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DETERMINATION OF THE SPECIFIC SURFACE OF CELLULOSE FIBRES

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Abstract:

The determination of the surface character of cellulose fibres is important not only in the papermaking technology and environmental protection, but the technologies of the sizing, the filling, and the coloration are all influenced by the specific surface of the pulp fibres.

In the experimental part of scientific work it was studied how the sizes of molecular, colloidal and coarse surface areas are dependent on the beating degree of cellulose fibres from different types of and differently cured pulps. For this purpose the adsorbed quantities of particles with different size were measured with molecular size methylene-blue, colloidal size iron-hydroxide ($Fe(OH)_3$) and micronized titanium-dioxide (TiO_2) which formed saturated monolayers. The specific surface areas of pulp fibres were found to be increased with increasing beating degree, on a typical manner of the different pulp. From the measured surface parameters mentioned above three new different surface types were calculated and nominated as primary-, secondary and tertiary surfaces.

Keywords:

cellulose fibre, fibre surface, specific surface, molecular size methylene-blue, colloidal size iron-hydroxide, micronized titanium-hydroxide,

1 INTRODUCTION

In order to produce high quality paper products, it is very important to alter the construct of the fibre surface because the properties of the products of the paper industry depend on the raw- and auxiliary materials' surface quality. The paper's mechanical parameters, flexibility, and permeatibility are influenced by the content and the method by which the pulp is produced.

During pulp production, the type of cooking, chemical penetration, the type of chemical reaction, as well as the technological method used to separate lignin from plant fibres alters the surface characteristics of the pulp (Figure 1). At the same time, the success of these technogologies depends on the properties of the fibre surface. During paper production, the water-based heterogenous contents significantly influence the qualitative properties of the paper. [1]

For those producing paper, it is very important to know how the mechanism of the interaction between the fibre and the filling material, such as absorption and adhesion, works in an electrolytical water-based environment. To optimize and improve knowledge about processes like beating and suspending, it is necessary to determine the exact physical and chemical mechanism of the previously described processes.

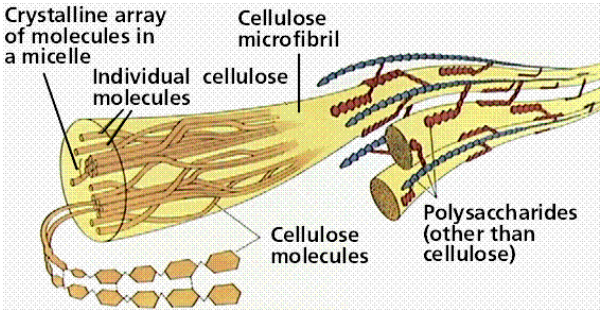

Figure 1: The structure of the cellulose fibre [2]

The determination of the colloidal structure and specific surface of the pulp fibres has been studied by international as well as Hungarian researchers for a long time.

It is advantageous to conduct the experiments in liquid medium because the surface characteristic of the fibres alters irreversibly in dry condition. Scientific articles about surface properties of pulp fibres and the specific surface of the pulp have been published worldwide since the 1940s and 1950s.

In the Obuda University, after a long period of scientific research, the so-called Three-Way Method.The essence of this method is the absorption of the positively charged particle onto the negatively charged surface of the fibre. In order for this method to be useful, a monomolecular layer needs to be formed on the fibre surface. With respect to the monomolecular adsorption, the parameters of the electrolyte concentration, the pH level, the initial and equilibrium concentration, adsorption time, and the temperature have to be optimized. It is also very important that the adsorptives should stay in discrete forms.

The main objectives of the scientific work were to optimize the Three-Way Method, to develop it further, and to determine the industrial usefulness of the new result. An additional aim of the research was to determine how the surface characteristics and different specific surface values of the fibres changed during the beating process. Furthermore, it was a question whether there is a significant relationship between the specific surface of the fibres and the mechnical properties of the paper made up from these fibres. [3][4]

2 EXPERIMENTAL PART OF SCIENTIFIC

2.1 Materials

Cotton, wheat, and pine fibres, cooked using different methods and beaten to different degrees, were examined by methylene blue, iron-hydroxide, and titanium-dioxide adsorption. These different fibre materials from the sample collection were beaten to 30, 50, and 70 beating degrees (SR) using Valley beating instruments according to the standards (Figure 2).

