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Effect of extraction on the coatings produced from nanoparticle gels obtained from hardwood and softwood bark

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Abstract. For coatings, non-extracted hardwood (birch) and softwood (pine) bark and that extracted in biorefinery were used. Lyophilic extractives (fats, waxes, etc.) were extracted with hexane and hydrophilic extractives (polyphenols, tannins, etc.) by means of successive extraction with solvents with increasing polarity, i.e. hexane, ethyl acetate, and ethanol water (1:1). The bark was destructed by the thermocatalytic destruction method and then dispersed in a water medium at a concentration of 8-10%. As a result, gel-like dispersions were obtained, which contained nanoparticles. It has been established that the coatings improve the Gurley air resistance and increase the mechanical properties (tensile strength, burst strength, stretch) of paper sheets. The coatings decrease the tensile strength in a wet state. The coatings made from extracted bark nanoparticle gels affect the properties of paper sheets to a greater extent. It is because extractive substances hinder the bond formation between the cellulose fibres and nanoparticles.

1. Introduction

Recently, various coatings have been used for improving the barrier and mechanical properties of papers. Thus, chitosan-caseinate bilayer coatings lead to a decrease in the water vapour permeability of paper sheets [1]. Chitosan coatings improve also the gloss, oxygen barrier properties and water absorption capacity [2, 3]. The use of microfibrillated cellulose as a surface coating on various papers considerably reduces the air permeability and improves the oil barrier properties of papers [4]. In our work [5], we also have established that the coatings made from bark nanoparticle gels and their mixtures with chitosan and sodium carboxymethylcellulose (Na-CMC) solutions improve the barrier and mechanical properties of paper sheets.

In this work, the effect of extraction of bark on the mechanical and barrier properties of paper sheets with coatings produced from hardwood and softwood bark nanoparticle gels was investigated.

2. Experimental

For coatings, nanoparticle gels from hardwood (birch) and softwood (pine) bark were obtained. Non-extracted bark and that extracted in biorefinery [6] were used. Lyophilic extractives (fats, waxes, etc.) were extracted with hexane in a Soxhlet apparatus and hydrophilic extractives (polyphenols, tannins, etc.) by means of successive extraction with solvents with increasing polarity, i.e. hexane, ethyl acetate, and ethanol water (1:1). The bark was destructed by the thermocatalytic destruction method developed at the Laboratory of Cellulose of the Latvian State Institute of Wood Chemistry [7]. The bark was impregnated with a thermocatalytic destruction catalyst – weak hydrochloric acid solution – and then thermally treated at a temperature of 120 ºC until a dry state. The partially destructed bark was dispersed in a water medium in a ball mill at a concentration of 8-10%. As a result, gel-like dispersions were obtained, which contained nanoparticles, average size of ~300 nm. Size of particles was determined by Zetasizer Nano ZS90 (Malvern Panalytical Ltd, UK), where measurements were made using dynamic light scattering (DLS) method, and therefore were influenced more by longitudinal size of particle. Diameters of these particles usually are smaller than 100 nm, however it cannot be correctly measured by DLS.

Using the obtained nanoparticle gels, coatings were made on both sides of paper sheets (made from 100% recycled fibres, grammage 90 g/m^2, thickness 0.11 mm) produced by the Ligatne Paper Mill (Latvia). Coatings with area of 0.04725 m^2 were made using K-Control Coater 202 (RK Print Instruments Ltd., UK). Gel concentration was 4-10%. In the suspension form, the coatings' thickness was 24, 40, 60 and 100 µm. Owing to the partial diffusion of the gel into the paper pores and water evaporation, the coatings' thickness after drying decreased. Final thickness was determined as a difference (divided by two) in the thicknesses of uncoated and coated paper.

Air resistance and mechanical properties of paper sheets were investigated. Air resistance according to Gurley (SCAN-P) was determined using an L&W Air Permeance Tester. Tensile strength was determined on a Frank Tensile Tester (Frank-PTI, Austria) according to the International Standard ISO 1924-1:1992(E). Burst strength was determined on a Frank Burst Tester for Paper (Frank PTI, Austria) according to the International Standard ISO 2758-1983(E). Determination of the tensile strength in a wet state was based of the TAPPI Standard 220 om-87. The StD of mechanical indices was below ± 4%.

3. Results and Discussion

3.1. Effect of coatings obtained from bark nanoparticle gels on the air resistance of paper sheets

Figure 1 demonstrates the Gurley air resistance of paper sheets versus thickness of coatings made from 6% non-extracted and extracted birch and pine bark nanoparticle gels. In the case of non-extracted bark, air resistance slightly increases with increasing thickness of coatings. In the case of extracted bark, the air resistance considerably increases with increasing coating thickness. It increases especially greatly in the case of birch bark. Thus, at the coating thickness of 30 µm, the air resistance of the coatings made from extracted birch and pine bark nanoparticle gels increases by 177 and 28 %, respectively, in comparison with the case of uncoated paper.

