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THESES OF THE Ph.D. DISSERTATION

DETERMINATION OF THE COLLOIDAL STRUCTURE OF PULP FIBRES

LÁSZLÓ KOLTAI

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DOCTORAL SCHOOL: **Cziráki József Wood Science and Technology**
(Head: Dr. András Winkler DSc.)

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(Head: Dr. András Winkler DSc.)

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SUPERVISOR: **Dr. Károly Németh DSc.**

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 mechanical parameters of the paper, the flexibility, and the permeability are influenced by the content and the method by which the pulp is produced.

In the process of cellulose fibre production, the type of cooking, chemical penetration, the type of chemical reaction, and the technological method used to separate lignin from plant fibres alter the surface characteristics of the pulp. At the same time, the success of these technologies depends on the properties of the fibre surface.

During paper production, the water-based heterogeneous contents significantly influence the qualitative properties of the paper.

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 the processes like beating and suspending, it is necessary to determine the exact physical and chemical mechanism of the previously described processes.

2. The Antecedents of the Scientific Research Work

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

It is advantageous to conduct the experiments in a liquid medium because the drying irreversibly alters the surface characteristics of the fibres. Scientific articles about surface properties of pulp fibres and the specific surface of the pulp have been published in the international sphere since the 1940s and 1950s.

In 1974, the Fibre Technology Committee of the Hungarian Academy of Sciences suggested a system of measurement of fibrous materials. Among the various surface measurement methods, the suggestion of measuring particle absorption was a pivotal one.

In the Budapest Polytechnic, after a long period of scientific research work, the so-called 'Three-Way Method' was developed by Sándor Rohrsetzer and József Erdélyi. 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 stay in a discrete form.

3. The Aims of this Scientific Work

The aims of the scientific work were to optimize the Three-Way Method, develop it further, and 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.

Further, it was a question whether there is a significant relationship between the specific surface of the fibres and the mechanical properties of the paper made using these fibres.

4. The Methods of the Research Work

In the research work, cotton, wheat, and pine fibres which were cooked using different methods and beating degrees were examined by methylene-blue, iron-hydroxide, and titanium-dioxide adsorption.

These different fibre materials from the sample collection were beaten in laboratory using Vallei-beater onto 30, 50, and 70 beating degrees according to the standards.

After the beating process the construction of the fibre-materials (the measure of the fibrillation) were determinated with a *WAT-250 D(W96P)* - type video microscope.

After the beating a part of the wet fibre sample were taken an Ernst-Hage type laboratory former, and 15 pieces of paper of about 80 g/m^2 were made. The rest of the sample was taken to the same laboratory former device to filter it. Afterwards, the still-wet sample of filtered fibres was taken in a hermetically sealed polyethylene bag and stored 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 tap water), 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 changed to be between 3.8 and 4.0 with 0.01 mol/l HCl solution or 0.01 mol/l NaOH solution.

After having climatic preparation the tearing resistance, the bursting strength and tensile strength parameters were determined.

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

In order for a monomolecular layer to form, 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, and the adsorption time was optimized with Langmuir type isotherm. Using the highest value of the adsorptive isotherm, and the diameter values of the particles the molecular, the colloidal, and the micronised specific surface values were calculated.

The different specific surfaces of the cellulose fibres were measured with a micro colourant methylene-blue particle measuring 0.77 nm in diameter, of a C.I.52015 type; an iron hydroxide ($Fe(OH)_3$) particle measuring 5.0 nm in diameter; and a titanium dioxide (TiO_2) particle measuring 524.0 nm of type RFD-1. The iron-hydroxide was hydrolysed from concentrated iron-chloride solution ($Fe(OH)_3$) with powdered ammonium-carbonate ($(NH_4)HCO_3$).

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 methylene-blue surface was designated 'molecular surface', the iron hydroxide surface was designated 'colloidal surface', and the titanium dioxide was designated 'rough surface'.

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 of the thesis also includes the study of the 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 calculations between changes of the mechanical values and the surface values were used.

5. Theses of the Research Work

The following results were reached after the research work was summarized

1) 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 a pH level of 3,8-4,1 at 297 K, and with a 3,0 mmol/l volume of 20,0 cm^3 liquid, a maximal monomolecular layer forms within 5 hours, independently the fibre-type.

2) 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.

3) Previous fibre surface definitions were perfected, and three new denominations were introduced as the 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.

4) 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 (TiO_2) and iron-hydroxide ($Fe(OH)_3$) surface methods. Around 75 SR, the results of bleaching do not change the specific surface values significantly.

5) There is a strong positive correlation 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 increase in a typical way which characterises the different pulps. The methylene-blue surface value of the cotton fibres changed between 18-38 m^2/g, the iron-hydroxide surface value of it changed between 2-28 m^2/g, and the titanium-dioxide surface value of it changed between0,6-2,6 m^2/g. The methylene-blue surface value of the straw fibres changed between 25-32 m^2/g, the iron-hydroxide surface value changed between 10-29 m^2/g, and the titanium-dioxide surface changed between 0,3-2,6 m^2/g. The methylene-blue surface value of the spruce fibres changed between 33-49 m^2/g, the iron-hydroxide surface value changed between 13-36 m^2/g, and the titanium-dioxide surface changed between 2-4 m^2/g.

6) 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, and the value of the primary surface is changed between 0.3 and 4 m^2/g. The secondary surface value increased significantly by the beating degree, its value is changed between 2.1 and 35 m^2/g. The tertiary surface value decreased with the beating degree in most of the fibres, and its value changed between 17 to 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.