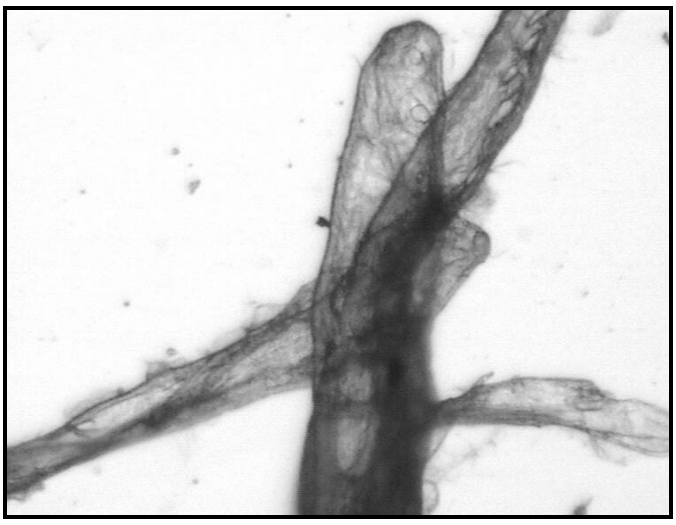

Figure 2: Tracheida fiber before the beating

After the beating process the structure of the fibre-materials were studied with a *WAT-250 D(W96P)* - type video microscope (Figure 3).

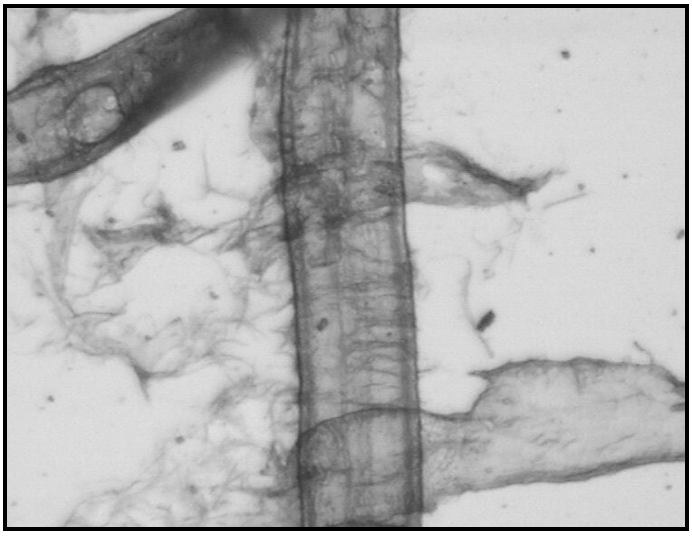

Figure 3: Tracheida fiber after the beating

After beating a part of the wet fibre sample were taken an Ernst-Hage type laboratory sheet-forming device, and 15 pieces of paper of about 80 g/m^2 were made. The rest of the sample was taken to the same laboratory sheet-forming device to filter it. Afterwards, the still-wet sample of filtered fibres was taken in a hermetically sealed polyethylene bag and stored at temperature between 274-276 K, until its

use for the experiment. The pH level of the cellulose fibre samples was around 6.5 to 7 (that of tapwater), which was acceptable for laboratory paper forming, however the pH level had to be changed for the surface study.

Consequently, the pH level of the cellulose fibres were adjusted to be 3.8-4.0 with 0.01 mol/l HCl solution or 0.01 mol/l NaOH solution.

2.2 Methods

After having climatic preparation, the tearing, ripping and cracking parameters were determined.

The differently cured, various types of cellulose fibers were also studied according to valid cellulose chemistry laboratory standards.

In order to form monomolecular layer, the parameters of the surface adsorption were optimized. Because the mass of the layers is influenced by the repulsion of the particles, the aim was to minimize this effect.

