

USE OF FINE FIBRE CELLULOSE FOR REINFORCING PAPER

MARIANNA LAKA,* MARITE SKUTE,* INESE FILIPOVA,* VELTA FRIDRIHSONE,**
 ULDIS GRINFELDS,* JURIS ZOLDNERS,* MARTINS SPADE*** and IGORS SIVACOV***

*Latvian State Institute of Wood Chemistry, 27, Dzerbenes Str., LV-1006 Riga, Latvia

**Institute of Polymer Materials, MSAC, Riga Technical University, 3, Paula Valdena Str.,
 Riga LV1048, Latvia

***Riga Stradins University, 16, Dzirciema Str., Riga LV1007, Latvia

✉ Corresponding author: Marianna Laka, lamar@edi.lv

Received March 20, 2019

In various production processes, for example, in the production of disposable absorbent underwear, a large amount of fine fibre cellulose results as a by-product. Our objective was to obtain from it nanocellulose gels for using them in papermaking for reinforcing paper. Fine fibre cellulose nanoparticle gels were obtained by the thermocatalytic destruction method developed at the Laboratory of Cellulose of the Latvian State Institute of Wood Chemistry, followed by their dispersion, at the concentration of 8%, in water medium in a ball mill. A part of the obtained gels was used as filler in paper sheets produced from bleached softwood kraft pulp. The other part was used for obtaining coatings, which were cast on both sides of paper sheets produced from recycled paper by the Ligatne Paper Mill (Latvia). The investigations have shown that nanocellulose fillers improve the air resistance and mechanical properties of paper sheets. The coatings considerably increase the air resistance of paper sheets, although they decrease the tensile index in dry and wet states.

Keywords: fine fibre cellulose, nanocellulose, tensile index, burst index, air resistance

INTRODUCTION

In the production of disposable absorbent underwear, a large amount of fine fibre cellulose results as a by-product. In Latvia, it amounts to ~6000 kg per year. The mean length and width of these fibres is 0.91 mm and 0.024 mm, respectively. It would be expedient to process them, so that they could be used in paper sheets to improve their properties.

Recently, there have been reported a lot of studies in which cellulose, especially nanocellulose, is used as a filler or for making coatings for polymer and paper materials. Nanocelluloses have been increasingly used in composites, since their reduced size, high aspect ratio and stiffness give great strength to materials. Thus, Dufresne¹ investigated cellulose reinforced polymer nanocomposites. Several forms of cellulose nanomaterials, notably cellulose nanocrystals and cellulose nanofibrils, have been found to exhibit attractive properties and to be potentially useful for a large number of industrial applications, including paper and cardboard manufacture, reinforcing filler in polymer nanocomposites, basis for low-density foams, additive in adhesives and paints, as well as in the

manufacture of a wide variety of filtration, electronic, food, hygiene, cosmetic and medical products. In the study by Lourenco *et al.*,² strategies to improve filler flocculation and the papermaking properties, by using enzymatic cellulose microfibrils, are provided. Enzymatic cellulose microfibril fillers improve the flocculation of precipitated calcium carbonate, leading to higher retention in the fibre matrix and to higher dry and wet strength of the paper. He *et al.*³ obtained high filler retention by using a precipitated calcium carbonate – cellulose nanofibrils composite filler in paper sheets. The paper filled with the composite fillers had much higher burst and tensile strength than that filled with a conventional calcium carbonate filler. In many studies, nanocellulose was used for obtaining coatings, which were cast on the surface of paper sheets. Thus, nanofibrillated cellulose was used as a substrate to carry triclosan, which was then applied as a coating agent for imparting antibacterial properties to paper, while also improving its strength.⁴ Antibacterial activity tests indicated that the coated paper exhibited excellent antibacterial activity. The tensile and tear index of

the coated paper increased by 18.0% and 26.4%, respectively, compared to the blank paper. Also, the paper coated with ZnO-cellulose composites was found to possess antibacterial and antifungal activity.⁵ In the study by Zhu *et al.*,⁶ composite paper with coatings made from dissolved cellulose in ionic liquid was investigated. Both the dry and wet tensile strength was found to be dramatically increased, compared to the case of the control paper. The composite paper dramatically decreased the oxygen permeability and the hydrophilicity, exhibiting strong water resistant and shape-retaining properties in water. Therefore, the composite papers showed great potential for packaging application requiring higher humidity resistance.

Our earlier works have shown that fillers and coatings obtained from nanoparticle gels produced from wood processing wastes considerably improve paper properties.⁷⁻¹⁰ In this work, nanocellulose gels from fine fibre cellulose were obtained for their use in papermaking.

