Ministry of Education and Science of the Russian Federation
Northern (Arctic) Federal University named after M.V. Lomonosov

THE ISSUES IN MECHANICS OF PULP-AND-PAPER MATERIALS

PROCEEDINGS
4th INTERNATIONAL CONFERENCE
IN MEMORY OF PROFESSOR VALERY KOMAROV

September 14–16, 2017

Arkhangelsk
Russia

УДК 676.017
ББК 35.77
П 78

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Конференция проводится при финансовой поддержке Российского фонда фундаментальных исследований (проект № 17-08-20431\17)

П 78 **Проблемы механики целлюлозно-бумажных материалов**: материалы IV Междунар. науч.-техн. конф., посвящ. памяти профессора В.И. Комарова (Архангельск, 14–16 сентября 2017 г.) / Сев. (Арктич.) федер. ун-т им. М.В. Ломоносова. – Архангельск: САФУ, 2017. – 377 с.
ISBN 978-5-261-01259

Представлены материалы докладов по фундаментальным и прикладным исследованиям в области механики целлюлозно-бумажных материалов по следующим направлениям: физические основы и методы оценки механического поведения целлюлозно-бумажных материалов; новые технологические решения для повышения уровня механических свойств технической целлюлозы, бумаги и картона; перспективы развития ресурсосберегающих способов получения бумаги и картона из рециркулируемого сырья; нанотехнологии в получении новых видов целлюлозы и бумагоподобных материалов.

УДК 676.017
ББК 35.77

ISBN 978-5-261-01259

CRILL MEASUREMENTS FOR IMPROVED FINES MATERIAL – CHARACTERIZATION OF NANOCELLULOSE

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In this compilation, the crill method has been used to characterize nanocellulose. We conclude from the improvement in crill values that there is better potential to produce nanocellulose using the TEMPO method than using hydrogen peroxide pretreatment, as the process yields a uniform size distribution of nanocellulose microfibrils under 100 nm in size.

ИЗМЕРЕНИЯ КРИЛЯ В ВЫСОКОКАЧЕСТВЕННЫХ МАТЕРИАЛАХ – ОПРЕДЕЛЕНИЕ ПАРАМЕТРОВ НАНОЦЕЛЛЮЛОЗЫ

В данной работе для определения параметров наноцеллюлозы использовали метод измерения криля. Найденное улучшение показателей по крилю позволило сделать вывод, что потенциал для производства наноцеллюлозы методом ТЕМПО выше, чем при методе предварительной обработки перекисью водорода, поскольку метод ТЕМПО обеспечивает однородное распределение по размерам фибрилл наноцеллюлозы размером менее 100 нм.

This abstract is compiled with parts based on two published papers:

1. Crill: a novel technique to characterize nano-lignocellulose – Nord Pulp Pap Res j 29(2):190–194.
2. Qualitative evaluation of micro fibrillated cellulose using the crill method and some aspects of microscopy – Cellulose, vol. 23(6), p. 3611(14).

Unit operations in pulping comprise primary and later stages of refining, the overall aim of which is to modify fibre and pulp characteristics to improve the design of final product properties. The need to monitor and control the refining process by means of rapid online measurements is vast and increasing, as pulp mills must be more cost effective to meet today's competition. Increasing process uniformity and running close to specifications are examples of cost-reduction strategies that require accurate and reliable measurements.

Steenberg et al [1]. first defined the existence of thin particles called crill in the 1960s. They studied the effect of the small fraction of the crill that is completely separated from the fibres during refining, finding that tensile strength was reduced when this crill fraction was removed from the pulp. They did not study the influence of the dominant, larger fraction of the crill still attached to the fibres due to the limitations of contemporary laboratory methods.

Crill measurements are based on a method in which light transmitted from two sources passes through a pulp suspension and is analysed. Measurements of how this light interacts with the pulp particles are made in the UV and IR spectral regions, in what is called “the crill method”.

In an attempt to circumvent the well-known limitation of optical instruments such as the FibreLab, FibreMaster, and MorFi analysers in characterising tiny fibres or “hyper-fines”, and with the longer-term objective of having a rapid and accurate method for the online characterisation of nano-ligno-cellulose, the crill method is regarded as alternative to the more conventional techniques currently used in assessing the fibrillar structure of nanofibres. The objective was to highlight the potential of a new technique for characterising the particle size of micro/nanofibres known as crill. The technique provides reliable estimates of the particle size distribution of micro/nanofibres. The crill method is an established technique used at the mill scale for measuring hairy fibres. It is a robust, fast, and reliable method for assessing tiny fibrils. The crill value was plotted relative to homogenisation time, with which it was found to correlate (Fig. 1).

