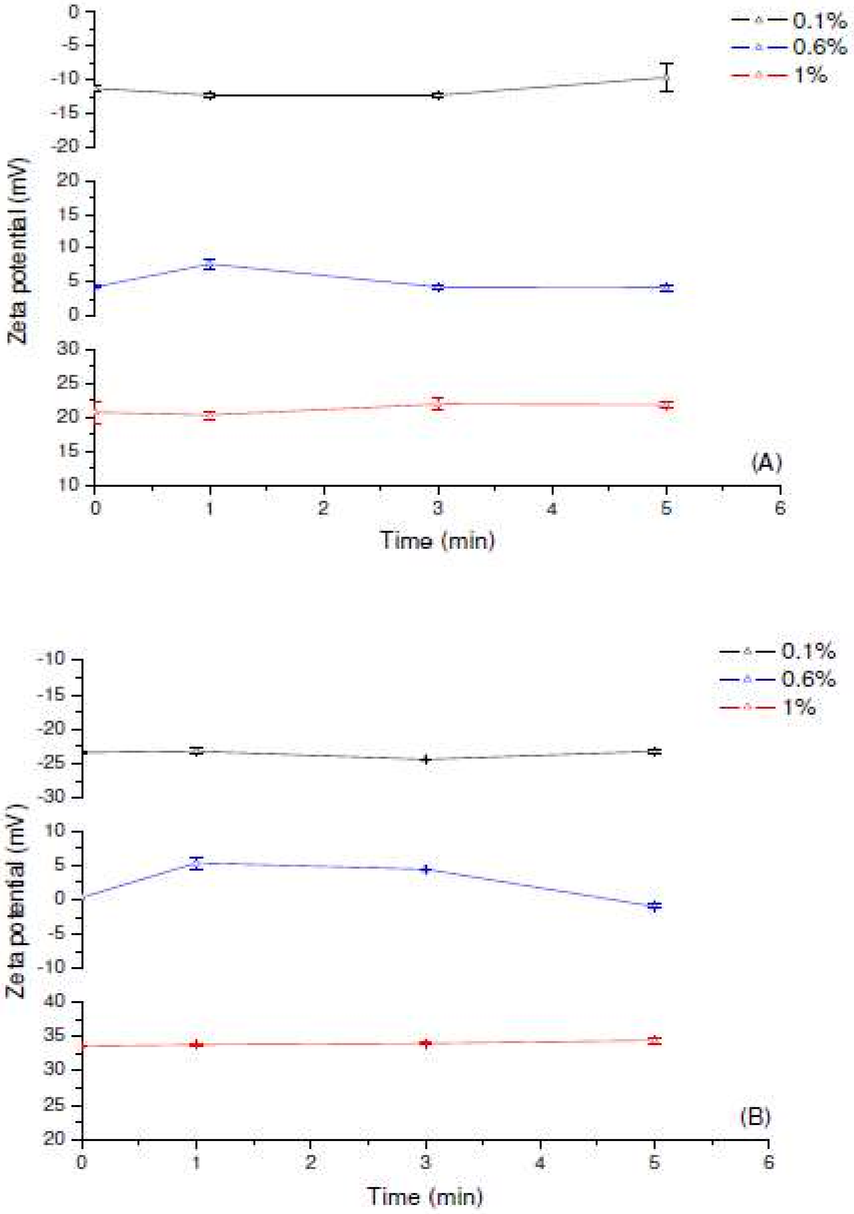


Figure 23. Zeta potential measurements for *Eucalyptus* pulp using (A) electrophoretic mobility and (B) streaming potential methods, as a function of the PAE concentration and the mixing time (Siqueira, 2012).

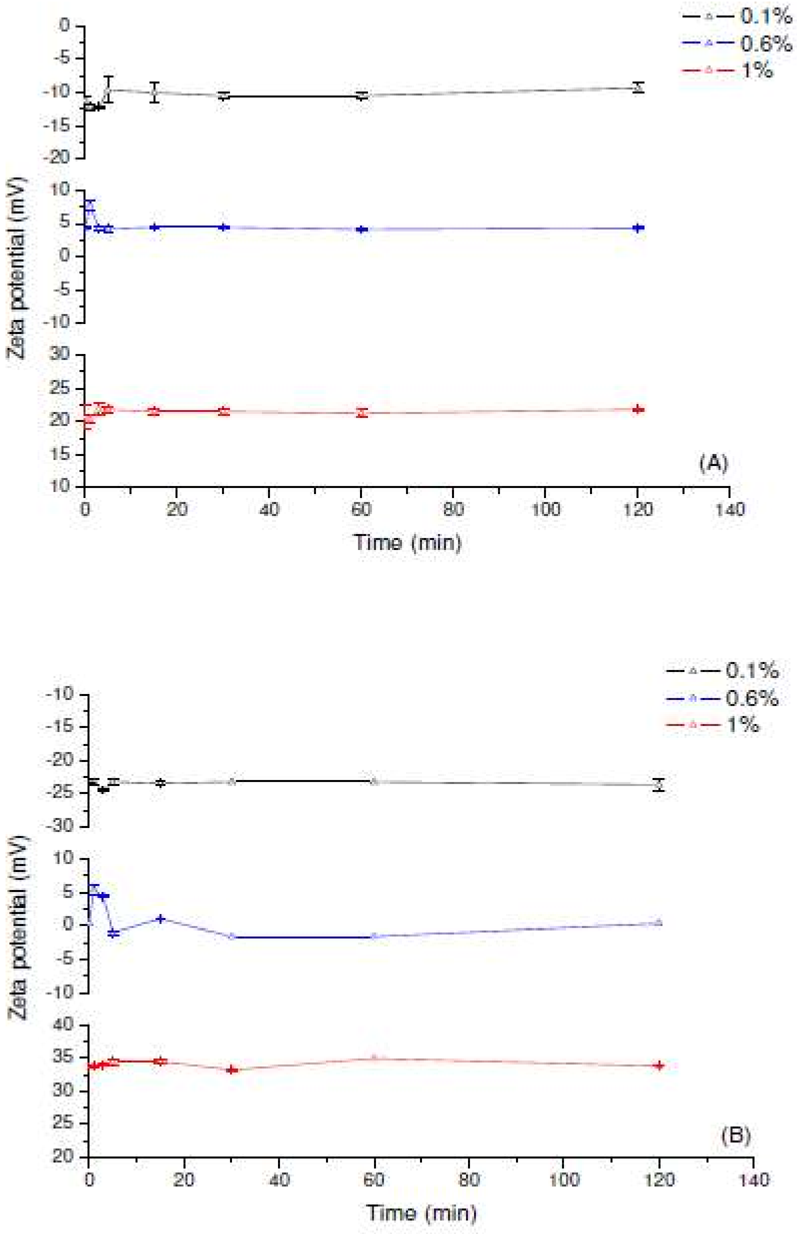


Figure 24. Zeta potential measurements of *Eucalyptus* pulp using (A) electrophoretic mobility and (B) streaming potential techniques as a function of PAE concentration and standing time (Siqueira, 2012).

Yoon (2007) showed that the PAE adsorption increased with time, in a few minutes the majority of PAE is being adsorbed, but, at longer times, it slowed down as the fiber surface became saturated (Figure 25).

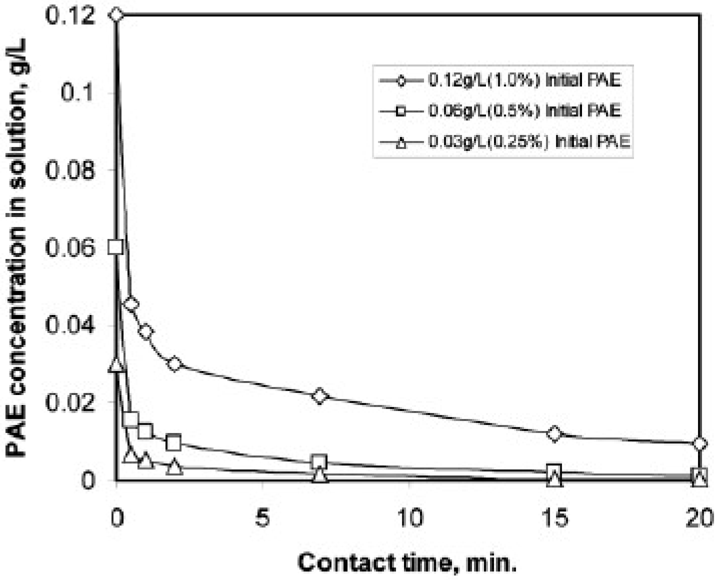


Figure 25. Change of concentration of PAE in aqueous cellulosic fiber suspension as a function of contact time (Yoon, 2007).

.

If the wet strength resin (PAE) has poor retention on the fibers of fines it may cause some consequences in the paper machine like generate foam, felt filling due to resin excess in the white water and it can affect the Yankee dryer coating, which become harder. So, the wet end condition can determine the retention of the resin, it is possible to use polymers to control the charge in the process and it can improve the PAE resin performance. When the process has high levels of anionic trash the use of fixing agents or anionic trash collectors (ATC) may control the overall conductivity and charge of the system. The ATC are typically polyamine-epichlorohydrin polymers, which are added to the papermaking process in a point before the PAE resin. These ATCs has cationic charge higher than the cationic charge of PAE resins. Therefore, ATCs form very effectively and neutral complexes with anionic species, cleaning the water of the papermaking system. Although ATCs are very useful at removing species that affect the PAE resin retention, their use should be done carefully to avoid over-cationization of the system. A value of ionic demand around −20 μEq/ml is a good target that helps the metering of ATCs (Thorn & Au, 2009)

In addition, cationic polymers and anionic polymers can be added in the papermaking process to increase the PAE resin retention. Anionic polyacrylamides

(APAM) and carboxymethylcellulose (CMC) are typical examples of anionic polymers used for this purpose. The use of these anionic polymers improve PAE resin retention due to the creation of more anionic sites on a fiber saturated with PAE resin. The anionic polymer interacts with the PAE resin, which is already retained on the fiber, allowing the polymer to be retained as well. The retention of these secondary polymers introduces additional anionic sites which can attract, interact and retain higher amounts of cationic PAE resin. This process will result in the formation of a large polymer complex or coacervate, as shown in Figure 26. Because of the higher molecular weight of CMC and APAM polymers this large polymer complex is able to bridge wider fiber-fiber spans, it improves the wet strength performance. Usually, the anionic polymers are added after the addition of the PAE resin, so good mixing is essential. A critical point is the ratio between the cationic and anionic polymers, an incorrect ratio can form deposits in the machine (Thorn & Au, 2009).

