

NANO-STRUCTURAL CONCEPT OF PAPERMAKING

M. Ioelovich and O. Figovsky

Polymate Ltd, 23100 Migdal HaEmek, Israel

KEYWORDS: Cellulose, Nano-structure, Papermaking

INTRODUCTION

Paper is a sheet composite consisting of cellulose-based fibers and additive of fillers, pigments, sizing agents, processing aids etc. Various paper types are known such as printing paper, writing paper, packaging paper, technical paper types and others. World production of the paper is estimated in 150-200 metric tons per year. Main raw-materials for papermaking are wood cellulose, cotton and other cellulose fibers. Soft- and hardwood cellulose is cheap and available material producing in the volume of 100-150 million tons per year. World resource of cotton fibers is about 20-25 million tons per year, and only its lower part is used in papermaking for production of special paper types.

The papermaking process includes steps of preparing the paper composition, wet beating, forming of wet sheet, pressing, drying, calendering and probable surface finishing (printing, dyeing, coating, etc.)¹. Beating or pulping is the obligatory step of papermaking required to obtaining the strong paper.

Despite that process of paper forming was studied for many years, certain substantial problems were not solved. Only in recent years the papermaking process can be studied deeply and detailed owing to progress in technique and methods of nano-structural investigations². Purpose of this work is to study contribution of cellulose nano-fibrils in formation of the structure and physico-mechanical properties of the paper.

MATERIALS AND METHODS

Paper-grade bleached sulfate softwood cellulose of International Paper Inc was used as initial material for papermaking. To prepare nano-size cellulose (NC), the initial material was hydrolyzed with hydrochloric acid at moderate temperatures; and the washed hydrolyzed cellulose was diluted and disintegrated by high-pressure homogenizer APV-2000 at the pressure of 100 MPa to obtain aqueous slurry of NC³.

The initial cellulose was beaten by Escher-Wyss mill at 10% solid content in water. The NC-slurry was added to mechanical pulp in amounts from 5 to 20% to solid cellulose and mixed together in the Waring blender.

Paper samples were formed on Rapid-Kothen sheet apparatus at 1% fiber concentration in presence of sizing agent (0.1% AKD to solid) and retention aid (0.5% PAA to solid). Then the wet sheets were pressed and dried. After conditioning at standard conditions, the paper samples were tested by Instron 4201 - Test System.

To carry out the structural investigations the wet mechanical pulp and NC-slurry were freeze-dried. Then the prepared samples were investigated by XRD, SEM and TEM methods.

RESULTS AND DISCUSSIONS

XRD investigations showed that elementary crystallites of native softwood cellulose have lateral size of 3.5-4 nm, while cellulose isolated from softwood by sulfate cooking with following bleaching contains nano-crystallites with lateral size of 7-8 nm formed via irreversible co-crystallization of adjacent elementary crystallites⁴. Release surface of the elementary nano-fibrils from the amorphous lingo-hemicellulose matrix at the wood's cooking process permits direct contact of the elementary fibrils with each other and forming lateral aggregates - secondary nano-fibrils with diameter ca. 10 nm coupled together with strong crystalline joints. Besides, morphology of isolated cellulose fibers consists of fibrillar bundles and lamellas with lateral size of 20-40 nm and fragments of S1-layer with thickness of 100-300 nm.

The prepared NC-slurry contains rod-like nano-particles having crystalline modification of C1 (Fig. 1 and 2, Table 1).