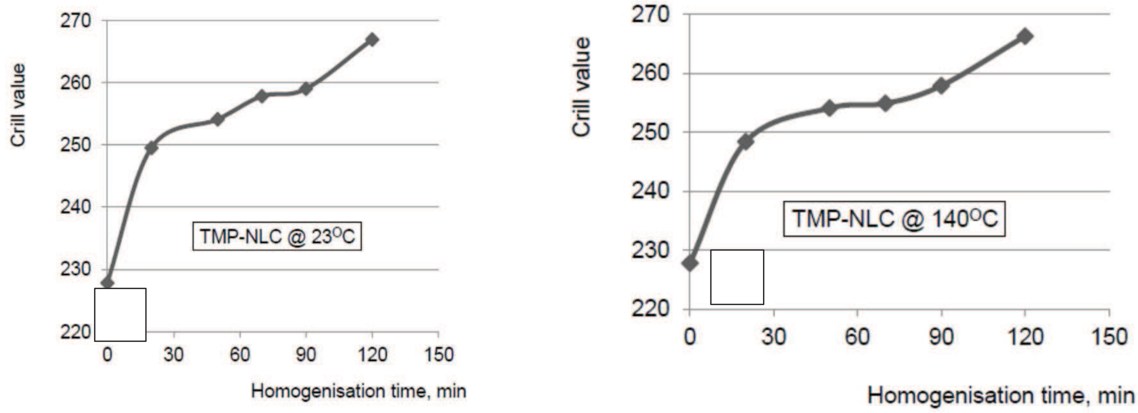

Fig 1. (A) Crill value of TMP-NLC homogenised at 23°C as a function of homogenisation time, (B) Crill value of TMP-NLC homogenised at 140°C as a function of homogenisation time

The crill method possesses the inherent ability to assess the particle size of a fibre/crill within a very short time frame (i.e., a few seconds) and without any damage to the pulp suspension under investigation, making it a non-destructive method. It should be noted that using the crill method to characterise NLC makes it possible to reduce the use of time-consuming microscopy techniques in characterising the particle size distribution. When considering the number of homogenisation passes versus the non-homogenised reference samples, we noticed that with 1 % hydrogen peroxide pre-treatment, the crill values for the untreated samples were 210 and 205 units for the TMP and CTMP samples, respectively, and that after 18 homogenisation passes, the crill values increased to 232 and 224 units, respectively, for a 22-unit improvement for the TMP and a 19-unit improvement for the CTMP samples (Fig. 2 and 3). With 4 % hydrogen peroxide pre-treatment (see Fig. 2 and 3), the crill values for the untreated samples were 218 and 214 units for the TMP and CTMP samples, respectively, increasing after 18 homogenisation passes to 234 and 229 units, respectively, for a 16-unit improvement for the TMP and a 15-unit improvement for the CTMP samples.

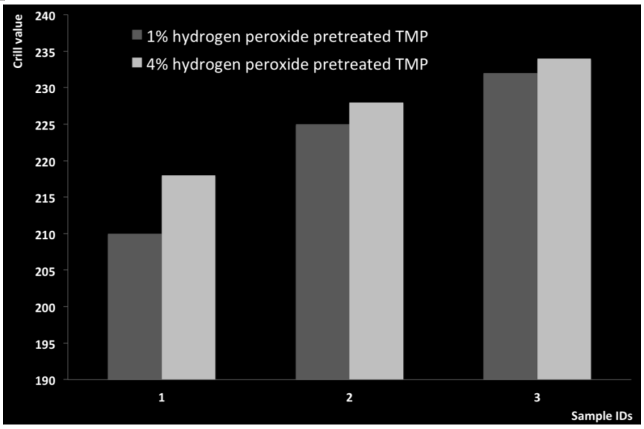

Fig 2. Crill values for TMP-based MFC relative to chemical (i.e., hydrogen peroxide) treatment and number of homogenisation cycles. Note: “sample 1” is non-homogenised, “sample 2” is homogenised for 9 cycles, and “sample 3” for 18 cycles