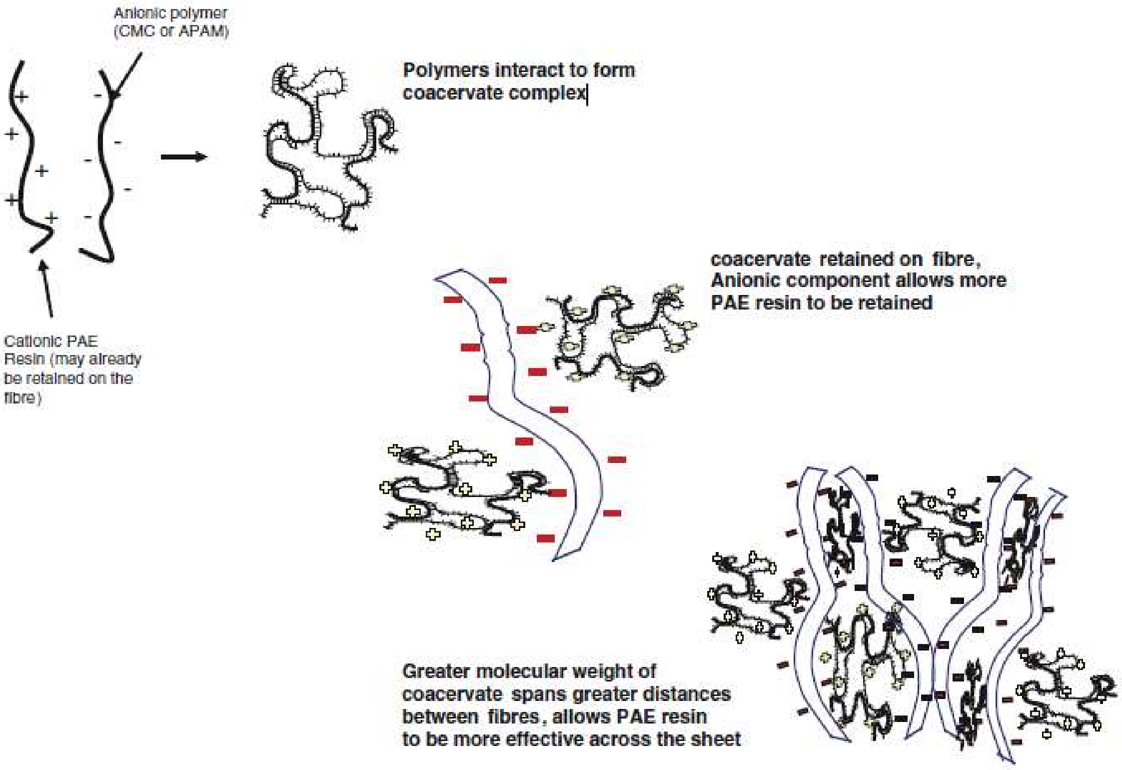


Figure 26. Formation of a large polymer complex or coacervate (Thorn & Au, 2009).

Another interesting study was conducted by Su et al. (2012), where they quantified the effect of PAE concentration on paper strength development. It was formed sheets with different concentrations of wet strength resin and analyzed the correlation between dry and wet tensile index. The Figure 27 shows that paper strength increased with polymer addition, but it reaches a maximum value of wet tensile index (4.6 Nm/g) at the PAE concentration of 10 mg/g (mg of PAE per g of dry pulp). After this point, the wet tensile index reduced to 4.2 Nm/g as a dosage of 20 mg/g of PAE and it maintain constant until 50 mg/g.

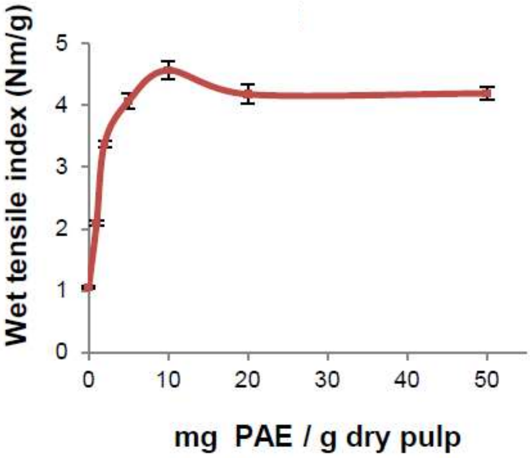


Figure 27. Effect of PAE concentration in wet tensile index (Su et al., 2012).

On the other hand, the dry tensile index reaches the maximum value (14.7 Nm/g) at a PAE concentration of 2 mg/g, then at higher PAE dosages there was a gradual decline in the dry tensile index (Figure 28).

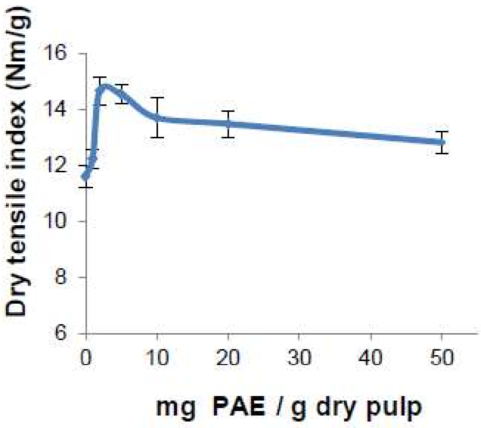


Figure 28. Effect of PAE concentration in dry tensile index (Su et al., 2012).

So, the maximum wet and dry strength index was achieved at different PAE concentrations. Analyzing the wet/dry strength ratio the Figure 29 shows that in the dosage of 5 mg/g this value increased significantly to 28%. The maximum value of this ratio was 33% at the dosage of 10 mg/g. After this concentration the ratio stabilized, at least to a PAE concentration up to 50 mg/g.

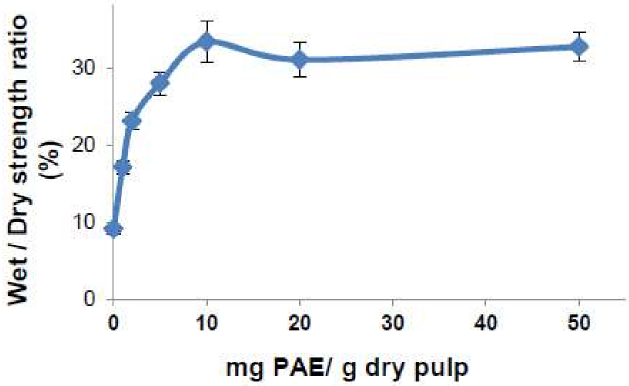


Figure 29. of PAE dosage on the wet and dry strength ratio (Su et al., 2012).

7. Materials and methods

The materials and equipment used in this work were supplied by the tissue company Santher located in Bragança Paulista – Brazil and Solenis S/A located in Paulinia – Brazil.

7.1. Raw materials

7.1.1. Pulp

The fiber matter used in this work was Bleached Hardwood Kraft Pulp (BHKP) made with *Eycalyptus urograndis*, a hybrid from the species *E. urophylla* and *E. grandis*. This pulp was produced by Suzano S/A, a Brazilian company, and the characteristics are shown in the Table 4. It was used this kind of cellulose because it is the most utilized in the manufacturing of paper towel in Santher, the tissue paper mill that supplied the pulp for this work.

Table 4. Bleached Hardwood Kraft Pulp (BHKP) characteristics

LOT IDENTIFICATION PROPERTIES				**Mill_Line T_L1** **Lot Z0605** **Date 05/06/2021** **Quantity 38**
ESPECIFICATION	**Unit**	**Method**	**Average**	**Standard deviation**
Brightness	%	ISO2470-1:16	**88.9**	**0.22**
Dry content	%	ISO638-08	**89.5**	**0.14**
Dirt	mm2/kg	ISO5350-2:06	**1.3**	**0.22**
Viscosity	dm³/kg	ISO5351:10	**805.9**	**2.6**
pH	-	ISO6588-12	**6.3**	**-**
Average fiber length	mm	TAPPIT234cm84	**0.8**	**-**
Coarseness	mg/100m	TAPPIT234cm84	**6.2**	**-**
Fibrous population	milhões	TAPPIT234cm84	**18.5**	**-**
TYPICAL PROPERTIES PFI 0 REV.	**Unit**	**Method**	**Average**	**Standard deviation**
Beating SR	°SR	ISO5267-1:01	**23.3**	**-**
Tensile index	kNm/kg	ISO1924-3:05	**28.1**	**-**
Specific volume	cm3/g	ISO534:11	**1.8**	**-**
TYPICAL PROPERTIES PFI 1500 REV.	**Unit**	**Method**	**Average**	**Standard deviation**
Beating SR	°SR	ISO5267-1:01	**38**	**-**
Tensile index	kNm/kg	ISO1924-3:05	**73.0**	**-**
Specific volume	cm3/g	ISO534:11	**1.4**	**-**
TYPICAL PROPERTIES PFI 3000 REV.	**Unit**	**Method**	**Average**	**Standard deviation**
Beating SR	°SR	ISO5267-1:01	**54.7**	**-**
Tensile index	kNm/kg	ISO1924-3:05	**91.7**	**-**
Specific volume	cm3/g	ISO534:11	**1.3**	**-**

7.1.2. Wet strength resin

The wet strength resin used was the Kymene 777LX produced by the company Solenis, this resin is formulated with polyaminoamide-epichlorohydrin (PAE) and has 12.5% of solids. This product works in a neutral to alkaline pH and develops a high level of permanent wet strength in the paper. It contributes to improve the efficiency of paper machines without affecting the water absorption capacity of the paper. This resin is the one that is used in Santher in products that demand wet strength.

7.1.3. Ionic charge control

The ionic charge control used was the Hercobond 2810 produced by the company Solenis, it has polyacrylamide in its formulation, it has anionic charge and solids content of 10%. This chemical was used due to the recommendation from Solenis to control the ionic demand of the process.

7.2. Methodologies

7.2.1. Stock concentration

The stock concentration is defined as the ratio of the oven-dry mass of material that can be filtered from a stock sample (aqueous suspension of pulp), to the mass of unfiltered sample; it is determined by the standard ISO 4119. The formula to calculate the stock concentration is showed below and the result is expressed in percentage.

$$C = \frac{m_2 - m_3}{m_1} . 100 \qquad (3)$$

Where:

m_1 is the mass of the initial sample

m_2 is the mass of the pulp filtered in the filter paper

m_3 is the mass dried in an oven at 105°C ± 2°C

C is the stock concentration in percentage

7.2.2. Specific load of the additives

The specific load in the industrial environment is measured in kilograms of additive per quantity of paper produced in ton, so, in this work, it was used this specific load. The calculation of the load of each additive was calculated based on the final mass of the formed sheet.

The formed sheets had the following dimensions: width of 0.25 m and length of 0.8 m, that is, an area of 0.2 m². The sheet weight was 9 ± 0.2 g, resulting in a weight of 45 ± 1.0 g/m².

There are wet strength resins with different solids concentration, such as 12.5% and 20%. The solids concentration is important because it is the active principle of the chemical. For example, the wet strength resin has 12.5% of polyaminoamide-epichlorohydrin, that is, the part of the additive which can react with the fibers. Due to, the amount of wet strength resin and the ionic charge control additive were calculated based on their quantity of solids. So, the specific load of the additives is showed in the equation 4.

$$Specific\ load = \frac{wet\ strenght\ resin\ (ml).density\left(\frac{g}{ml}\right).\left(\frac{kg}{1000g}\right).solids\ concentration(\%)}{paper\ mass\ (t)} = \frac{kg}{t}$$

(4)

7.2.3. Drainability measurement

The drainability measurement was made using the Schopper-Riegler test, which provides the resistance to drainage of a dilute pulp suspension. This measurement was done according the standard ISO 5267-1. It was used the Schopper-Riegler apparatus, a graduated beaker of 1000 mL with direct read of the °SR (Figure 30) and a precision scale of 0.1g.

Figure 30. Schopper-Riegler apparatus with a beaker graduated of 1000 mL with direct read of the °SR.