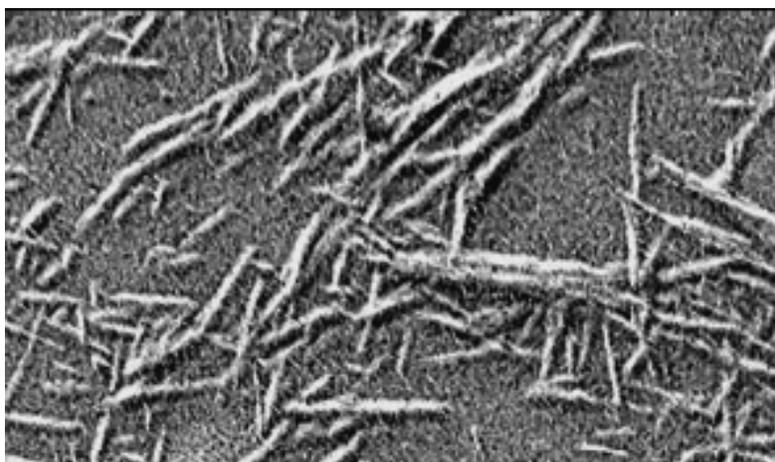


Fig. 1: Rod-like nano-particles of the NC-slurry

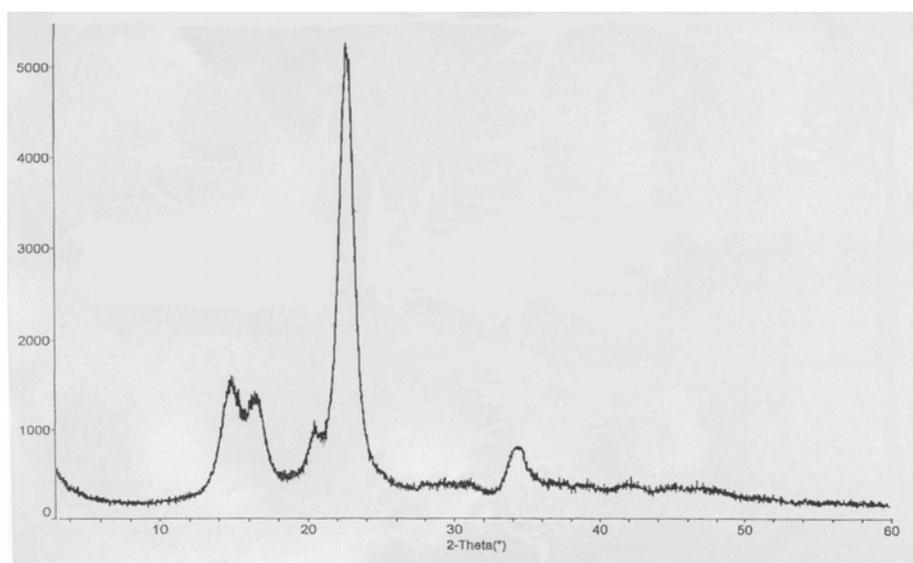


Fig. 2: X-ray patterns of NC

Table 1: Structural characteristics of NC

Characteristics	Value
Crystallinity degree, %	76-78
Lateral size of crystallites, nm	8-10
Length of crystallites, nm	50-60
Length of the nano-particles, nm	180-200
Width of nano-particles, nm	20-40
Sp. surface, m ² /m ³	1.5 x 10 ⁸

Beating of the initial cellulose has a negligible effect on crystallinity degree and sizes of crystallites (Table 2).

Table 2: Structural characteristics of cellulose samples

Characteristics	Initial sulfate cellulose	Sulfate cellulose after beating to 60 °SR
Crystallinity degree, %	64-65	63-64
Lateral size of crystallites, nm	7-8	7-8
DP	830-850	820-840

However, during the beating the significant changes in morphology of cellulose fibers are taken place. As follows from the structural investigations, the beating process causes fibrillation of the cellulose fibers with eliminating of submicron lamellas and fibrillar bundles (Fig. 3)

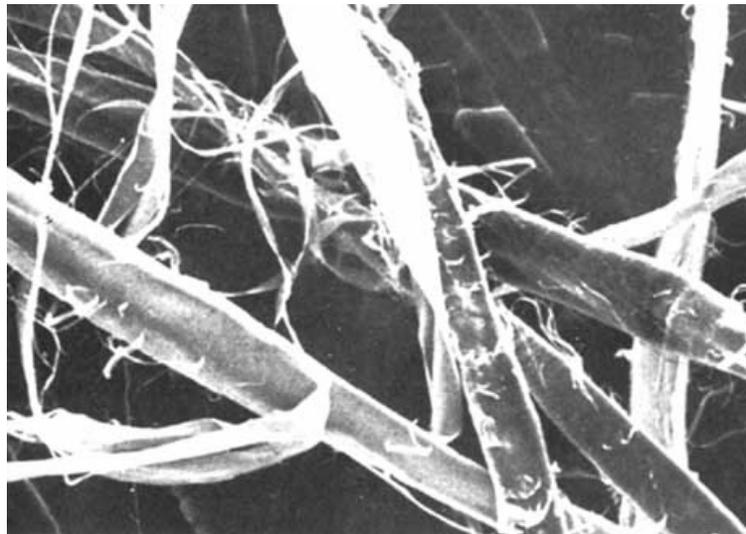


Fig. 3: SEM photo - fibrillated surface of cellulose fibers after beating up 35 °SR

With rise the beating degree (freeness value), the relative part of submicron fibrillar bundles increases, while their lateral size decreases. By means of statistics methods, a dependence of the average thickness of structures (**H**) formed as a result of beating on the freeness value (**°SR**) is found (Fig.4).