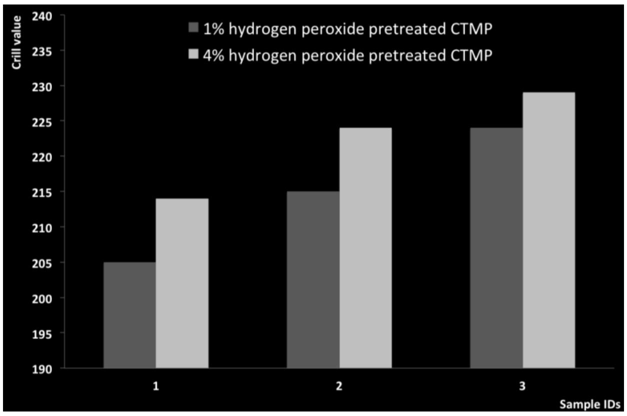

Fig 3. Crill values for CTMP-based MFC relative to chemical (i.e., hydrogen peroxide) pre-treatment and number of homogenisation cycles. Note: “sample 1” is non-homogenised, “sample 2” is homogenised for 9 cycles, and “sample 3” for 18 cycles

In addition, the TEMPO-oxidation reaction is usually conducted at a high pH of 9–10; during the reaction, we noticed a reduction in brightness (i.e., a pulp-yellowing effect) in the lignin-rich CTMP fibres. It is possible that the NaClO added to the pulp as a bleaching agent also generates chromophore groups on the lignin in alkaline media, leading to a change in colour. However, the crill results shown in Fig. 4 indicate that it was relatively easier to produce nanocellulose from the oxidized pretreated pulp samples than from the non-pretreated samples.

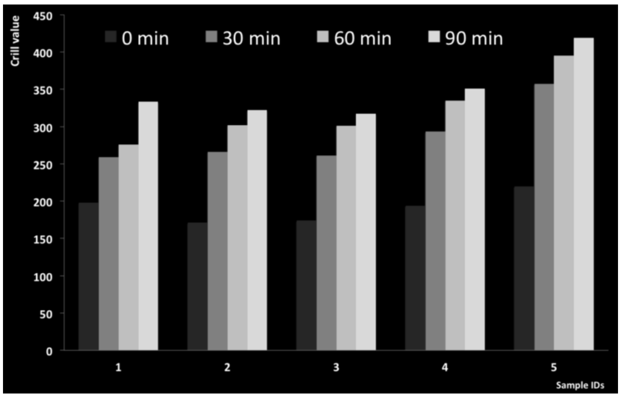

Fig 4. Crill values of CTMP-based MFC relative to chemical (i.e., TEMPO) treatment and high-shear homogenisation time. Note: "sample 1" is non-chemical pre-treated, "sample 2" is 3 mmol NaClO TEMPO pre-treated, "sample 3" is 5 mmol NaClO TEMPO pre-treated, "sample 4" is 7 mmol NaClO TEMPO pre-treated, and "sample 5" is 10 mmol NaClO TEMPO pre-treated

One reason for using TEMPO oxidation in the second was to induce fibre swelling and facilitate the mechanical disruption of the fibres during high-shear homogenisation. TEMPO oxidisation helps loosen the adhesion in the fibre wall and make it easier to reduce the fibre particle size from the microfibril to nano-fibril scale. The high fibrillation efficiency is a well-known advantage of the TEMPO-based nanocellulose production process; accordingly, in this work we compare the crill values with the homogenisation times and chemical treatment dosages. Such comparisons clearly indicate that the crill values improve with higher NaClO dosages and longer mechanical treatment times. We successfully produced nanocellulose through two different processing routes, i.e., hydrogen peroxide pre-treatment and TEMPO-mediated oxidation. We conclude from the improvement in crill values that there is better potential to produce nanocellulose using the TEMPO method than using hydrogen peroxide pre-treatment, as the process yields a uniform size distribution of nanocellulose microfibrils under 100 nm in size.

References

1. Steenberg, B., Sandgren, B., Wahren, D. (1960): Studies on Pulp Crill, Part 1. Suspended fibrils in paper pulp fines, Svensk Papperstidning Nr 12, pp. 395–397.