## Influence of Zeta Potential in Physical and Mechanical Properties of Recycled Paper

A. C. Nascimento Chemical Engineering School Faculty of Telemaco Borba – FATEB Telemaco Borba, Brazil

## ABSTRACT

The zeta potential is the electric potential near the surface of a particle in suspension. It is a way of quantifying the loading of the fibers, indicating the adsorption capacity of the fiber and if the additive was really adsorbed. Thus, one can predict stability of colloidal suspensions. The best retention of colloidal particles in a papermaking occurs when the zeta potential is near zero. Paper recycling is the use of waste paper to produce new roles, and has important environmental and social contribution. The objective is to form sheets with different percentages of recycled fiber and control the zeta potential to check its influence on the physical and mechanical properties. Sheets were formed using short fiber (Eucalyptus) and recycled (paper) and the zeta potential was controlled with the use of aluminum polychloride. Sheets were obtained in laboratory former, and kept in a controlled environment for realization of physical-mechanical tests. Tests for burst and tensile index showed better formation and resistance with the control of zeta potential and increased significantly with higher recycled paper. Tear index not followed a trend presenting distinct behavior with the use of aluminum polychloride. The zeta-potential have influence on the physico-mechanical properties of the paper, since it retains the colloidal particles, and these in turn, improve sheet formation.

## Keywords

Zeta potential, recycled fiber, physical and mechanical properties.

## **1. INTRODUCTION**

The fiber suspension to papermaking consists of a large number of components which differ from each other in various respects such as size, shape, surface area, surface roughness and electrical charge (Figure 1). The suspension of fibers and fine contains mineral filler and additives which aim at improving the process of papermaking and their properties. The fibrous material when dispersed in aqueous medium develops surface charge due to the presence of ionizable functional groups such as the hydroxyl and carbonyl. Which results in the inefficiency in the retention of particles of colloidal nature (such as fines and fillers) [10, 11, 14]. The cellulosic fibers normally carry a negative charge when suspended in water due to the presence of ionisable acidic groups in the hemicelluloses and lignin. The charge of fibers is a complex function of the chemical composition, state of ionization of the acid groups, and the nature and amount of additional substances adsorbed on the fiber surface. The population of ionisable groups depends on the origin of the fibers and on the chemical treatments such as pulping and bleaching. The characteristics of any particular fiber surface also depend greatly on the degree of mechanical treatment [4,7]. The number of charged groups

J. V. Moreira Chemical Engineering School Faculty of Telemaco Borba – FATEB Telemaco Borba, Brazil

present depends on the particular origin of the fibers and their charge distribution is expected to vary with changes in fiber morphology [2].



Figure 1. Constituents of fiber suspension. Adapted from [14].

Over a third of the paper produced worldwide is produced from recycled pulp and due to increasing environmental pressures, the paper mills are forced to higher levels of shutdown system, in other words, reuse the fibers coming from waste paper. However, there is a limitation in recycling paper. With each recycling, the quality of pulp deteriorates making with the recycled fibers have a higher drainage resistance due to their positions on repeated processes of pulping and drying [3].

The ionization of acid groups on cellulosic fibers forms loads that influence the formation of the paper. The supplied chemical interactions are complex. The load in papermaking systems plays an important factor in determining the aggregation of particles and the effect of different additives. The control of retention of fines and fillers in the papermaking process is needed for technical and economic reasons, for it depends the improvement of refining, the preservation the solids content after pressing and lower steam consumption. The hydrodynamic factors play an important role in the process of retention along with the colloidal interaction forces. In order to improve retention and drainage are typically added to pulp, soluble water flocculants polymeric. These include natural polymers (starch, carboxymethyl cellulose and gums) and synthetic flocculants (polyacrylamides, amines, polyamines, polyamides, polyethylene oxide) [5, 3].

Many techniques for determining characteristics load's fibers and chemical additives in papermaking are discussed in the literature. Among the techniques available the zeta potential was postulated as the control parameter. However, the information available in the literature about retention and drainage on recycled fibers and the influence of zeta potential is very limited. There is a strong need for understanding more quantitative of effects of different chemicals to control the zeta potential to improve retention and drainage recycled fiber, which could result in higher production rates and improved quality [3].

#### 1.1 Zeta potential

The zeta potential analysis is a well-established technique for characterization of particle surface charge from the viewpoint of classical theory of colloidal stability and has more than three decades of application in the paper industry. The zeta potential represents the electrostatic charge density induced near the surface of a particle by the action of ions and polymers in suspension. The magnitude and sign of the charge is derived from the measurement of particle motion applied in an electromagnetic field. Since these movements could be strong or weak and depends on the composition of the surface of the particles may occur zeta potential distributions (since not all particles share the same charge). This occurs when more than one type of material is present in the solution (mineral filler and fines) and when it has a high mechanical shearing after mixing. Thus, both the average of zeta potential as the shape of the distribution is important [11].