7.2.4. pH measurement

The pH measurement was performed using the pH meter UP-5 produced by Denver Instrument. This device was previously calibrated with buffer solutions of 4.0, 7.0 and 10.0.

The electrode which was in a KCl (3M) solution was washed with distilled water and gently dried with a paper towel, after this procedure the measurement was made by inserting the electrode into the sample, which contained enough amount for the electrode to be submerged, obtaining the pH value.

7.2.5. Ionic charge measurement

The ionic charge was determined using the equipment Mutek PCD-04 manufactured by the BTG company.

For this measurement, the stock pulp was filtered to remove the fines, using a BTG Mutek Becker sieve of 80 mesh. An amount of 10 mL of the filtered sample was collected and placed in the container along with the piston for measurement;

then this container was fitted to the device. In the Figure 31 it is possible to see the Mutek PCD-04.

Figure 31. Ionic charge equipment Mutek PCD-04.

After these steps, the equipment was turned on and the titration must be carried out with the opposite charge from the one indicated on the Mutek display, that is, if the charge is cationic, the anionic solution must be used to determine the ionic demand. On the other hand, if the device presents a negative result, the determination of the ionic demand will occur using the cationic solution.

To perform the titration, a 1 mL syringe was used and the titrant solution with 0.001N was added up to the load turning point shown on the equipment display. The result will be calculated as shown in the list below:

$$Ionic\ charge = 100.Titrant\ volume(mL) = \ \mu Eq/mL \qquad (5)$$

7.2.6. Zeta potential measurement

The determination of the zeta potential was done using the equipment Mutek SZP-10, produced by the company BTG. This measurement is very simple, a beaker with the pulp sample is positioned in the measure chamber and then it was selected

ON to start the measure, after 60 seconds the result is showed on the screen. The Mutek SZP-10 is showed in the Figure 32.

Figure 32. Zeta potential equipment Mutek SZP-10.

7.2.7. Pulp disaggregation

The pulp sample used in this work was collected in an industrial hydropulper produced by Valmet, which works with low stock concentration (4 – 6%). The cellulose was disaggregated using process white water without addition of any chemical. The characteristics of the disaggregated pulp are in the Table 5.

Table 5. Disaggregated pulp characteristics.

pH	8.1
Stock concentration [%]	4.3
Ionic demand [µEq/mL]	-6.0
Zeta Potential [mV]	-15.9
Drainability [ºSR]	18.0

7.2.8. Hand sheet preparation

For the preparation of hand sheets, it was chosen a grammage of 45 g/m². It was the lowest grammage that provides a good formation, without flocculation and it represents the grammage of a paper towel of two ply. A bad formation and flocculation in the paper sheet may affect measurements of dry and wet tensile strengths.

The sheet forming was done through a dynamic handsheet former. The equipment used was the FDA – Automated Dynamic Handsheet Former produced by Techpap (Figure 33). In this equipment the sheets formed have fiber orientation, so there are "machine direction" and "cross direction".

Figure 33. FDA – Automated Dynamic Handsheet Former produced by Techpap

The sheet was formed by the projection of pulp on a wire positioned in a rotating cylindrical jar. The wire was completely submerged in a water wall. The pulp projection was accomplished using an injector nozzle fixed on a delivery tube sweeping vertically up and down inside the rotating cylindrical jar. The final basis weight of the sheet depends on the consistency of the pulp, the number of nozzle sweeps and the pulp flow. A scoop system bails out the water wall after the sheet was formed and the water remaining in the sheet is drained by centrifugal force. After that the sheet was removed along with the wire from the cylindrical jar for pressing and drying steps.

7.2.8.1. Pulp preparation

Preparation of pulp suspension was done in the 22 L integrated pulp tank (Figure 34). It was prepared 5 L of the pulp suspension with a stock concentration of 0.20% to produce a sheet from 45.0 ± 1.0 g/m², then it was added the wet strength resin in the specific dosage (kg/t) related to final grammage. In the second part of this work, it was added the chemical to control ionic charge, this chemical was added in the pulp suspension, it was done to simulate the dosage in the fan pump a common point which is dosed in the paper machine. For each dosage of the wet strength resin it was waited 10 minutes to the PAE being absorbed and the fiber surface became saturated (Siqueira, 2012; Yoon, 2007) after this time the sheet was formed, this procedure was done to guarantee the fiber saturation and standardize the hand sheet preparation. In an industrial environment this time is not accomplished, usually the wet strength resin is dosed after the refining process. If the wet strength resin is dosed before the refiner, the mechanical action of this equipment can break the linkages between fiber and resin, reducing the efficiency of this chemical.

Figure 34. Tank with pulp suspension prepared

7.2.8.2. Equipment set-up

The equipment has a wire where the sheet is formed. In the Figure 35 it is possible to see the wire and the wire installation.

Figure 35. Wire (a), wire installation (b) and wire installed (c).

7.2.8.3. Sheet forming

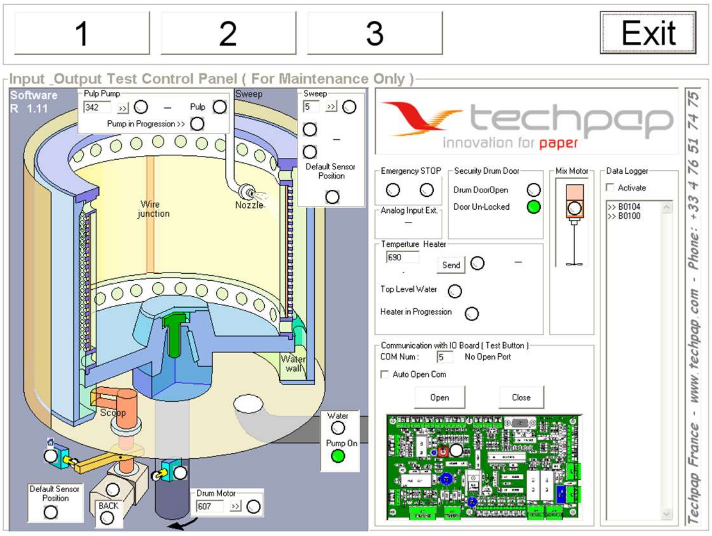
The sheet is formed by dynamic projection of pulp on a wire screen, which is placed in a rotating cylindrical perforated jar. The wire screen is drowned in a water wall.

The projection of pulp is done by an interchangeable injector nozzle, which is fixed on a wiping piston that moves it up and down along cylindrical water wall (Figure 36).

The final basis weight of the sheet depends on the type and consistency of the pulp used, the number of wiping as well as the pulp flow and number of pulp layers applied.

Figure 36. Sheet forming and injector nozzle.

A software is used to control the jar, wire speed, pulp flow and pulp speed. In the Figure 37 is showed the software interface. The jar velocity used was 456 m/min and the wire speed rotation was1200 m/min. The fiber retention in the sheet forming process was 90%.



Pulp Pump: 342
Sweep: 5
Temperture Heater: 690
COM Num : 5
Drum Motor: 607
Data Logger: >> B0104 >> B0100

Figure 37. FDA – Automated Dynamic Handsheet Former software.

After the final process, the sheet with the wire were removed, after that it was pressed using a metal roll and an absorbent paper (Figure 38). Finally, it was dried in another equipment that has a surface of stainless steel heated at 90ºC for 15 minutes (Figure 39). The paper sheet was dried until a dry content of 93 ± 1%.

Figure 38. Sheet pressing.

Figure 39. Sheet drying.

7.2.9. Measurement of the paper properties

The analysis of grammage, dry tensile strength, wet tensile strength and water absorption were carried out in a conditioned laboratory with room temperature of 21.5 °C and relative humidity of 42%.

7.2.9.1. Measurement of grammage

The determination of the grammage of the paper sheets of paper was carried out according to the ISO 12625-6 standard. For this, the sample area was measured in m², later this sample was weighed on a precision scale of 0.001g. The weight of the paper was determined using the calculation below:

$$Grammage = \frac{massa\ (g)}{área\ (m^2)} \qquad (6)$$

7.2.9.2. Measurement of dry tensile strength

The standard ISO 12625-4 was used to determine the dry tensile strength of the paper sheets. It was utilized an electronic dynamometer produced by Regmed model DI-21 it has load speed adjustment and accuracy of up to 0.1 kgf, having a measuring capacity of 20.00 kgf and working pressure from 3 kgf to 4.5 kgf; distance between the claws of 100 mm.

The size of the specimen used was:

- Width: 50 mm ± 1 mm.
- Length: enough to hold the claws, that is >100 mm.

The sample was placed between the claws, the sensor held the sample and then the test started; when the sample tore the dynamometer reader showed the result of the dry tensile strength in kgf (Figure 40).

The final result was obtained through the equation below and is expressed in gf/50mm.

$$Tensile\ strength = kgf.1000 = \frac{gf}{50mm} \quad (7)$$

Figure 40. Dynamometer (a) and dynamometer with the sample (b).

7.2.9.3. Measurement of wet tensile strength

The determination of wet tensile strength was through the standard ISO 12625-5. In this test, it was used the same dynamometer and test configuration to determine dry tensile strength.

The sample used to determine the wet strength was placed in the oven at a temperature of 105 ± 5°C for premature aging, the sample remained in the oven for 10 minutes. After removing the sample from the oven, it was waited for it to return to room temperature. After this step, the sample was folded and the fold was immersed in a beaker with water, moistening the sample as shown in the Figure 41.

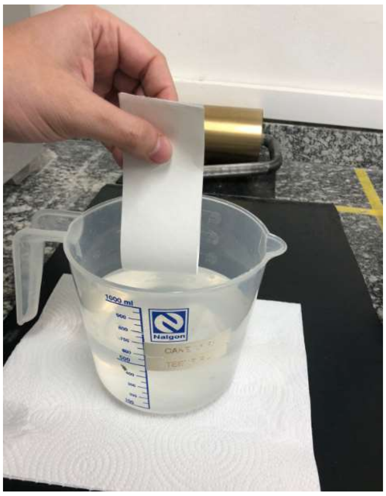


Figure 41. Wetting the sample for wet tensile strength analysis.

Afterwards, the sample was placed on five sheets of absorbent paper towels, which were on a flat and rigid surface. Another five sheets of absorbent paper towel were placed on top of the sample, then the metal roller (weighing 10 ± 0.5 kg and width 200 mm) was passed twice, one forward and one backward. The Figure 42 shows the wetted sample and the metal roller.

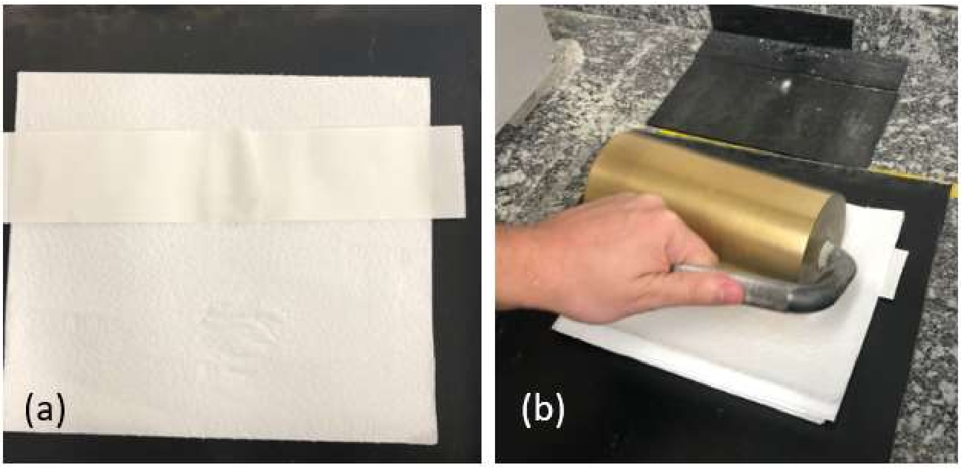


Figure 42. Wetted sample (a) and metal roller (b).