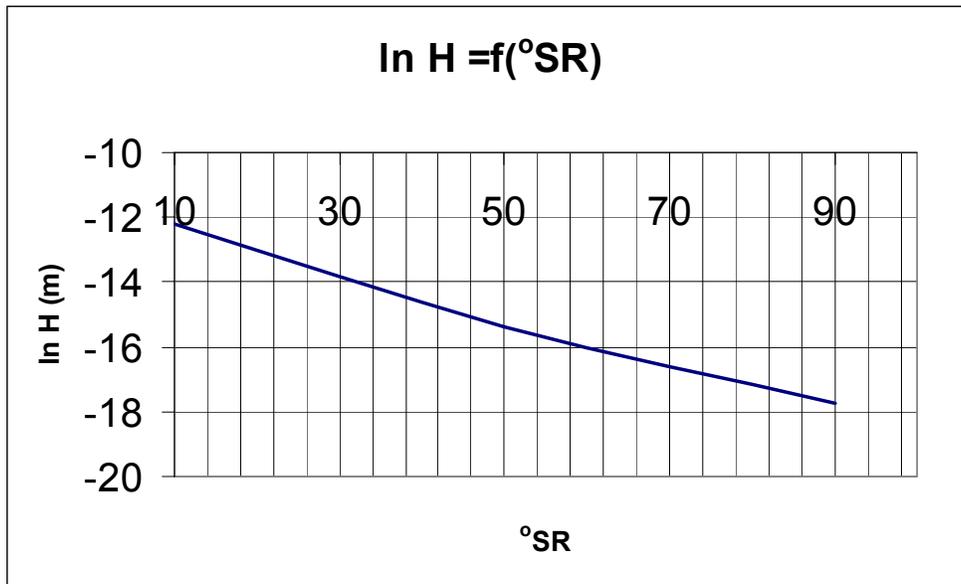


Fig. 4: Relationship $H=f(^{\circ}\text{SR})$

The non-beaten fibers having $^{\circ}\text{SR}$ 10-12 don't consist of fibrillated submicron bundles, because obtained H -value is close to thickness of cell wall for the initial cellulose fibers (4-5 μm). Increasing of the freeness value of the fibers to 80 $^{\circ}\text{SR}$ causes forming fibrillar bundles with average thickness of 40 nm.

At a drying process, the nano-scale fibrils join the adjacent cellulose fibers by means of strong contacts containing hydrogen bonds. As a result, the fibrous web bonded with interfiber contacts, characteristic to paper architecture is formed (Fig. 5).

Additive of NC-slurry to mechanical pulps has a significant effect on paper properties, because thin nano-cellulose particles form additional interfiber contacts. Moreover, these particles fill both micro- and nano-pores of the paper. As a result, sharp increasing of density and tensile strength of the paper is taken place (Fig. 6).