EXPERIMENTAL

Materials

Fine fibre cellulose resulted as a by-product from the production of disposable absorbent underwear by FARMEKO Ltd. (Latvia). It was obtained from bleached softwood kraft pulp. The paper sheets for the experiments with the nanocellulose filler were produced from TCF bleached softwood kraft pulp (Metsa-Botnia). In the investigations with coatings, paper sheets produced from recycled paper by the Ligatne Paper Mill (Latvia) were used.

Method for obtaining nanoparticle gels

Fine fibre cellulose nanoparticle gels were obtained by the thermocatalytic destruction method developed at the Laboratory of Cellulose of the Institute of Wood Chemistry.¹¹ According to this method, the fine fibre cellulose was impregnated with a thermocatalytic destruction catalyst (weak hydrochloric acid) and thermally treated at elevated temperatures (120 °C) until it reached a dry state. The destroyed material, at the concentration ~8%, was dispersed in water medium in a ball mill. As a result, gel-like dispersions, which contained nanoparticles, were obtained.

Use of nanoparticle gels in paper sheets

A part of the fine fibre cellulose gels, produced from the by-product obtained from FARMEKO Ltd. (Latvia), was dissolved and introduced as a filler into the paper furnish in different amounts. The filler content was 5, 10, 15, 20 and 25% (on dry matter). The other part of the obtained gels was used for obtaining coatings. They were applied on both sides of paper sheets produced by the Ligatne Paper Mill. Coatings

were obtained using a K-Control Coater 202 (RK Print Instruments Ltd., UK). Gel concentrations of 6% and 10.5% were used. In the suspension form, the coating thickness was 24, 40, 60 and 100 µm. Owing to the partial diffusion of the gel into the paper pores and water evaporation, the coating thickness decreased after drying. Final thickness was determined as the difference (divided by two) between the thickness of coated paper and that of uncoated one.

Investigation of barrier and mechanical properties of paper sheets

The air resistance and mechanical properties (tensile index in dry and wet states, burst index) of paper sheets were investigated. In the case of nanoparticle fillers, the paper sheets, as indicated above, were made from bleached softwood kraft pulp. In the case of coatings, paper sheets from recycled paper produced by the Ligatne Paper Mill (Latvia) were used. Air resistance was determined according to Gurley (SCAN-P), using an L&W Air Permeance Tester. Tensile index was determined on a Frank Tensile Tester (Frank-PTI, Austria), according to the International Standard ISO 1924-1:1992(E). Burst index was determined on a Frank Burst Tester for Paper (Frank PTI, Austria) according to the International Standard ISO 2758-1983(E). The determination of the tensile index in a wet state was based of TAPPI Standard 220 om-87. The StD of mechanical indices was below ± 4%.

RESULTS AND DISCUSSION

Effect of nanocellulose filler on barrier and mechanical properties of paper sheets

Figure 1 shows air resistance *versus* nanocellulose filler content. It can be seen that, with increasing the filler content up to 15%, the air resistance of paper sheets considerably increases and then practically does not change. At the filler content of 20%, the air resistance increases 1.27 times.

The nanocellulose filler also increases the mechanical properties of paper sheets produced from bleached kraft wood pulp. It can be explained by the fact that the nanoparticle fillers fill the microvoids between the cellulose fibres and thus improve the barrier and mechanical properties. Figure 2 demonstrates the tensile index in dry and wet states and burst index as a function of the nanocellulose filler content. All these indices increase with the nanocellulose filler content. At the filler content of 20%, the tensile index in a dry state, and the burst index and tensile index in a wet state increase 1.28, 1.24 and 1.22 times, respectively. These results are similar to those obtained earlier with regard to a

nanoparticle filler developed from bark.¹⁰ In the latter case, the nanoparticle filler obtained from extracted black alder and pine bark, increased the tensile index in a dry state 1.40 and 1.30 times, the burst index 1.25 and 1.14 times, and the tensile index in a wet state 1.73 and 1.67 times, respectively, when used in the content of 20%.

With increasing the nanocellulose filler content, the stretch of a paper sheet in a dry state also increases (Fig. 3). At a filler content of 20%, it increases 1.37 times. However, the stretch in a wet state decreases – at a filler content of 20%, the stretch in a wet state decreases 1.10 times.