As part of the preparation for the experiment, the electrolyte concentration, the pH level, the initial and equilibrium concentration, as well as the adsorption time were optimized with Langmuir type isotherm. Using the highest value of the adsorptive isotherm, the molecular-, the colloidal- and the micronised specific surface values were calculated. [5][6]

The different types of specific surface of the cellulose fibres were measured using methylene-blue particles measuring 0.77 nm in diameter (C.I.52015 type); iron-hydroxide particles measuring 5.0 nm in diameter; and titanium dioxide particles measuring 524.0 nm (type RFD-1). The iron hydroxide was hydrolysed from iron chloride with ammonium carbonate. So the most important parameters of the measurement were the diameters of the particles. Using 1 mg methylene blue we can measure about 1 m^2 surface, 10 mg iron-hydroxide can measure 1.2 m^2 surface and 1000 mg titanium-dioxide, can measure 1.12 m^2 surface. Considering the molecular weight of the adsorptiums, we can calculate the surface of the cellulose (Eq.1-2).

$$m^{\sigma} = \frac{V \cdot (C_k - C_e)}{m}$$

(Eq. 1.)

Where:

V: volume of the suspension [dm^3]

C_k: concentration of the solution before the adsorption [mol/dm^3]

C_e: concentration of the solution after the adsorption, [mol/dm^3]

m: weight of the cellulose [g]

m^{σ}: weight of the adsorptioned particles [mol/g]

$$S = m^{\sigma} \cdot N \cdot S_0$$

(Eq. 2.)

Where:

m^{σ}*: weight of the adsorptioned particles [mol/g]*

N: Avogadro- Loschmidt number [$6 \cdot 10^{23}$ *particle/mol]*

S_o*: surface of one adsorptioned particle [* m^2*/1 particle]*

S: specific surface [m^2*/g]*

To characterise the fibre surface, the previous research carried out in this field was further developed and perfected. To use the adsorptive diameter data, the surface measured by methylene-blue, by iron-hydroxide and by titanium-dioxide was designated 'molecular surface', 'colloidal surface' and 'rough surface', respectively.

From the previously measured surface parameters, three new different surface types were calculated and defined as primary, secondary and tertiary surfaces. The primary surface value is equal to the rough surface value, the secondary surface is the difference between the colloid and the rough surface values, and the tertiary surface is the difference between the molecular and the colloid surface values.

This new concept system is useful for optimizing the processes which modify the fibre surface and for optimizing the paper-making processes such as sizing, filling, and coloration, as well as the properties of different paper products.

The research also includes the study of connection between the variation of the surface character of the fibres and the mechanical properties of the papers made from the different fibrous materials. For this purpose, correlation between changes of the mechanical values and the surface values were calculated.

3 RESULTS

By the method which measures the specific surface using methylene-blue, it was determined that for 1,0 ± 0,5 g absolutely dry mass of fibres, at 3,8-4,1 pH, at 297 K, and a 3,0 mmol/l volume of 20,0 cm^3 liquid, the total monomolecular layer forms within 5 hours (Figure 4).

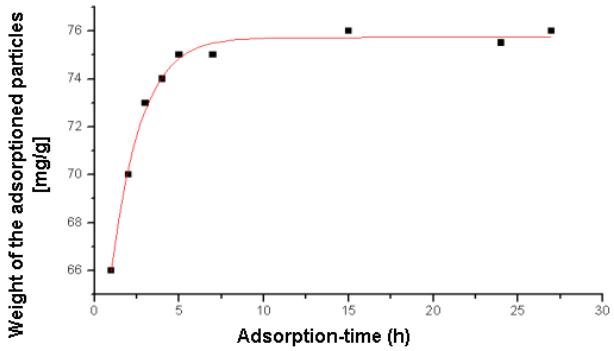

Figure 4: The adsorption-time of the methylene-blue monomolecular layer

Between the specific surface determined by the Three Way Method and the cellulose fibre type it was determined that the result of bleaching is significant in the fibres with a low beating degree by the titanium dioxide and iron hydroxide surface methods. Around 75 SR, the results of bleaching do not influence the specific surface values significantly.