After this step, the sample was placed between the dynamometer claws (Figure 43) until the sensor held the sample and the test started. When the sample tore, the dynamometer reader showed the result in kgf and the final result is obtained through the equation (5).

Figure 43. Wet tensile strength analysis.

7.2.9.4. Measurement of water absorption capacity

The determination of water absorption was carried out based on the ISO 12625-8 standard, measuring the absorption water absorption capacity through the immersion test method.

The analysis started weighing around 5g of paper sheet, this sample was rolled up in a little basket and then they were placed in a beaker (Figure 44).

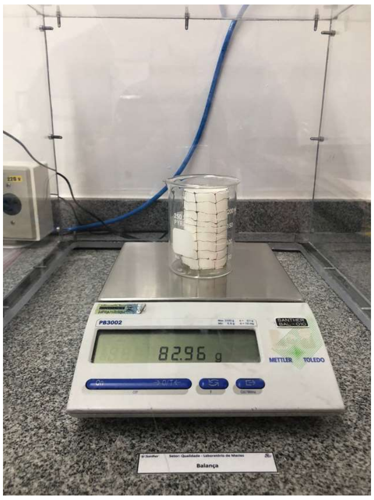


Figure 44. Paper sample in the basket for water absorption capacity analysis.

After that, there was another beaker which was filled with water. The basket and paper set were submerged in water for 30 seconds and then removed, waiting 60 seconds for the water to flow out (Figure 45).

Figure 45. Paper sample filled with water.

Then the sample was putted in an empty beaker and weighed again. The water absorption capacity is expressed in grams of water per grams of paper, and it was determined through the calculus below:

$$Water\ absorption\ capacity = \frac{m_3 - m_1}{m_2 - m_1} = \frac{g_{water}}{g_{paper}} \qquad (8)$$

Where:

m_1 is the mass of the basket and the beaker

m_2 is the mass of the paper sample, the basket and the beaker

m_3 is the mass wet paper sample, the basket and the beaker

8. Results and discussion

This work was divided in two parts for a better understanding of the influence of ionic charge, zeta potential and the ionic charge control additive for the tissue paper water absorption capacity, dry and wet tensile strength. As the examined paper sheets were not creped, the elongation, thickness and handfeel index were not measured, because these characteristics are mostly developed by the creping process.

The first part of this work deals with the analysis of paper produced “without ionic charge control”. The laboratory prototypes of tissue paper were formed employing a dynamic former with a weight of 45 ± 1.0 g/m². Each sheet formed had different specific dosages of wet strength resin: 0; 3.25; 6.5; 13 and 26 kg/t. The resin loads until 13 kg/t are commonly used in some products in tissue manufacturing, the load of 26 kg/t was chosen to analyze the extreme values of wet tensile strength, ionic charge and zeta potential. In each assay of paper sheet forming, the stock pH, ionic charge and zeta potential were assessed. After the sheet was formed it was measured the dry tensile strength, wet tensile strength and water absorption capacity. As in the sheet formation it was possible to obtain fiber orientation, all the measurements were done in the cross direction, because in tissue paper industries the wet strength tensile is measured only in this direction.

The second part of this work deals with the analysis of paper produced “with ionic charge control”. The paper sheets of same weight with the same specific loads of wet strength resin as in the first part of the study were produced. However, in this second series of assays, during the pulp preparation process, the pulp suspension ionic charge was controlled by adding the ionic charge control additive. The amount of this additive was enough to maintain the value of ionic charge between -10 and -21 µEq/ml. After that the paper sheets were formed. The value of ionic demand was kept in this range because a positive ionic demand can generate foam in the white water system, affecting the paper sheet forming and Yankee dryer coating.

In each part of this work, it was formed one sheet per specific dosage of wet strength resin, so it was prepared one pulp suspension per specific dosage and the measurements of pH, ionic charge and zeta potential were done one time; the grammage was also measured one time. The measurements of dry strength, wet strength and water absorption capacity were done in triplicate and average.

The results of all measurements of the two experimental parts are summarized in Table 6 and in Table 7.

Table 6. Results of the first part, without ionic charge control.

Grammage [g/m²]	Load of wet strength resin [kg/t]	pH	Ionic charge [µEq/mL]	Zeta Potential [mV]	Dry strength without ionic charge control [gf/50mm]	Wet strength without ionic charge control [gf/50mm]	Water absorption capacity without ionic charge control [gwater/gpaper]
45.8	0	8.1	-6	-15.9	2528 ± 158	120 ± 13	5.53 ± 0.46
45.3	3.25	8	-2	-5.7	2521 ± 305	478 ± 12	4.92 ± 0.11
44.8	6.5	7.9	4	-1.4	2609 ± 108	534 ± 24	4.84 ± 0.04
45.4	13	7.7	6	2.6	2792 ± 108	654 ± 21	4.97 ± 0.17
45.1	26	7.6	8	6.5	2739 ± 231	714 ± 40	5.20 ± 0.13

Table 7. Results of the second part, with ionic charge control.

Grammage [g/m²]	Load of wet strength resin [kg/t]	Load of ionic charge control additive [kg/t]	pH	Ionic charge [µEq/mL]	Zeta Potential [mV]	Dry strength with ionic charge control [gf/50mm]	Wet strength with ionic charge control [gf/50mm]	Water absorption capacity with ionic charge control [gwater/gpaper]
44.4	0	0.2	7.8	-18	-20.7	2883 ± 70	116 ± 11	5.76 ± 0.04
44.8	3.25	0.6	7.9	-14	-22.3	3206 ± 48	475 ± 21	5.28 ± 0.09
45.2	6.5	1.4	7.5	-10	-16.6	3287 ± 76	562 ± 16	4.87 ± 0.09
44.3	13	1.9	7.4	-14	-17.3	3414 ± 76	795 ± 49	5.36 ± 0.08
45.7	26	2.8	7.2	-21	-16.9	3617 ± 45	925 ± 34	5.14 ± 0.08

Through the results obtained it was plotted some graphics to visualize better all the relationships between loads of wet strength resin, ionic charge additive, ionic charge, zeta potential, dry and wet tensile strength and water absorption capacity.

Dry strength

In both experiments, without and with ionic charge control, the values of dry tensile strength increase as the load of strength resin increased (Figure 46). The dry tensile strength without ionic charge control increased 8% in the maximum dosage of wet strength resin, while when it was controlled the ionic charge the dry tensile strength increases 25% at the maximum dosage. Since the ionic charge control additive contained polyacrylamide in its composition, this chemical reagent and the PAE of the wet strength resin contribute to increase the dry tensile strength.

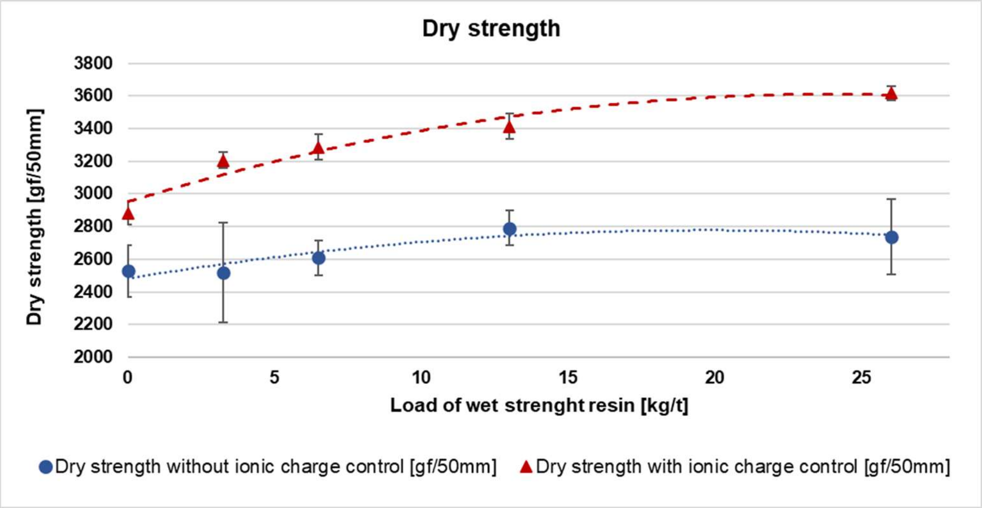


Figure 46. Dry tensile strength with and without ionic charge control additive.

As can be seen from Figure 47 and Figure 48, there is no clear correlation could be found between the ionic charge of the stock and the dry strength of the formed papers.

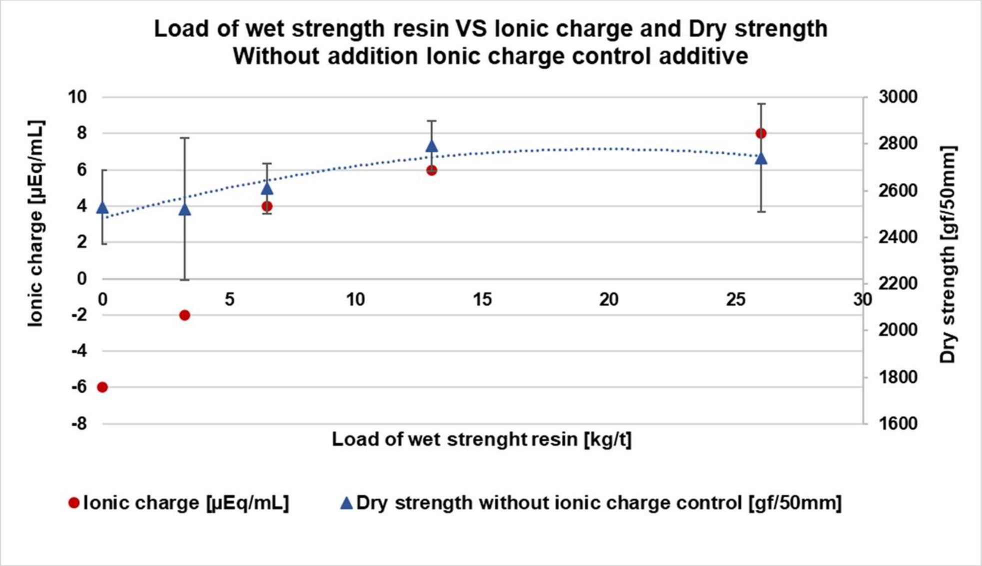


Figure 47. Load of wet strength resin *versus* ionic charge and paper dry strength without addition of ionic charge control additive.