The development of an electrostatic charge occurs when the solids are dispersed in water. In papermaking systems, this load may come from dissociated carboxylic groups, sulfonic acid groups and adsorption of substances such as hemicelluloses, lignin dissolved, retention agents and cationic starches on the particle surface (generally the fiber). Mineral fillers, such as kaolin and titanium dioxide also develop surface charge throughout ionization interface particle/ water and for adsorption of other charged substances.



Figure 2. Description of the double layer theory an arrangement of load. Adapted from [14].

The electric potential of the surface is determined by the type and surface density of charged groups. The particles present in papermaking are usually anionic in nature. Therefore the Figure 2 was performed with negatively charged surface. We can observe that the representation of the double layer occurs over the surface of hydrophobic particles suspended in water, being the zeta potential ( $\zeta$ ) potential as measured between the plane of shear and the layer of ions of opposite charge (positive) strongly adsorbed over the particle negative (electrostatic forces and van der Waals interactions - the electrostatic forces are a result of the fact that the particle surfaces are charged while the van der Waals depend on the chemical nature of the solid phase). As moves away from the particle negative the electric potential tends to reduce, providing increased mobility to the particles. The term zeta potential applies to electrical loads that exist in the dispersions of nature colloidal. A colloidal particle (fines or load) suspended in the pulp is surrounded by a dense layer of ions having a specific electrical charge. This layer in turn is surrounded by another layer, more diffuse than the first which has its own electrical charge. The liquid in dispersion has its own electrical charge. The difference in the electrical charge between the dense layer of ions surrounding the particle and the suspending liquid medium is called zeta potential and is usually measured in mV [6, 12].

As a result of the movement of heat dependent and an increase in the dilution, an increasing proportion of these ions are located in the adjacent volume of liquid phase, where its concentration drops to zero with increasing distance from the surface. This part of the double layer electric is called the diffuse layer (Figure 3).



Figure 3. Double layer electrochemical and course of potential at the interface.

The level of surface potential  $\Psi 0$  cannot be measured.  $\Psi \delta$  is the hypothetical potential in the outer layer of Stern. The potential of the cutting plane (which in the ideal case coincides with the outer edge of the Stern layer) along the diffuse layer facing the solution is called electrokinetic potential or zeta potential [16].

Thus the zeta potential is a way of quantifying the loading of the fibers. Does not depend on sample size and help predict how fast the suspension will agglomerate. It may be affected by pH, conductivity, temperature and ionic strength of the medium. The zeta-potential indicates the adsorption capacity of the fiber and if the additive was adsorbed. Thus, one can predict stability of colloidal suspensions [8].

## **1.2** Effects of utilization of secondary fibers in the papermaking process

Recycling is the utilization of waste paper pulp fibers, papers culled during the manufacturing process and scrap for the production of new papers. Nearly all types of paper used can be availed. Technically, the fibers contained therein are likely to replace virgin fiber raw materials, such as chemical pulp, semichemical or mechanical.

Despite the paper recycling be a promising activity, there are technical problems and technology with the product at the end of the process, as a loss of quality and final properties of recycled paper in relation to the original product. As a result of these losses are generated limitations of quality of the cellulosic fibers in the successive recycling processes. To circumvent these problems the paper industry has several technical devices such as refining, adding virgin fibers and application of additives. All these contribute to complement the demand of potential of links interfibrillar lost with the recycling process [8].

## 1.3 Retention

The fiber charge is an important factor in papermaking processes because many of the interactions between soluble and particulate fractions of papermaking furnishes are charge-induced. The effects of fiber charge on retention of additives at the wet end of paper machines are the main subject in many studies [15, 9, 2].

To measure the retention of fiber and additives on the screen of papermaking are used two parameters: global retention and retaining the first step. The global retention is the ratio between the total material (fibers, fillers, additives) that is being fed in the machine, and that is getting trapped in the dry sheet. This retention further includes the step of forming the stage of recovery of the fibers outside the machine, usually a flotation stage. While retaining first step is the ratio between the total material fed into the input box and what is retained on the screen. The first pass retention can also be measured or expressed in only one of the components of the mass, as the first step of retaining of fibers, fines or fillers.