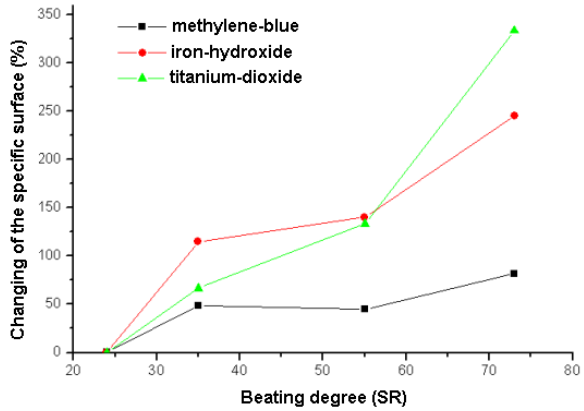

Figure 5: Relationship between the values of the three adsorptives surface types and the beating degree

As a result of the relationship between the values of the three new surface types and the beating degree, it was determined that the primary surface increased significantly by the beating degree. The values of the primary surface were changed between 0.3-4 m^2/g. The secondary surface value increased significantly by the beating degree. Values changed between 2.1-35 m^2/g. The tertiary surface value decreased with the beating degree in most of the fibers. Values changed between 17-8 m^2/g. This indicates that the molecular order of magnitude of the fibre surface opened in the colloidal order of magnitude of the fibre surface during the beating process (Figure 5 and Figure 6).

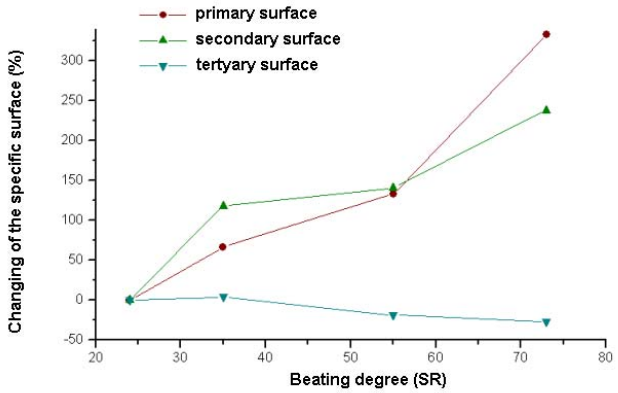

Figure 6: Relationship between the values of the three surface types and the beating degree

4. CONCLUSIONS

As a result of sample fibre measurements, a strong correlation between the beating degree and beating time was determined. So it was possible to interpolate an empirical and exponential Boltzman graph or a linear graph to represent the beating process.

Strong positive correlation was experienced between the result of the specific surface values of the Three Way Method and the beating degree. By increasing the beating degree, the specific surface measurements also increased in a typical way which characterized the different pulps

The previous fibre surface definitions were perfected and three new designations were introduced: the primary, the secondary, and the tertiary surfaces. The primary surface value is equal to the rough surface value, the secondary surface value characterizes the difference between the colloid and the rough surface values, and the tertiary surface is the difference between the molecular and the colloid surface values.

4 REFERENCES

[1] Broderic, G.; Paris, J.; Valade, J.L.: Fiber development in chemmimechanical pulp refining", Tappi Journal, 1996, Vol.79, No. 4, pp.193-201.

[2] The structure of the cellulose fibre
http://www.emc.maricopa.edu/faculty/farabee/biobk/biobookchem2.html (online, 25.10.2010)

[3] Kaewprasit, C.; Hequet, E.; Abidi, N.; and Gourlot J.P.: „Application of Methylene Blue Adsorption to Cotton Fiber Specific Surface Area Measurement Part I. Methodology", Journal of Cotton Science, 1998, No.2, pp.164-173,

[4] Karlson, O.; Westermark, U.: „Evidence for Chemical Between Lignin and Cellulose in Kraft Pulps", Pulp and Paper, 1996, Vol. 22, No.10, pp. 397-400.

[5] Koltai, L., Baksay, M-né., Rohrsetzer, S., : Determinations of the Colloidal Structure of Pulp Fibres by Adsorption in Liquid Medium - The role of pulping Process, Acta Polytechnica Hungarica, 2008, Vol. 5, No.3, pp.87-92.

[6] Vilar, V.J.P.; Botelho, C.M.S.; Boaventura,R.A.R.: „Methylene blue adsorption by algal biomass based materials", Journal of Hazardous Materials, 2007 Vol. 74 No. 1-2, pp. 120-132.

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