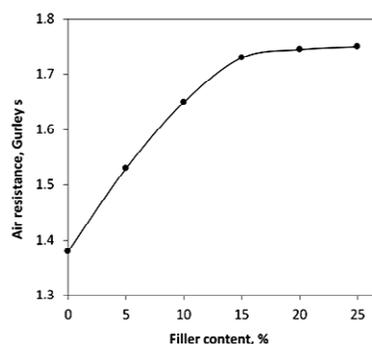


Figure 1: Air resistance of paper sheets *versus* nanocellulose filler content

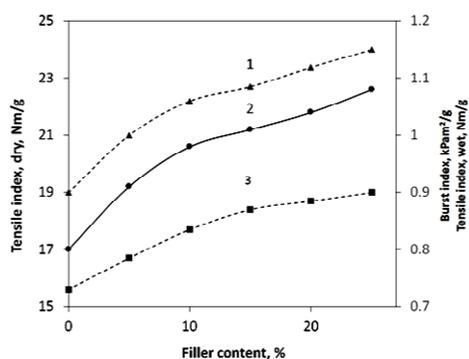


Figure 2: Burst index (1), tensile index in a dry state (2), and tensile index in a wet state (3) of paper sheets *versus* filler content

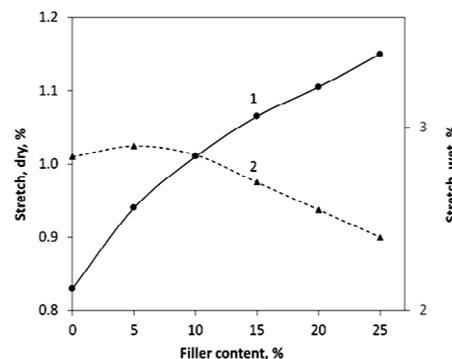


Figure 3: Stretch in a dry state (1) and in a wet state (2) of paper sheets *versus* filler content

Effect of nanocellulose gel coatings on air resistance and mechanical properties of paper sheets

Figure 4 demonstrates the dependence of the air resistance of paper sheets on the thickness of the coating made from fine fibre nanoparticle gels. It can be noted that the coatings considerably increase the barrier properties of the paper sheets. This is because the coatings cover the surface of the paper sheets and protect them from external effects. Air resistance increases with increasing coating thickness and depends on the gel concentration. Thus, at the coating thickness of 20 μm and the gel concentration of 6% and 10.5%, air resistance increases 22.5 times and 35 times, respectively. In the case of the coatings obtained

from bark nanoparticle gels,¹⁰ air resistance increases no more than twice.

Figure 5 shows the tensile index of paper in dry and wet states and the burst index as a function of coating thickness for coatings obtained from 6 and 10.5% fine fibre nanoparticle gels. With increasing coating thickness, the burst index does not change, but the tensile index in dry and wet states decreases. This can be explained by the fact that the coatings obtained from the fine fibre nanocellulose gels are weaker than the paper sheets obtained from recycled fibres produced by the Ligatne Paper Mill, and can contain a lot of defects. At the coating thickness of 20 μm , the tensile index in dry and wet states decreases ~ 1.3 times and 1.2 times, respectively. With increasing

coating thickness, the stretch of paper increases in a dry state (1.6 times at both gel concentrations),

although, in a wet state, it decreases (Fig. 6).

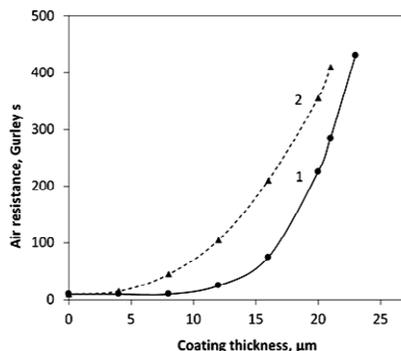


Figure 4: Air resistance of paper sheets with coatings made from 6% (1) and 10.5% (2) nanoparticle gels *versus* coating thickness

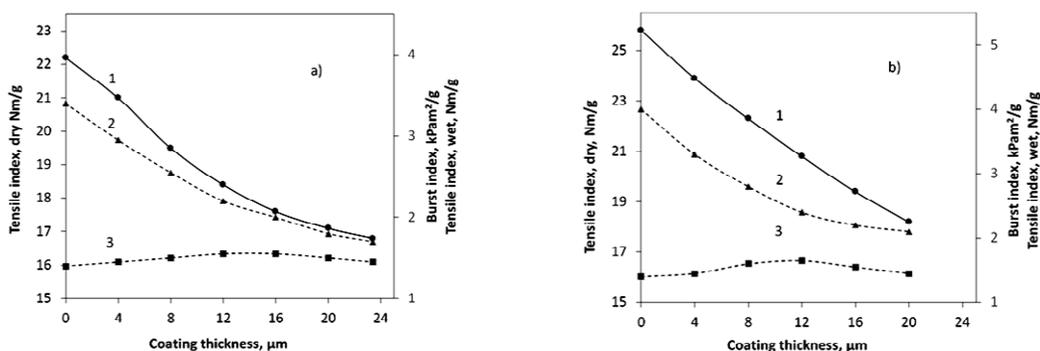


Figure 5: Tensile index in a dry state (1) and in a wet state (2), and burst index (3) of paper sheets with coatings from 6% a) and 10.5% b) nanoparticle gels *versus* coating thickness