The economy in the use of various additives is concerned primarily with global retention, since the not retained in the sheet portion is lost with the residual white water system, however it is known that the recovery system seeks to close the circuits of machine system for reducing the volume and effluent and minimize losses. Several sheet's properties such as formation, opacity, brightness, porosity, strength and smoothness can be affected by the withholding agent (flocculant) [12]. Therefore this study will assess the sheet's resistance formed with recycled papers when the zeta potential is controlled, in order to verify the importance of retaining the physical and mechanical properties.

## 1.4 Physical and mechanical properties

The properties of paper are highly dependent on the properties of the pulp fibers. In addition to the specific surface area, the bonding ability of single fibers is highly relevant to the physical strength of the paper produced. Previous study suggests that fiberfiber bonding strength is affected by the electrokinetic properties of the fibers, especially those related to surface charge [1, 4].

The grammage is the determination of the mass in grams per square meter paper or paperboard. Most papers are bought and sold according to their grammage, so this property is very important for consumer and producer. The tear resistance is the force perpendicular to the plane of the paper required to tear one or more sheets of paper through a specified distance. The fiber length is an important aspect in the development of resistance to tearing. The burst strength is defined as the pressure needed to produce the burst of the material while applying pressure uniformly increasing, transmitted by an elastic diaphragm, of a circular area equal to 962 mm<sup>2</sup>. Pulps with lower levels of fines and longer fibers generally produce papers with improved resistance to burst. Tensile strength is the maximum tensile force per unit width of the paper or card can support before breaking under defined conditions. The interfibrillar connections occurring in the formation of the paper will be critical to discuss this property.

## 2. EXPERIMENTAL

## 2.1 Materials

The industrial Eucalyptus pulp unbleached was kindly donated by Klabin Monte Alegre (Telemaco Borba, Parana, Brazil) (Figure 4). This pulp is obtained by cooking the wood chips into the digester with the addition of white liquor, which comprises sodium hydroxide and sodium sulphide. The withholding agent used to lower the zeta potential was the aluminum polychloride that was purchased from Stalge Sunrise (Brazil). To obtain pulp of recycled paper were used old newspapers.



Figure 4. Industrial Eucalyptus pulp unbleached.

## 2.2 Preparation of pulps

The industrial pulp, consistently around 4%, were washed (due to residual alkali contained in the pulp), dewatering, air dried, and packed in plastic bags.

The newspaper sheets were disaggregated in a laboratory pulper, without addition of chemicals and using water at 50°C, air dried and packed in plastic bags.

# **2.3** Formation of the paperboard sheets to the physic-mechanical

The sheets were obtained in laboratory type trainer Tappi, 200  $g/m^2 \pm 5$  in accordance with standard TAPPI 205 om-81. They were stored in air-conditioned environment with temperature of  $23 \pm 1^{\circ}$ C and relative humidity of  $50 \pm 2\%$  to achieve the physical and mechanical tests. Were prepared ten sheets with 0, 50 and 100% recycled fiber and ten sheets with the same compositions but with adjustment of the zeta potential.

## 2.4 Determination of charge

Determination of zeta potential was measured after the addition of aluminum polychloride in the pulp with a consistency of 0.5%. The determination was performed with the equipment Mutek SZP-06 manufactured by BTG (Figure 5).



#### Figure 5. Measuring zeta potential - Mütek SZP-06. (Source: Google Images).

The fiber potential analyzer is designed to determine the zeta potential of fibers according to the Helmholtz-Smoluchowski equation by simultaneously measuring conductivity, pressure and the streaming current potential. The measuring principle is based on the streaming current potential measuring method in a fiber plug.

## 2.5 Physic-mechanical tests

#### 2.5.1 Grammage

It is the determination the mass in grams per square meter paper or paperboard. The weight is obtained by Equation 1 where the forming area used is  $201 \text{ cm}^2$ .

$$Grammage = \frac{sheet \ weight \ (g)}{forming \ area \ (m^2)}$$
(1)

#### 2.5.1.1 Tear Resistance

The tear resistance is measured in equipment Elmendorf Pendulum SE 009 and it is the force perpendicular to the paper required to tear one or more sheets of paper through a specific distance (43 +/-0.5 mm). The fiber length is an important dimension in the development of resistance to tearing. It also said that intrinsic resistance of the fibers, related to the thick cell wall, is proving influential in the development of resistance to tearing, these features were more significant in long fibers.

#### 2.5.1.2 Burst Resistance

The burst resistance test runs on equipment Bursting Strength Tester and is defined as the pressure required to produce the burst of the material, by applying a uniformly increasing pressure, transmitted by an elastic diaphragm, a circular area equal to 962 mm<sup>2</sup>. Pulps with lower levels of fines and longer fibers in general, produce papers with higher resistance to burst.