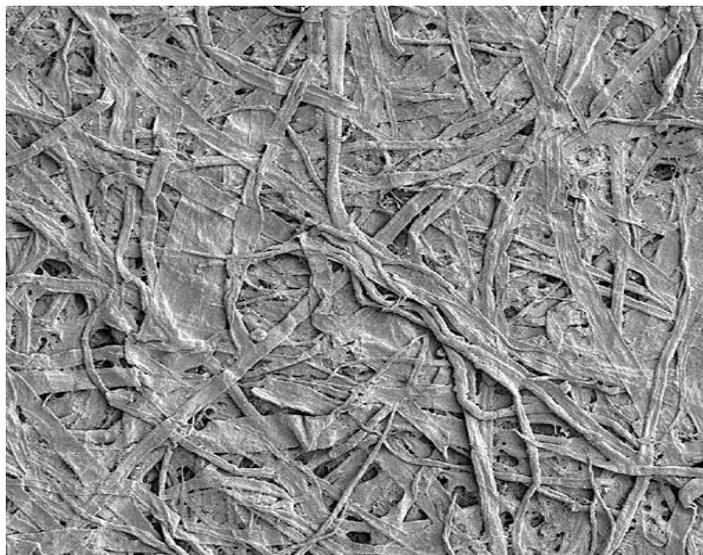


Fig. 5: Structure of the dried paper

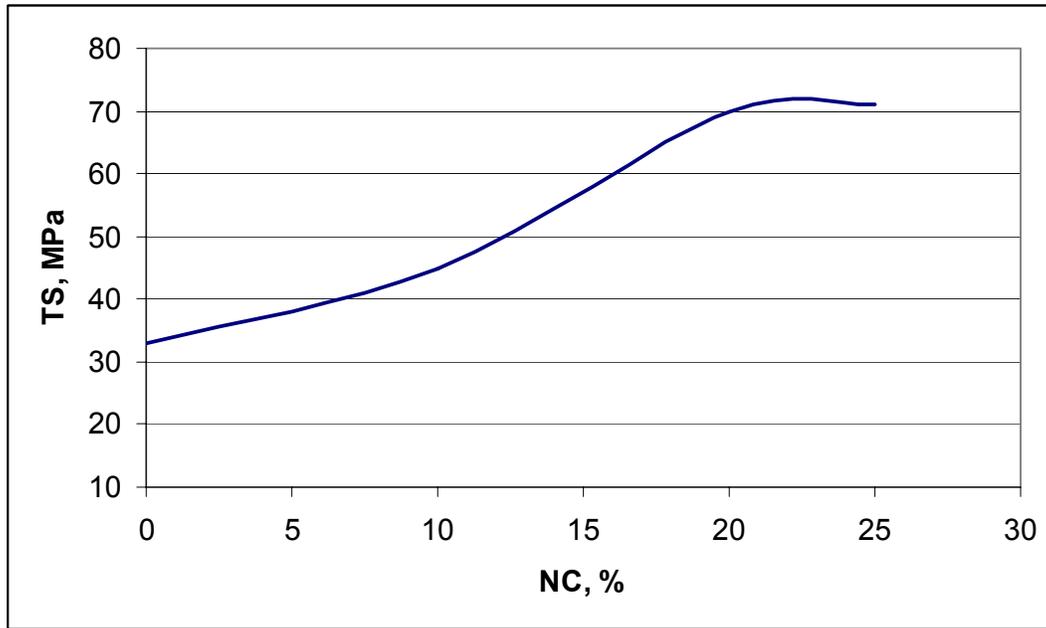


Fig. 6: Dependence TS of paper on amount of NC-additive to 35 °SR mechanical pulp

CONCLUSION

The hydrogen bonds play a major role in forming the interfiber paper contacts⁵. In order to achieve the interfiber hydrogen bonds, the direct contacts between fibers should be provided: no-contacts, no-bonds⁶. However, roughness of the cellulose fibers hinders forming the direct contacts. Due to fiber roughness the minimal distance between fiber surfaces even in the strong paper samples is 10-20 nm^{6,7}, which is much more than distance of 0.27-0.3 nm that is required for forming of the direct hydrogen bonds. The direct contact between the adjacent fibrillated fibers is provided by means of the long and thin nano-fibrils and their bundles filling the inter-fiber gaps.

Drying process of a wet paper sheet is accompanied by constriction of fibrils under effect of water surface tension. If the water layer between nano-fibrils is 20 nm, then constriction pressure of the nano-fibrils under the water surface tension is about 7 MPa. In the case that only four water molecules remain between the nano-fibrils, then constriction pressure increases to about 140 MPa. After all water molecules evaporate, the direct contact of the adjacent nano-fibrils with forming strong hydrogen bonds can be taken place.

Based on data that average energy of hydrogen bonds in paper samples is 20 kJ/mol, distance of these bonds is 0.3 nm and surface of one glucopyranose link is 0.27 nm², an average tensile strength (TS) of the direct interfiber contact caused by hydrogen bonds can be calculated.

The calculation gives TS value of 450 MPa that is close to experimentally determined tensile strength of the interfiber contact in the strong paper⁷. Lots of the contacts are formed between the fibers. Therefore, mechanical properties of paper samples are limited by strength of the individual cellulose fibers and their orientation in the paper sheet.

Thus, forming nano-scale fibrils at cellulose beating process and following their constriction at drying of the wet sheet promotes obtaining the dense and strong paper caused by hydrogen

bonds. Additive of nano-cellulose slurry to mechanical pulps improves mechanical properties of paper, because the nano-particles having high developed surface can form additional interfiber hydrogen bonds.

REFERENCES

1. **Grant, J.**, “A laboratory handbook of pulp and paper manufacture”, **Second edition, E. Arnold Publ., London, 1961.**
2. **Nano-Pulp and Paper Company**, “Highlights in global markets and emerging technologies”, **<http://www.nanopulpanpaper.com>**
3. **Ioelovich, M. and Leykin A.**, “Microcrystalline cellulose: nano-structure formation”. *Cellulose Chem. Technol.*, **Vol. 40, No. 5, pp 313-317, 2006.**
4. **Ioelovich, M.**, “Distribution of cellulose crystallites”. *Cellulose Chem. Technol.*, **Vol. 40, No. 7, pp 519-523, 2006.**
5. **Nissan, A.H., Byrd, V.I., Batten, G.I. and Ogden, R.W.**, “Paper as an H-bond dominated solid in the elastic and plastic regimes”, *TAPPI*, **Vol. 68, No 9, pp 118-122, 1985.**
6. **Hubbe, M.A.**, “Bonding between cellulosic fibers in the absence and presence of dry-strength agents”, *BioResources*, **Vol. 1 No 2, pp 281-318, 2006.**
7. **Reizinsh, R.**, in: “Wood cell wall and its transformations under chemical treatments”, **Science, Riga, 1972.**