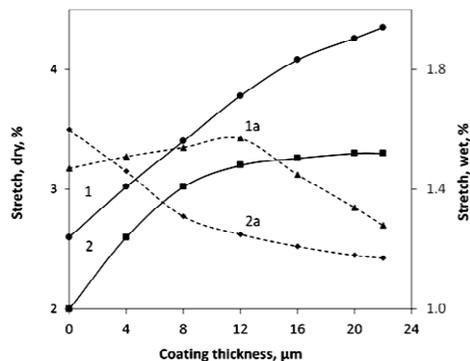


Figure 6: Stretch of paper sheets in dry and wet states (a) for coatings from 6% (1) and 10.5% (2) nanoparticle gels *versus* coating thickness

CONCLUSION

From fine fibre cellulose, nanocellulose gels were developed and then used either as fillers in paper sheets or to produce coatings, which were cast on both sides of paper sheets.

The nanocellulose fillers obtained from fine fibre cellulose have been found to improve the

barrier properties (Gurley air resistance) and the mechanical properties of paper sheets. This can be explained by the fact that the fillers fill the microvoids among fibres and the paper becomes stronger. In the case of coatings made from these nanocellulose gels, the barrier properties of the paper sheets were considerably improved, owing

to the protection of the surface of the paper sheets from the external influence.

To conclude, owing to improved barrier and mechanical properties, paper manufactured with fine fibre nanocellulose fillers and coatings can be used for packaging applications.

ACKNOWLEDGEMENT: The study is financed by the Latvian State Institute of Wood Chemistry, Bioeconomy Grants “Regeneration and modification of cellulose for obtaining environment friendly materials” (RENMODCELL) and “Complex processing of the hemp and its products” (HEMPWISDOM).

REFERENCES

- ¹ A. Dufresne, *Curr. Opin. Colloid Int. Sci.*, **29**, 1 (2017), <https://doi.org/10.1016/j.cocis.2017.01.004>
- ² A. F. Lourenco, J. A. F. Gamelas, P. Sarmiento and P. J. T. Ferreira, *Carbohydr. Polym.*, **224**, 115200 (2019), <https://doi.org/10.1016/j.carbpol.2019.115200>
- ³ M. He, B.-U. Cho and J. M. Won, *Carbohydr. Polym.*, **136**, 820 (2016), <https://doi.org/10.1016/j.carbpol.2015.09.069>
- ⁴ K. Liu, L. Chen, L. Huang, Y. Ni and B. Sun, *Carbohydr. Polym.*, **117**, 996 (2015), <https://doi.org/10.1016/j.carbpol.2014.10.014>
- ⁵ M. Jia, X. Zhang, J. Weng, J. Zhang and M. Zhang, *J. Cult. Herit.*, **38**, 64 (2019), <https://doi.org/10.1016/j.culher.2019.02.006>
- ⁶ R. Zhu, X. Liu, P. Song, M. Wang, F. Xu *et al.*, *Carbohydr. Polym.*, **200**, 100 (2018), <https://doi.org/10.1016/j.carbpol.2018.07.069>
- ⁷ M. Laka, S. Chernyavskaya, A. Treimanis, I. Birskā and L. Vikele, in *Procs. 4th International Scientific Conference on Hardwood Processing*, Florence, Italy, October 7-9, 2013, pp. 354-355
- ⁸ M. Laka, L. Vikele, L. Rozenberga and S. Janceva, in *AIP Conf. Procs.*, 2016, pp. 020112-1-020112-4, <https://doi.org/10.1063/1.494987>
- ⁹ M. Laka, A. Treimanis, S. Chernyavskaya, M. Skute, L. Rozenberga *et al.*, *Holzforschung*, **69**, 745 (2015), <https://doi.org/10.1515/hf-2014-0271>
- ¹⁰ M. Laka, M. Skute, S. Janceva, V. Fridrihsone, I. Sable *et al.*, *Solid State Phenomena, Mater. Eng.*, **267**, 12 (2017), <https://doi.org/10.4028/www.scientific.net/SSP.267.12>
- ¹¹ M. Laka and S. Chernyavskaya, Latvian Republic Patent 11184 (1996)