#### 2.5.1.3 Tensile Resistance

Tensile strength is the maximum traction force per unit width of the paper or card supports before they break, under defined conditions. It is in direct tension force needed to break the paper, when applied longitudinally or transversely. The paper sample is pulled to rupture in the equipment Tensile Tester L & W - SE 062/064. The interfibrillar connections occurred in the formation of the role will be critical to discuss this property..

#### 3. RESULTS AND DISCUSSION

The results of the behavior of sheets with different percentages of addition of recycled fibers exhibited gradual gains for nearly all physical and mechanical properties. Table 1 shows the values obtained by analysis of short fiber sheets with different compositions of recycled fibers as well as the values of the zeta potential:

Table	1.	Results	of p	ohysical	tests
-------	----	---------	------	----------	-------

Composition of recycled paper (%)	Tensile Index (Nm/g)	Burst Index (kPa. m <sup>2</sup> /g)	Tear Index (mN. m <sup>2</sup> /g)	Zeta Potential (mV)
0	25.31	1.34	6.85	-183.00
50	21.99	1.33	8.02	-202.90
100	29.48	1.54	4.10	-139.60

For calculation purposes, we use the following equations:

Tensile Index = 
$$\frac{Tensile(kN/m)}{grammage(g/m^2)} \times 1000$$
 (2)

Burst Index= 
$$\frac{Burst(kPa)}{grammage(g/m^2)}$$
(3)

Tear Index = 
$$\frac{Tear(mN)}{grammage(g/m^2)}$$
 (4)

As you cannot precisely control the grammage of the sheet formed it used the calculation of the index. Thus we can compare the tests because they are adjusted according to the weight of each sheet.

As seen to best retention of particles occurs when the potential is near zero. To this, it was added aluminum polychloride mass. Table 2 shows the results obtained with zeta potential close to zero:

Composition of recycled paper (%)	Tensile Index (Nm/g)	Burst Index (kPa. m <sup>2</sup> /g)	Tear Index (mN. m²/g)
0	18.79	0.95	8.03
50	25.79	1.19	11.72
100	33.14	1.90	9.32

Table 2. Results of physical tests

Figure 6 shows a comparison of the tensile index:



Figure 7. Comparison of burst index.

It is observed that the burst index increases as increasing the recycled fiber composition. But with control of zeta potential this increase is more pronounced.

Figure 8 shows a comparison of tear index:



It is observed that the tear index follows a parabolic trend. Up to 50% recycled fiber had an increase, but with 100% recycled fiber been a sharp decline. The work required to tear a sheet is made of two major contributions: i) the work to cut the fibers, ii) the work needed to separate the fibers do not "cut" of its neighboring links. Therefore the increased tear index can be explained by the

increase in strength, because with better retention (zeta potential = 0) at fiber-fiber connection is greater.

As can be observed zeta potential influences the physicalmechanical properties of the paper. Therefore it retains the colloidal particles, and these in turn, improve sheet formation. According to the analysis obtained we can emphasize that the use of recycled fibers may contribute to the improvement of physicomechanical paper. Note that each point of the graphs is the average reading of ten analyzes.

## 4. CONCLUSION

The zeta potential is a very important factor in the manufacture of paper. It was observed that the sheets formed with zeta potential close to zero had a tendency better. The use of recycled paper actually increased the physical-mechanical properties of the paper. We observe that with increasing percentage of recycled paper in the sheet the properties increases. It is because recycled pulp fibers have the function to fill the empty spaces of intertwining short fiber pulp causing better paper formation.

#### 5. SYMBOLS USED

- $\zeta \quad \text{zeta potential} \ (mV)$
- $\Psi$  surface potential (mV)

### 6. ACKNOWLEDGMENTS

The research support by the Klabin Monte Alegre (Brazil) is gratefully acknowledged.