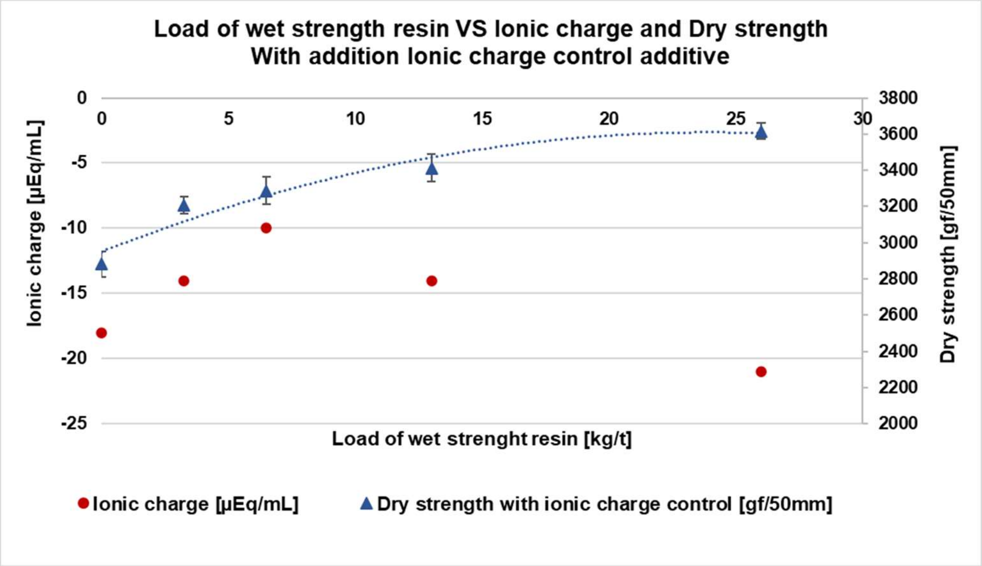


Figure 48. Load of wet strength resin *versus* ionic charge and paper dry strength with addition of ionic charge control additive.

The relation between zeta potential and dry tensile strength is shown in the Figure 49 and Figure 50. In the experiment without ionic charge control the dry tensile strength has tendency to level off when the zeta potential value is positive, and which is observed after the dosage of 13 kg/t of wet strength resin (Figure 49). It indicates that the fiber surface has no more points to linkage, so it was not formed more hydrogen bonding between fibers and the dry tensile strength do not increase anymore. At the same time, when adding the ionic charge additive, it is possible to obtain higher dry strength values (Figure 50). This fact clearly indicate that the addition of ionic charge controller allowed the improvement of hydrogen bonding between fibers and the crosslinking between polyacrylamide and fibers.

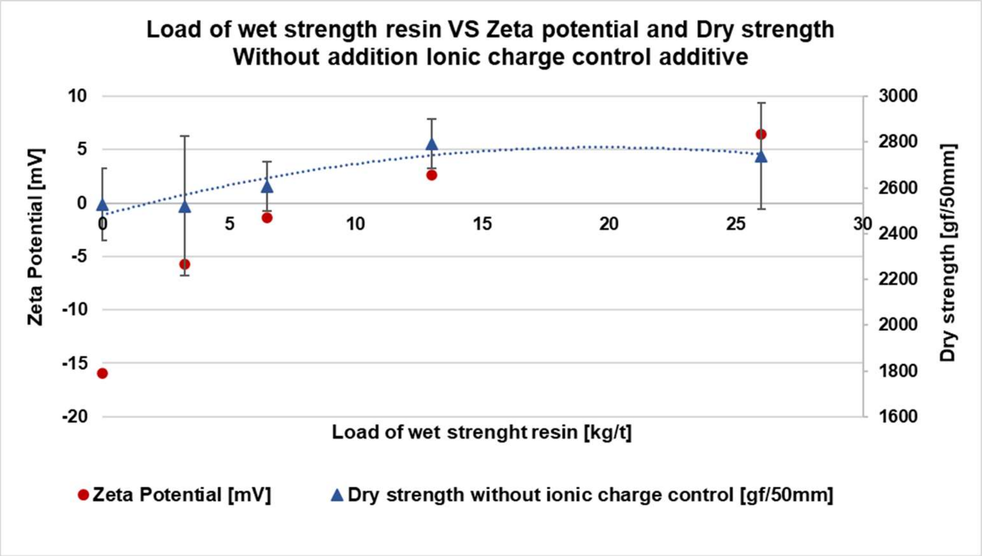


Figure 49. Load of wet strength resin *versus* zeta potential and paper dry strength without addition of ionic charge control additive.

.

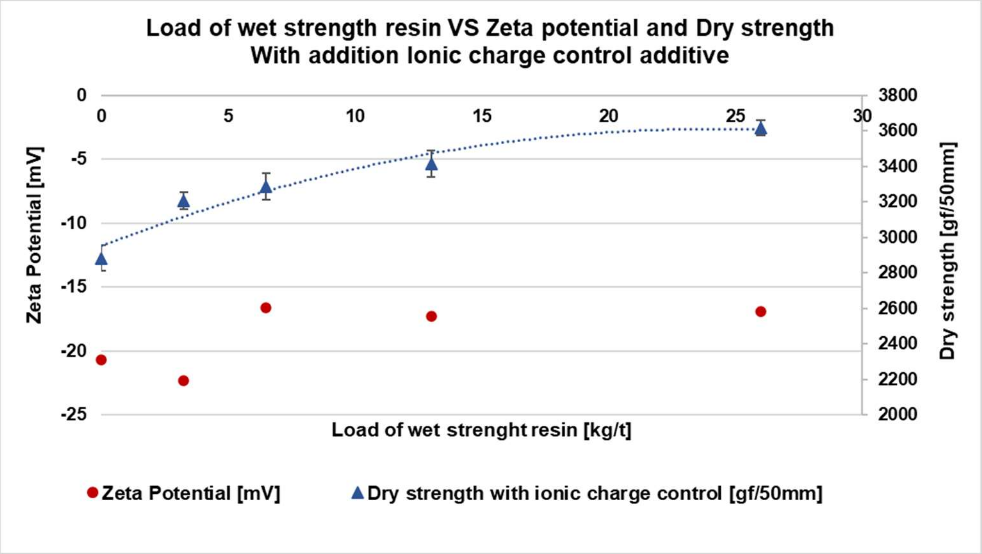


Figure 50. Load of wet strength resin *versus* zeta potential and paper dry strength with addition of ionic charge control additive.

Wet strength

The Figure 51 shows the results of wet strength tensile with and without ionic charge control of pulp suspension. These results clearly show that when it is used the ionic charge control additive, the values of wet tensile strength are significantly enhanced. The paper sheet with 26 kg/t of wet strength resin without ionic charge control additive has lower wet tensile strength than the paper sheet with 13 kg/t with ionic charge control additive. Hence, when optimizing of the wet strength resin dosing, it is possible to obtain the same wet tensile strength with less wet strength resin dosing using this ionic charge control additive.

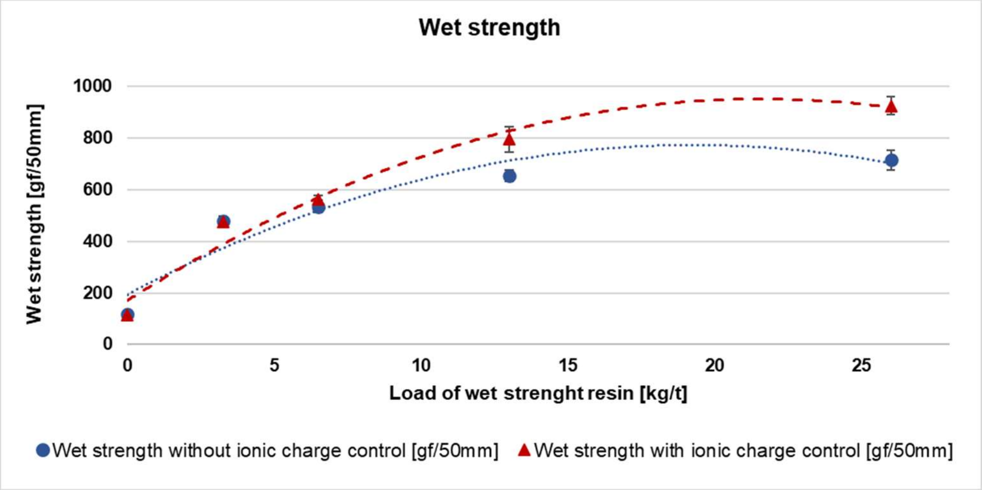


Figure 51. Wet tensile strength with and without ionic charge control additive.

The figures Figure 52, Figure 53, Figure 54 and Figure 55 show the relation between the wet strength resin load, wet tensile strength of the paper, ionic charge used and the values of zeta potential.

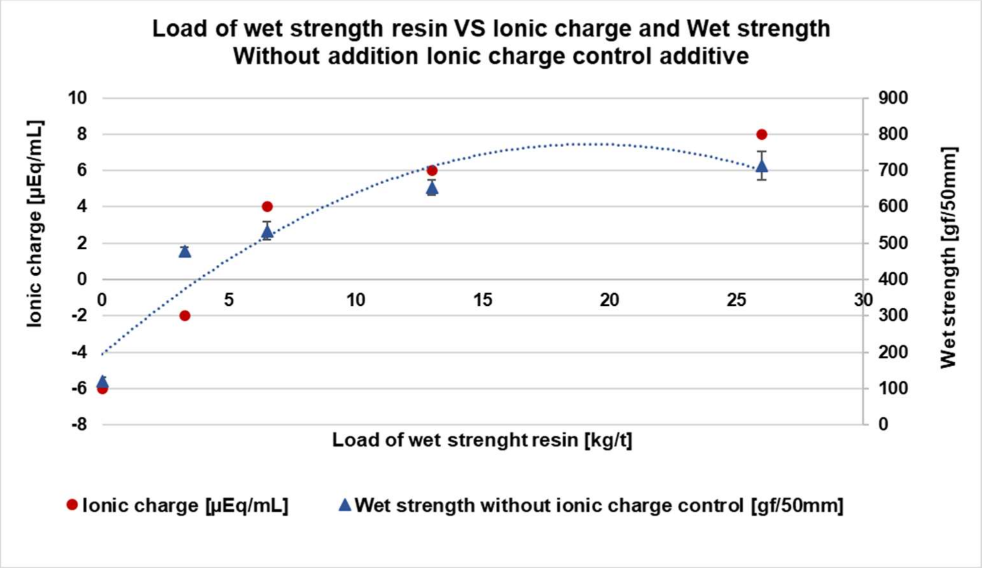


Figure 52. Load of wet strength resin *versus* ionic demand and paper wet strength without addition of ionic charge control additive.

.