7) In the results of the measurements of the papers made from fibrous materials and the Three Way Method's specific surface value, it was determined that there is a strong relationship (the correlation coefficient is above 0.92) between the tensile index and the iron hydroxide specific surface, and between the tensile index and the iron hydroxide specific surface. There is a weak relationship between the tear index and the specific surface values. The

methylene-blue value is also weakly correlated with the mechanical parameters. This indicates that the beating process changed mostly the rough and colloid surfaces, but the molecular surfaces changed only to a small degree.

8) In the results of the measurements of the papers made from fibrous materials and the three new specific surface values, it was determined that the strongest relationships are between the primary and the secondary surfaces, and the primary surface and tensile index. There is also quite a strong relationship between bursting index and the primary and secondary surfaces. The tear index has a weak relationship with the primary and secondary surfaces.

6. Important Publications Related to the Research

Journal Articles in Hungarian and English

1. **Koltai, L**: Papíripari rostanyagok fajlagos felületének összehasonlító vizsgálata Gallóné H. J. (szerkesztő): A Könnyűipari Műszaki Főiskola Csomagolás- és Papírtechnológiai Tanszékén 1997-ben végzett papírgyártó-feldolgozó ágazatos hallgatók szakdolgozatainak rövid kivonata.
Papíripar, XLII. évf. 2. sz. 1998.

2. Rohrsetzer, S.–Erdélyi, J.–Baksay, M.,-**Koltai, L**.-Annus, S.: Víztartalmú papíripari cellulózrostok kolloidkémiai szerkezetének megállapítása molekuláris kolloid és durva részecskék adszorpciójával, illetve adhéziójával
Magyar Kémiai Folyóirat 106. évfolyam, 4. szám, 2000. április

3. Erdélyi, J.–Baksay, M-né.-**Koltai, L**.-Annus, S.: Rostok fajlagos felületének meghatározása vízközegben
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4. **Koltai, L**.–Majsai, K.–Gallóné, H. J.: Csomagolóipari papírok rostanyagának összehasonlító fajlagos felület és mechanikai tulajdonság vizsgálata I.- Elméleti alapok
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6. **Koltai, L**.– Borbély, E.– Erdélyi, J.: Papíripari rostanyagok kolloidkémiai szerkezetének vizsgálata víz közegben színezékrészecskék adszorpciójával,
Anyagvizsgálók Lapja, 16./1. 2006.

7. **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, (ISSN 1785-8860) Vol. 5. No.3, 2008.

8. **Koltai, L**. : Papíripari rostanyagok felületi jellegének meghatározása I. – Elméleti alapok
Papíripar LIII. Évf. 1. sz. 2009.

9. **Koltai, L**. : Papíripari rostanyagok felületi jellegének meghatározása II. – Vizsgálati eredmények
Papíripar LIII. Évf.3. sz. 2009. – megjelenés alatt

Conference Presentations

1. **Koltai, L**.: Papíripari rostanyagok fajlagos felületének összehasonlító vizsgálata
MTESZ-PNyME-BMF Fiatal Diplomások Fóruma-Budapest, 2004. november 23.

2. **Koltai, L**., Majsai K., Erdélyi J.: Papírok rostanyagának fajlagos felület és mechanikai tulajdonság vizsgálata
IN-TECH-ED'05 konferencia Budapest, 2005. szeptember 8-9.

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4. **Koltai, L**.: Búzaszalma cellulózrost kolloidkémiai szerkezetének meghatározása
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1. **Koltai, L.**, - Majsai K., - Erdélyi J. : Papírok rostanyagának fajlagos felület és mechanikai tulajdonság vizsgálata – Összefoglaló/Proceedings *IN-TECH-ED'05 Budapest, 2005. pp.275-279. (ISBN 963-7154-52-3)*

2. **Koltai, L.** – Baksay, M. – Rohrsetzer, S.: Determinations of the Colloidal Structure of Pulp Fibres by Adsorption in Liquid Medium - The role of pulping Process
BMF -Conference 2007.- New Aspects in the Innovation of a Traditional Industry Budapest, 2007. pp.189-192. (ISBN 978-963-7154-66-9)

3. **Koltai, L.**,-Baksay, M.-né,-Gallóné, H. J.: Búzaszalma cellulózrost kolloidkémiai szerkezetének meghatározása
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4. **Koltai, L.**: Papíripari rostanyagok videomikroszkópos vizsgálata
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Scientific Conference Posters in Hungarian

1. **Koltai, L.**: Papíripari rostanyagok videomikroszkópos vizsgálata
Tudomány és innováció a jövő szolgálatában - workshop – KSZGYSZ-BMF Budapest, 2008. november 7.

Publications Marginally Related to the Research

1. **Koltai, L.**: A papír szerepe a csomagolásban - Csomagolópapírok
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2. **Koltai, L.**- Oroszlány, G.-Nagy, E.: A papír szerepe a csomagolásban – Reklámtáskák papírból
   Transpack- csomagolási, anyagmozgatási és logisztikai magazin, VIII.évf./I.sz. 2008. február

3. **Koltai, L.**: A papír szerepe a csomagolásban – Poharak papírból
   Transpack- csomagolási, anyagmozgatási és logisztikai magazin, VIII.évf./II.sz. 2008. április

4. **Koltai, L.**: Hullámtermékek, több mint egy évszázada a csomagolóiparban – I. rész
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5. **Koltai, L.**: Hullámtermékek, több mint egy évszázada a csomagolóiparban – II. rész
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