#### REFERENCES

- Ampulski, R.S. 1985. The influence of fibre surface charge on tensile strength. In Tappi Papermakers Conference Proceedings. (Denver, USA, April 15-17, 1985), 9–16.
- [2] Bhardwaj, N.K., Duong, T. D., Hoang, V. and Nguyen, K.L. 2004. Determination of fiber charge components of Lo-Solids unbleached kraft pulps. Journal of Colloid and Interface Science, 274 (Jun. 2004), 543-549.DOI= http://dx.doi.org/10.1016/j.jcis.2003.12.062.
- [3] Bhardwaj, N.K., Kumar, S., Bajpai, P.K. 2005. Effect of zeta potential on retention and drainage of secondary fibers. Colloids and Surfaces A. 260 (Jun. 2005), 245-250. DOI= http://dx.doi.org/10.1016/j.colsurfa.2005.03.011
- [4] Bhardwaj, N.K., Hoang, V. and Nguyen, K.L. 2007. A comparative study of the effect of refining on physical and electrokinetic properties of various cellulosic fibers. Bioresource Technology.98 (May 2007), 1647-1654. DOI= http://dx.doi.org/10.1016/j.biortech.2006.05.040
- [5] Carrasco, F., Mutjé, P., Pelach, M.A. 1998. Control of retention in paper-making by colloid titration and zeta potential techniques. Wood Sci. Techno. 32 (Apr. 1998), 145-155. DOI= http://link.springer.com/article/10.1007/BF00702595
- [6] Hubbe, M., Rojas, O., Lucia, L. A. and Jung, T. M. 2007. Consequences of the nanoporosity of cellulosic fibers on their streaming potential and their interactions with cationic polyelectrolytes. Cellulose. 14, 6 (Dec. 2007), 655-671. DOI= http://link.springer.com/article/10.1007%2Fs10570-006-9098-4

- [7] Lindström, T. 1991. Electrokinetics of the papermaking industry. In Paper Chemistry. Ed. Roberts, J.C., Blackie & Son Ltd., Glasgow, 28. Available: https://books.google.com.br/books?id=9Q38CAAAQBAJ&p g=PA22&dq=Paper+Chemistry.+Ed.+Roberts,p.+28,+1991 &hl=pt-BR&source=gbs\_toc\_r&cad=3#v=onepage&q=Paper%20Ch emistry.%20Ed.%20Roberts%2Cp.%2028%2C%201991&f= false
- [8] Nascimento, A.C., Moreira, J.V., Santos, R.A., Marques, R.G., and Iarosz, K.C. 2009. Influência de fibras recicladas nas propriedades físico-mecânicas do papel (In Portuguese). Revista de Engenharia e Tecnologia. 1, 1 (Dec. 2009), 93-71. Available: http://www.revistaret.com.br/ojs-2.2.3/index.php/ret/article/viewFile/16/53
- [9] Pietschker, D. A. 1985. Practical application of zeta potential. Tappi Journal. 68, 4, (Apr. 1985), 84-86. http://www.scopus.com/inward/record.url?eid=2-s2.0-0022050890&partnerID=10&rel=R3.0.0&md5=98c84c9db4f c973eb589364007683a14
- [10] Porobská, J., Alince, B., Van De Ven, T.G.M. 2002. Homoand heteroflocculation of papermaking fines and fillers. Colloid Surface A. 210, 2-3, (Nov. 2002), 223-230. DOI= http://dx.doi.org/10.1016/S0927-7757(02)00370-9
- [11] Sanders, N.D., Schaefer, J.H. 1992. A comparison of zeta potential distribution and colloid titration of papermaking materials: particle surface charge vs. polyelectrolyte adsorption. In Papermaking Conference. (Atlanta, USA, April, 1992) TAPPI Proceedings, 463-472.

- [12] Scott, W.E. 1996. Principles of wet end chemistry. In Tappi Press. (Atlanta, USA, 1996), 22-25. Available: http://www.tappi.org/content/pdf/member\_groups/paper/010 1r241.pdf
- [13] Shin, J. H., Han, S. H., Sohn, C., Ow, S. K. and Mah, S. 1997. Highly branched cationic polyelectrolytes: filler flocculation. Tappi Journal, 80, 11 (Nov. 1997), 179-185.

Silva, D. J. 2010. Química da parte úmida em processo de fabricação de papel – Interações em interfaces sólido-líquido (In Portuguese). Doctoral Thesis. Polytechnic of University of Sao Paulo. Available: http://www.teses.usp.br/teses/disponiveis/3/3137/tde-13082010-115730/en.php

- [14] Stratton, R. A. and Swanson, J. W. 1980. Electrokinetics in papermaking - a position paper. In TAPPI Annual Meeting. (Atlanta, USA, February 24-27, 1980) Tappi Press, 79-83. http://www.scopus.com/record/display.url?eid=2-s2.0-0018923965&origin=inward&txGid=0584DD6541635C772 5B48D5403F76DC7.fM4vPBipdL1BpirDq5Cw%3a12
- [15] Thiele, B., Kopp, J.W. 1997. Charge balances of paper machine systems – a method of process optimization. Wochenbl. Papierfabr, 125, 11-12 (1997). 542-556