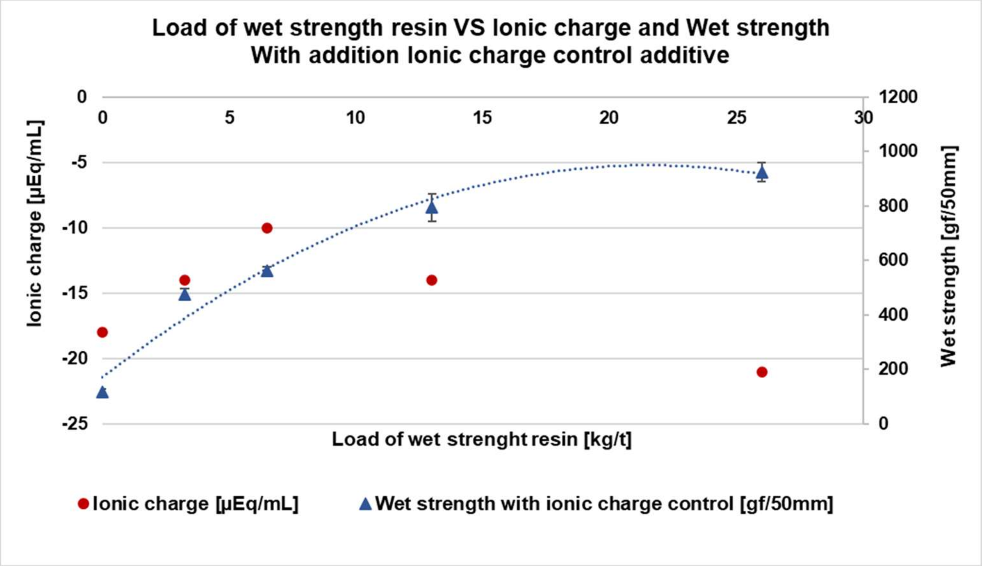


Figure 53. Load of wet strength resin *versus* ionic demand and paper wet strength with addition of ionic charge control additive.

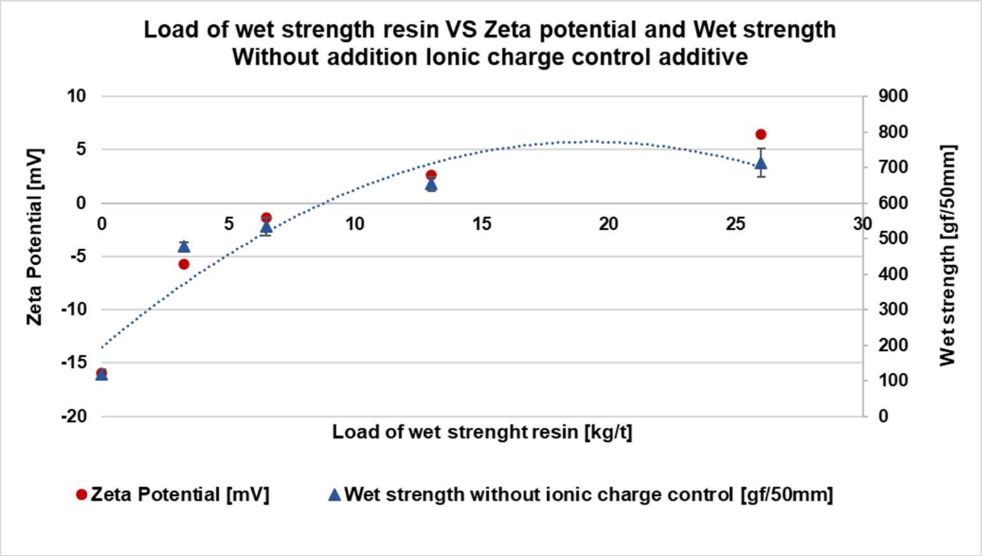


Figure 54. Load of wet strength resin *versus* zeta potential and paper wet strength without addition of ionic charge control additive.

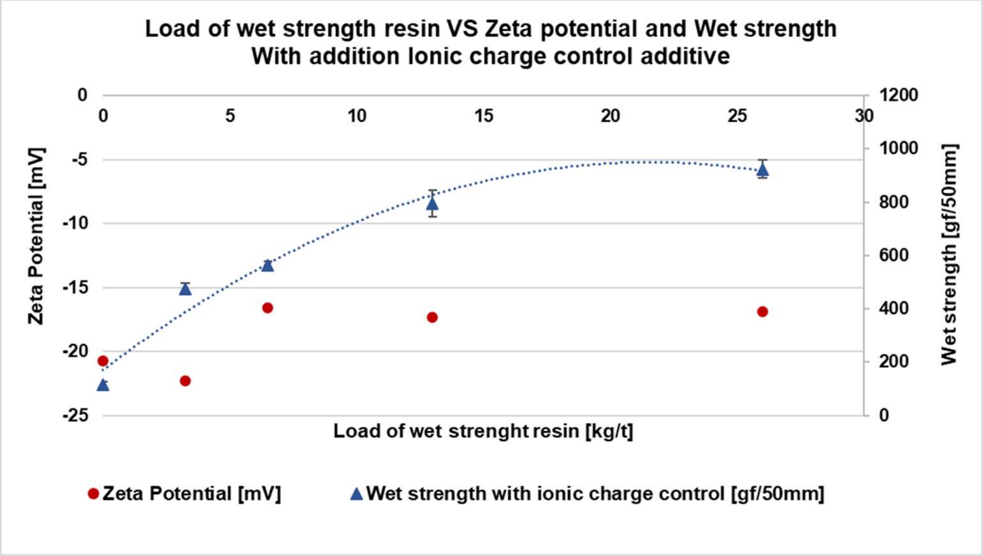


Figure 55. Load of wet strength resin *versus* zeta potential and paper wet strength with addition of ionic charge control additive.

Analyzing the ionic charge and zeta potential it is possible to see that when the ionic charge is controlled possessing negative values, the wet tensile strength achieves greater values. The values of ionic charge in the experiment with ionic charge control were kept between -10 to -21 μEq/mL (Table 7, Figure 53).

In the experiment without ionic charge control, the ionic charge became positive with the dosage of 6.5 kg/t of the wet strength resin (Table 6, Figure 52). It appears to be that a wet strength resin does not adsorbed completely on the pulp fibers in suspension being presented in aqueous phase to a significant extent. In this point the zeta potential is close to zero, -1.4 mV, as the zeta potential gives an idea of how much points on fiber surface are available for linkages; so, there are some points in fiber surface that would be bonded with the wet strength resin. In the experiment without ionic charge control additive the values of wet tensile strength increased a little after the zeta potential became positive, as shown in Figure 54. It occurs because of the PAE homo-crosslinking which are weaker than the co-crosslinking that happen between the azetidinium groups of PAE resin and carboxyl groups of the fiber. Such a co-crosslinking is more pronounced in the experiment with the addition of ionic charge control additive (Figure 55). In this case, the addition of the ionic charge control additive improves the retention and allow more wet strength resin to be absorbed by cellulose fibers. In the dosage of 13 kg/t of wet strength resin the value obtained of wet tensile strength when it was added the ionic charge control additive reached 141 gf/50mm more than the paper sheet without this additive. The fiber surface with this dosage of resin has a negative zeta potential (-16.6 mV), which indicates that the ionic charge control additive generates more points for bonds between fibers and wet strength resin. On the other hand, in the same dosage of wet strength resin without charge control the zeta potential is 2.6 mV, near to zero, indicating that the fiber surface is saturated.

The author Su et al. (2012) also showed that there is a saturation point of the fiber surface when it is increased the dosage of wet strength resin. As it be seen in Figure 52 and Figure 54, when the ionic charge and zeta potential became positive the value of wet tensile strength increased a little, in other words, it can be considered a saturation point of the chemical dosage and wet tensile strength. In this work, it was expected to find this saturation point of wet strength resin even though the ionic charge is controlled in the papermaking process. In the second part of this study, the ionic charge was controlled between -10 to -21 μEq/mL and the zeta potential measurements had values between -16.6 to -22.3 mV. As in this part the wet tensile strength continued to increase between the upper resin dosages (13 and 26 kg/t), it shows that the ionic charge control additive created more anionic sites on the fiber surface. The polyacrylamide interacts with the PAE that is retained on the fiber surface and this fact allowed to keep more anionic sites on the fiber surface, being possible another interaction with the PAE of the wet strength resin. Thus, more bonds of PAE in the fiber network caused higher wet strength of the paper sheet.

In a paper machine there are others function and process chemicals, so, other interactions occur on the wet end and other machine sections. The retention time of the wet strength resin may be different while changing the dosage point, a simple change, can bring different results. The ionic charge control additive can be added in the fan pump suction, after the dosage of the wet strength resin, the dosage on this point can create more anionic sites on fiber surface making possible more wet strength resin being absorbed. Another possibility in the dosage of the ionic charge control additive is it addition before the dosage of the wet strength resin, in this case this anionic chemical first can interact with others cationic chemicals, generating less competition with the wet strength resin for the anionic sites presented in the pulp.

Relation between wet/dry tensile strength

It was also analyzed the relation between the values of the wet tensile strength and dry tensile strength (Table 8). For both experiments, the ratio kept practically the same. The Figure 56 shows this correlation. Analyzing these results, the tendency is that the maximum ratio between wet/dry tensile strength is close to 26%. So, if a company is developing a new product with wet strength this ratio can be a limiting of the product design.

Table 8. Relation between wet and dry tensile strength

Load of wet strength resin [kg/t]	**Wet/Dry tensile strength without charge control [%]**	**Wet/Dry tensile strength with charge control [%]**
0	4,7% ± 0,3%	4,0% ± 0,3%
3,25	19,1% ± 1,9%	14,8% ± 0,8%
6,5	20,5% ± 0,8%	17,1% ± 0,7%
13	23,5% ± 1,6%	23,3% ± 1,4%
26	26,2% ± 2,9%	25,6% ± 1,1%

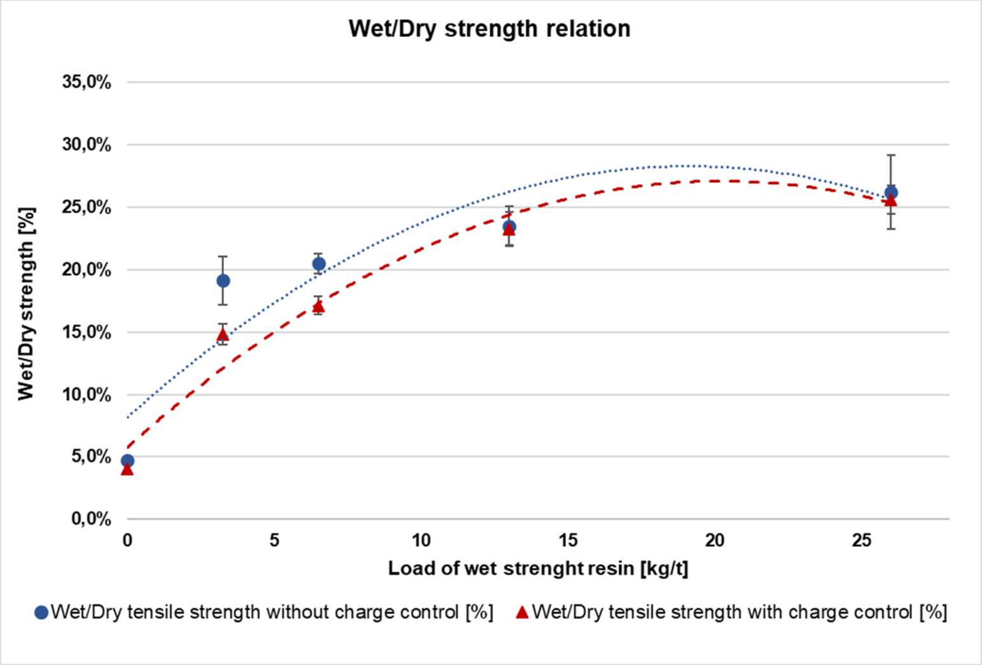


Figure 56. Relation between wet and dry strength with and without charge control.

Chemical’s consumption

Regarding the chemical’s consumption, the dosage of ionic charge control additive was not too high to maintain the ionic charge anionic. The average dosage of this chemical was around 15% of the wet strength resin dosage (Figure 57).

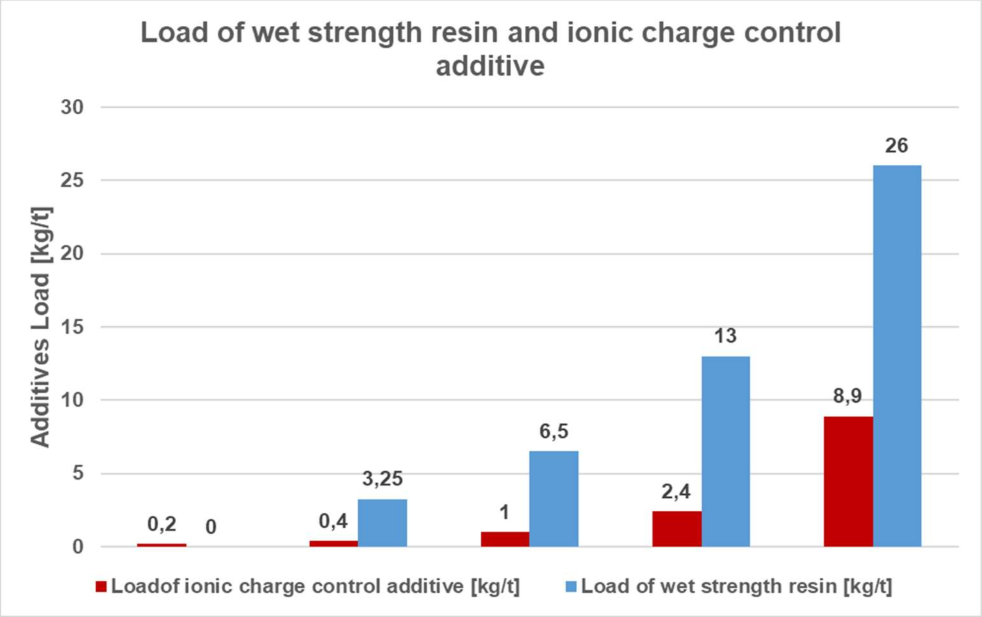


Figure 57. Load of wet strength resin and ionic charge control additive.

In a financial perspective the use of the ionic charge control additive represents, in the maximum dosage of wet strength resin, an increase in the cost of the application of 2.1 €/t (Table 9).

However, this cost is justified by greater values of the wet tensile paper strength, which reached of 211 gf/50mm.

Considering a paper with around 700 gf/50mm of wet tensile strength when it was controlled the ionic charge this value is obtained with a wet strength resin load of 13 kg/t, instead of 26 kg/t without ionic charge control. It represents a saving in the chemical cost of 5.84 €/t.

Another benefit to control the ionic charge in the paper machine is that the foam generation, forming and Yankee dryer coating problems may be avoided.

Table 9. Cost of chemicals per ton.

Load of Wet strength agent resin [kg/t]	Load of Ionic charge control additive [kg/t]	Cost [€/t] Without ionic charge control	Cost [€/t] With ionic charge control
0	0.2	0.00	0.15
3.25	0.6	1.82	2.28
6.5	1.4	3.64	4.70
13	1.9	7.28	8.72
26	2.8	14.56	16.69

Wet strength resin = € 0.56/kg; Ionic charge control additive = € 0.76/kg.

Water absorption capacity

In the Figure 58 is shown the values of water absorption capacity. In the paper sheets without wet strength resin the water absorption capacity have a slightly different value than the sheets with dosage of wet strength resin. The PAE impacts negative but not significant on water absorption capacity, because the PAE adsorbed forms crosslinking bonds with fibers and this restrict or prevent the fiber swelling, that is why the water absorption capacity decrease with the addition of wet strength resin. The water absorption capacity is mostly related to the creping process because there are breaking of some bonding's in this process, allowing the fiber swelling.

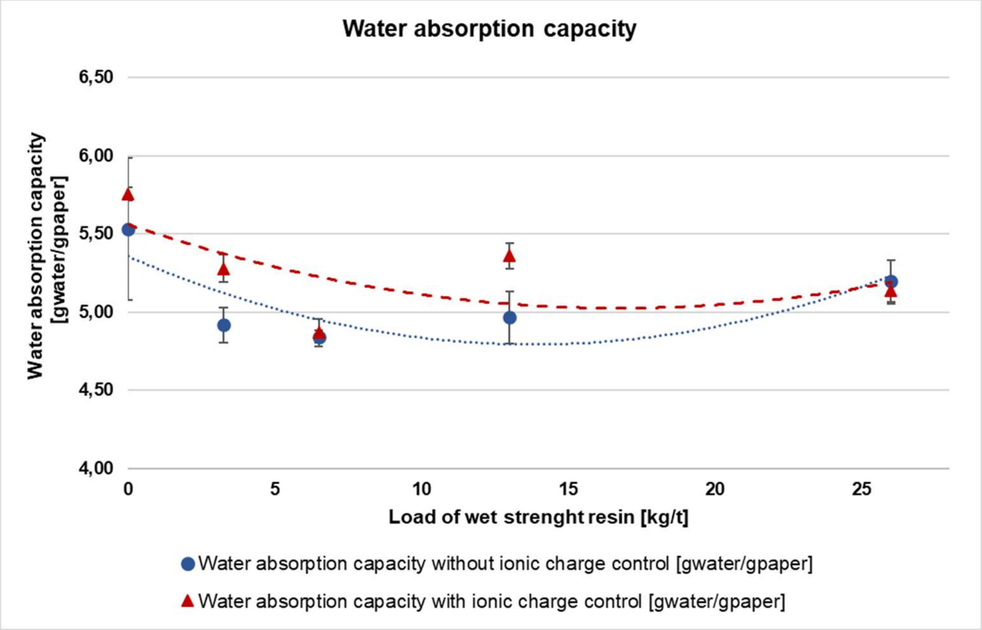


Figure 58. Water absorption capacity with and without charge control.

9. Conclusions

The objectives of the work were to better understand and optimize the dosage of wet strength in tissue paper production. In paper towel manufacturing the consumption of wet strength resin represents the main percentage of the chemicals cost, reducing or avoiding overdosing of this product is fundamental to save money.

Using the ionic charge control additive is important to maintain paper machine stability. Cationic values of ionic charge in the pulp suspension can result in some problems on machine such as foam generation in the white-water system, sheet formation and can affect the Yankee dryer coating. Furthermore, the use of the ionic charge control additive also helps to increase dry tensile strength, the average gain was 650 gf/50mm. It happened due to this additive has in its composition polyacrylamide, which contributes to the dry strength of the paper.

The measurements of wet tensile strength when the ionic charge was not controlled showed that there was a saturation of the fiber surface by wet strength resin, which was confirmed by the positive zeta potential measurements and because the sheet did not present an enhanced wet tensile strength gain. On the other hand, when it was used the ionic charge control additive, the ionic charge was kept between -10 to -21 µEq/mL, even with the increase in the dosage of the wet strength resin. Zeta potential values also remained negative, between -16.6 to -22.3 mV, indicating that the fiber surface still had points for linkage with the wet strength resin. In higher loads of wet strength resin (13 and 26 kg/t), the control of the ionic charge showed to be a good way to achieve greater values of wet tensile strength. For sheets formed with a load of 13 kg/t of wet strength resin, 1.9 kg/t of ionic charge control additive was used to maintain the ionic charge negative (-14 µEq/mL). The wet tensile strength of this sheet was 795 gf/50mm, a higher value than the wet tensile strength of the sheet formed with 26 kg/t of wet strength resin without ionic charge control.

The wet/dry tensile strength ratio tends to a stability at maximum dosages studied in this work, around 26%, this ratio is important because in a product development that requires wet tensile strength this percentage should be considered as limiting in the product design.

In conclusion, the ionic charge control of the fibrous suspension optimizes the consumption of the wet strength resin, the polyacrylamide interacts with the polyaminoamide-epichlorohydrin that are retained on the fiber surface creating more anionic sites, as there is the possibility of a greater amount of polyaminoamide-epichlorohydrin interacts with this coacervate, so higher values of wet strength values are obtained.

References

Alves, E. D., Pinheiro, O. S., Costa, A. O. S., & Costa, E. F. J. (2015). Estudo do processo de obtenção celulose Kraft com ênfase no forno de cal. *Revista Liberato*, *16*(26), 205–217. Retrieved from http://www.liberato.com.br/sites/default/files/arquivos/Revista_SIER/v.16%2C n.26 %282015%29/11-art02-kraft-24-nov.pdf

Bajpai, P. (2018). Papermaking Chemistry. I (Chapter 10, pp. 207-236). Elsevier (Ed.), *Biermann's Handbook of Pulp and Paper* Volume 2: Paper and Board Making. https://doi.org/10.1016/b978-0-12-814238-7.00010-6

Bonicenha, J. J., Barbosa, L. C., & Santos, M. (2020). Controle avançado de demanda iônica em máquina de papel. *IX Congresso Brasileiro de Engenharia de Produção*, pp. 273–285. https://doi.org/10.47573/aya.88580.2.6.16

Boudreu, J. (2013). *New Methods for Evaluation of Tissue Creping and The Importance of Coating, Paper and Adhesion* (Doctoral dissertation). Karlstad University.

Cadena, E. M., Garcia, J., Vidal, T., & Torres, A. L. (2009). Determination of zeta potential and cationic demand in ECF and TCF bleached pulp from eucalyptus and flax. Influence of measuring conditions. *Cellulose*, *16*(3), 491–500. https://doi.org/10.1007/s10570-009-9275-3

Campos, E. S. (2012). *Curso de fabricação de papéis "tissue"* (p. 185). p. 185. Retrieved from https://www.eucalyptus.com.br/artigos/outros/2012_Curso_Fabricacao_papel_tissue.pdf

Coelho, A. M. (2009). *Otimização do processo de crepagem para a produção de papel tissue* (Lato Sensu monography). Universidade Federal de Viçosa.

de Assis, T., Pawlak, J., Pal, L., Jameel, H., Reisinger, L. W., Kavalew, D., … Gonzalez, R. W. (2020). Comparison between uncreped and creped handsheets on tissue paper properties using a creping simulator unit. *Cellulose*, *27*(10), 5981–5999. https://doi.org/10.1007/s10570-020-03163-0

de Assis, T., Reisinger, L. W., Pal, L., Pawlak, J., Jameel, H., & Gonzalez, R. W. (2018). Understanding the Effect of Machine Technology and Cellulosic Fibers on Tissue Properties – A Review. *BioResources*, *13*(2), 4593–4629. https://doi.org/10.15376/biores.13.2.DeAssis

Domis, E. de O. (2010). *O uso de enzima no refino de fibras celulósicas na fabricação de papel* (Lato Sensu monography). Universidade Federal de Viçosa.

Dunlop-Jones, N. (1991). Wet-strength chemistry. In *Paper Chemistry* (pp. 76–96). https://doi.org/10.1007/978-94-011-6474-0_6

Ek, M., Gellerstedt, G., & Henriksson, G. (2009a). Paper Products Physics and Technology. In M. Ek, G. Gellerstedt, & G. Henriksson (Eds.), *Pulp and Paper*

Chemistry and Technology (Vol. 4). https://doi.org/10.1515/9783110213461

Ek, M., Gellerstedt, G., & Henriksson, G. (2009b). Wood Chemistry and Wood Biotechnology. In M. Ek, G. Gellerstedt, & G. Henriksson (Eds.), *Pulp and Paper Chemistry and Technology* (Vol. 1). https://doi.org/10.1515/9783110213409

Fengel, D., & Wegener, G. (1983). *Wood: Chemistry, Ultrastructure, Reactions*. In D. Fengel & G. Wegener (Eds.). Berlin, New York: De Gruyter. https://doi.org/10.1515/9783110839654

Ferreira, G. A. B. (2019). *Comparação de desempenho de adesivos de coating para cilindro yankee* (Lato Sensu monography). Universidade Federal de Viçosa.

Gharehkhani, S., Sadeghinezhad, E., Kazi, S. N., Yarmand, H., Badarudin, A., Safaei, M. R., & Zubir, M. N. M. (2015). Basic effects of pulp refining on fiber properties—A review. *Carbohydrate Polymers*, *115*, 785–803. https://doi.org/10.1016/j.carbpol.2014.08.047

González, M. (2017). *Optimización del uso de agentes de resistencia en máquinas papeleras - caso real CMPC Tissue Planta Puente Alto* (Graduation work). Universidade de Chile. Retrieved from http://repositorio.uchile.cl/bitstream/handle/2250/146395/Optimizacion-del-uso-de-agentes-de-resistencia-en-maquinas-papeleras-caso-real-CMPC.pdf?sequence=4

Haettich, T., & Vazquez, J. (2018). Gerenciamento de partículas - uma abordagem inovadora para maximizar a qualidade do papel e a operacionalidade da máquina de papel. *O Papel*, *79*(8), 91–96. Retrieved from http://www.revistaopapel.org.br/noticia-anexos/1547063413_037fe2f3efaa8bd7def851223ca64a9f_961396338.pdf

Hergen. (2020). Cilindros Yankee. Retrieved December 2, 2020, from http://www.hergen.com.br/produtos/pampa-tissue/cilindros-yankee/

Hergen. (2021). Refiners. Retrieved December 12, 2021, from https://www.hergen.com.br/en/products/stock-preparation/refiners/

Hirn, U., & Schennach, R. (2015). Comprehensive analysis of individual pulp fiber bonds quantifies the mechanisms of fiber bonding in paper. *Scientific Reports*, *5*(1), 10503. https://doi.org/10.1038/srep10503

Holik, H. (2006). Handbook of Paper and Board. In H. Holik (Ed.), *WILEY-VCH Verlag GmbH & Co*. https://doi.org/10.1002/3527608257

Hubbe, M. A., Rojas, O. J., Lucia, L. A., & Jung, T. M. (2007). Consequences of the nanoporosity of cellulosic fibers on their streaming potential and their interactions with cationic polyelectrolytes. *Cellulose*, *14*(6), 655–671. https://doi.org/10.1007/s10570-006-9098-4

IMARC. (2020). Tissue Paper Market: Global Industry Trends, Share, Size, Growth, Opportunity and Forecast 2020-2025. Retrieved November 2, 2020, from https://www.imarcgroup.com/global-tissue-market

International Organization for Standardization. (2016). *ISO 12625-6:2016 - Tissue paper and tissue products — Part 6: Determination of grammage*.

International Organization of Standartization. (1999). *ISO 5267-1:1999 Pulps – Determination of drainability – Part 1: Schopper-Riegler method*.

International Organization of Standartization. (2016a). *ISO 12625-4:2016 - Tissue paper and tissue products — Part 4: Determination of tensile strength, stretch at maximum force and tensile energy absorption*.

International Organization of Standartization. (2016b). *ISO 12625-5:2016 - Tissue paper and tissue products — Part 5: Determination of wet tensile strength*.

International Organization of Standartization. (2016c). *ISO 12625-8:2016 - Tissue paper and tissue products — Part 8: Water-absorption time and water-absorption capacity, basket-immersion test method*.

Kirwan, M. J. (2013). *Handbook of Paper and Paperboard Packaging Technology* (Second edition). https://doi.org/10.1002/9781118470930

Lima, A. S. (2012). A química da parte úmida em produção de papel: conceitos e aplicações (Lato sensu monography). Universidade Prebisteriana Mackenzie.

Lindström, T., Wågberg, L., & Larsson, T. (2005). On the nature of joint strength in paper – a review of dry and wet strength resins used in paper manufacturing. In *13th Fundamental Research Symposium* (Vol. 1, pp 457 - 562). Retrieved from https://www.researchgate.net/publication/267385974

Liu, J. (2004). Effects of chemical additives on the light weight paper (Doctoral dissertation). Georgia Institute of Technology.

Manfredi, M., Colodette, J. L., Oliveira, R. C. de, & Barbosa, B. M. (2014). Efeitos da sequência de branqueamento na ação de alvejantes óticos em celulose kraft de eucalipto. *CERNE*, *20*(2), 223–230. https://doi.org/10.1590/01047760.201420021434

Marques, T. R. (2013). *Análise da demanda iónica de um processo papeleiro - influência de variáveis de processo* (Master's thesis). Universidade de Coimbra. Retrieved from https://estudogeral.sib.uc.pt/bitstream/10316/40233/1/Analise da demanda ionica de um processo papeleiro.pdf

Mihara, I., Sakaemura, T., & Yamauchi, T. (2008). Mechanism of paper strength development by the addition of dry strength resin and its distribution within and around a fiber wall. *Nordic Pulp & Paper Research Journal*, *23*(4), 382–388. https://doi.org/10.3183/npprj-2008-23-04-p382-388

Milanez, A. F., & Rost, É. M. (2005). Tissue Paper - Revisão tecnológica. Retrieved December 12, 2020, from https://www.researchgate.net/publication/270820766_Tissue_Paper_-_Revisao_tecnologica

Nachtergaele, W. (1989). The Benefits of Cationic Starches for the Paper Industry. *Starch - Stärke*, *41*(1), 27–31. https://doi.org/10.1002/star.19890410108

Obokata, T., & Isogai, A. (2007). The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *302*(1–3), 525–531. https://doi.org/10.1016/j.colsurfa.2007.03.025

Oliveira, E. L. (2002). *Condicionamento de feltros nas máquinas de papel* (Lato sensu monography). Universidade Federal de Viçosa.

Pan, K., Phani, A. S., & Green, S. (2016). *Mechanics of Creping in Tissue Making* p. 35. Retrieved from https://mech.ubc.ca/files/2016/08/Mechanics-of-CrepingKui-Pan_UBC.pdf

Parason. (2021). Confiner. Retrieved December 12, 2021, from https://parason.com/products/refining/confiner/

Pires, E. D., Cabral, C. R. A. (2011). *Propriedades e características que influenciam o consumidor do papel tissue* (Graduation work). Faculdade de Pindamonhangaba.

Ramires, H., Oliveira, R. C., Rubini, B., Demuner, B., Pavan, P. (2013). Aumento da proporção de fibras de eucalipto na formação de paéis tissue e avaliaçaõ de suas propriedades. *The 46th ABTCP International Pulp and Paper Congress, October, 8-10. 2012, Sao Paulo Brazil.*, 8–10. Retrieved from https://www.eucalyptus.com.br/artigos/outros/2013_Fibras_eucalipto_tissue_paper.pdf

Ramires, H. O. R. (2013). *Alternativas tecnológicas para melhores de propriedades mecânicas de papéis tissue e sua aplicação para diferentes polpas kraft de eucalipto* (Master's thesis). Universidade Federal de Viçosa.

Roberts, J. C. (1996). The Chemistry of Paper. Cambridge. In *RSC Paperbacks*. https://doi.org/10.1039/9781847552068

Robusti, C., Viana, E. F., Júnior, F. F., Gomes, I., Tognetta, L., Santos, O., Dragoni, P. (2014). *Celulose e Papel - Papel* (1st edition). Senai-SP Editora.

Sabino, F. D. (2020). *Aditivos para desenvolvimento das propriedades dos papéis tissue* (Mather's tesis). Universidade de Aveiro. Retrieved from https://www.ua.pt/pt/incubator/sobre

Santos, C. P., dos Reis, I. N., Moreira, J. E. B., & Brasileiro, L. B. (2001). Como se fabrica papel. *Química Nova Na Escola*, *14*, 1–5. Retrieved from https://www.yumpu.com/pt/document/read/12489746/papel-como-se-fabrica-qnesc

Silva, D. de J. (2010). *Química da Parte Úmida em Processo de Fabricação de Papel - Interações em interfaces sólido-líquido* (Doctoral Dissertation). Universidade de São Paulo.

Silva, V. L. (2007). *Aditivos utilizados no processo de secagem de papéis tissue* (Graduation work). Universidade Federal de Viçosa.

Siqueira, E. J. (2012). *Polyamidoamine epichlorohydrin-based papers : mechanisms of wet strength devel- opment and paper repulping* (Doctoral Dissertation). Université de Grenoble.

Sixta, H. (2006). *Handbook of Pulp*. Lenzing. WILEY-VCH.

Soares, V. C. (2007). *Desenvolvimento de processo e produtos para controle de substâncias em estado coloidal (Stickies) na produção de papel reciclado* (Masther's tesis). Universidade Federal de Viçosa.

Stumm, D., & , R. Grenz, W. D. (2009). Surface charge determination for balancing charge quantities and modelling the reactivity furnish for the efficient application of wet strength agents. *Papermaking Research Symposium*, 1–4. Retrieved from https://www.ptspaper.de/fileadmin/PTS/PTSPAPER/01_Ueber_uns/Dokumente/Veroeffentlichungen/2009_PRS2009_Surface.pdf

Su, J., Mosse, W. K. J., Sharman, S., Batchelor, W., & Garnier, G. (2012). Paper strength development and recyclability with polyamideamine-epichlorohydrin (PAE). *BioResources*, *7*(1), 913–924. https://doi.org/10.15376/biores.7.1.0913-0924

Thorn, I., & Au, C. O. (2009). Applications of Wet-End Paper Chemistry. In I. Thorn & C. O. Au (Eds.), *Applications of Wet-End Paper Chemistry: Second Edition* (2nd Edition). https://doi.org/10.1007/978-1-4020-6038-0

Uner, B. (2002). *Adhesion Mechanism between Polymer and Metal Interface* (Doctoral dissertation). North Carolina State University. Retrieved from https://repository.lib.ncsu.edu/handle/1840.16/3598

Valmet. (2020). Tissue machine. Retrieved December 12, 2020, from https://www.valmet.com/rollcovers/tissue.html

Venditti, R. (2020). Enzyme Applications in Pulp and Paper : An Introduction to Applications (919), 40. Retrieved from https://faculty.cnr.ncsu.edu/richardvenditti/wp-content/uploads/sites/24/2018/10/csirEnzymeApplicationsinPulpandPaperrav.pdf

Wang, Y., De Assis, T., Zambrano, F., Pal, L., Venditti, R., Dasmohapatra, S., … Gonzalez, R. (2019). Relationship between human perception of softness and instrument measurements. *BioResources*, *14*(1), 780–795. https://doi.org/10.15376/biores.14.1.780-795

Yoon, S. H. (2007). Analysis on adsorption equilibrium of polyamide-epichlorhydrin in aqueous fibrous suspension by colloid titration. *Journal of Industrial and Engineering Chemistry*, *13*(3), 345–351.