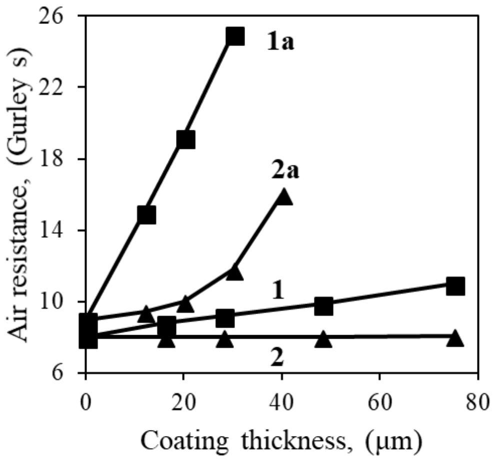

Figure 1. Gurley air resistance versus thickness of coatings made from 6% non-extracted and extracted (a) birch (1) and pine (2) bark nanoparticle gels.

Similarly, Gurley air resistance increases with increasing coating weight (Figure 2). At the coating weight of 0.45 g, Gurley air resistance increases for coatings made from non-extracted birch and pine bark nanoparticle gels by 20 and 9%, respectively, and for those from extracted ones – by 62 and 47%.

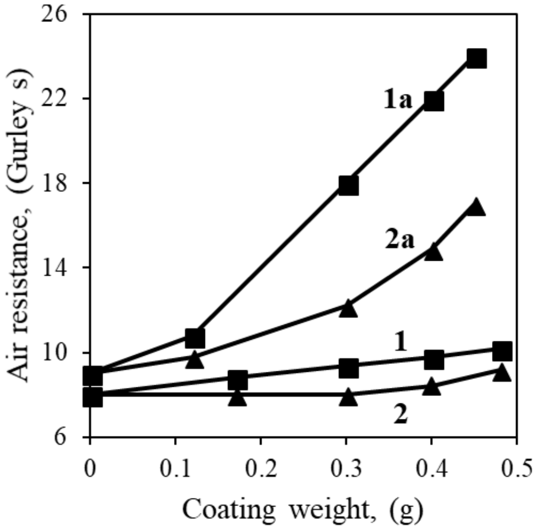

Figure 2. Gurley air resistance versus weight of coatings made from 6% non-extracted and extracted (a) birch (1) and pine (2) bark nanoparticle gels.

The higher Gurley air resistance of the paper sheets with coatings made from bark nanoparticle gels can be explained by the fact that nanoparticles cover the micro- and submicrovoids between the fibres and fibrils, and improve the barrier properties. The greater effect of the coatings made from extracted bark nanoparticle gels is because the extractive substances hinder the bond formation between the cellulose fibres and nanoparticles.

The effect of coatings on the Gurley air resistance increases with the nanoparticle gel concentration (Figure 3). Thus, for coatings made from extracted birch bark and pine bark nanoparticle gels (coating thickness in the suspension form was 100 µm) at a concentration of 4 %, Gurley air resistance increases by 117 % and 55 %, but at a concentration of 10 %, by 180 % and 120 %, respectively, in comparison with uncoated paper. For coatings made from non-extracted birch and pine bark nanoparticle gels, Gurley air resistance differs a little and, with increasing concentration, increases slightly. At a concentration of 10 %, it increases by 37 % on the average.

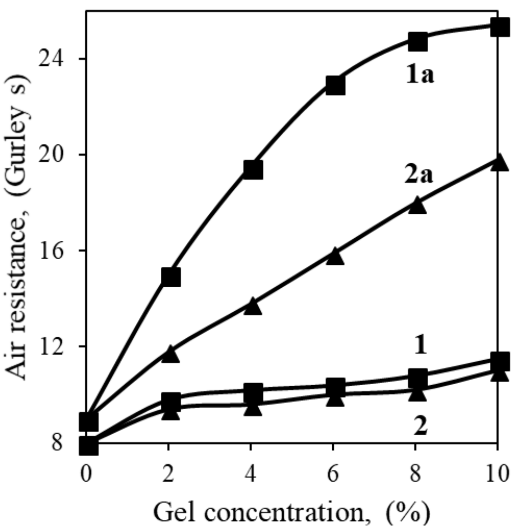

Figure 3. Gurley air resistance versus the concentration of the nanoparticle gel made from non-extracted and extracted (a) birch (1) and pine (2) bark.

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3.2. Effect of coatings obtained from bark nanoparticle gels on the mechanical properties of paper sheets

The coatings made from extracted bark nanoparticle gels affect also the mechanical properties of paper sheets to a greater extent in comparison with those made from non-extracted bark nanoparticle gels. Figure 4 demonstrates the tensile strength in a dry state and burst strength of paper sheets versus coating thickness for coatings from birch bark (4a) and pine bark (4b) 6 % nanoparticle gels. The tensile strength of paper sheets with coatings from the gels obtained from non-extracted bark nanoparticle gels practically does not change with increasing coating thickness. In the case of coatings made from extracted bark nanoparticle gels, tensile strength increases with increasing coating thickness. At a coating thickness of 30 μm, tensile strength increases by 9.5 % for birch bark, and by 5.0 % for pine bark. Burst strength increases more with increasing coating thickness. At a coating thickness of 30 μm, burst strength for coatings made from non-extracted birch and pine bark nanoparticle gels increases by 21.4 and 11.5 %, respectively, and for coatings made from extracted bark by 46.2 and 22.8 %.

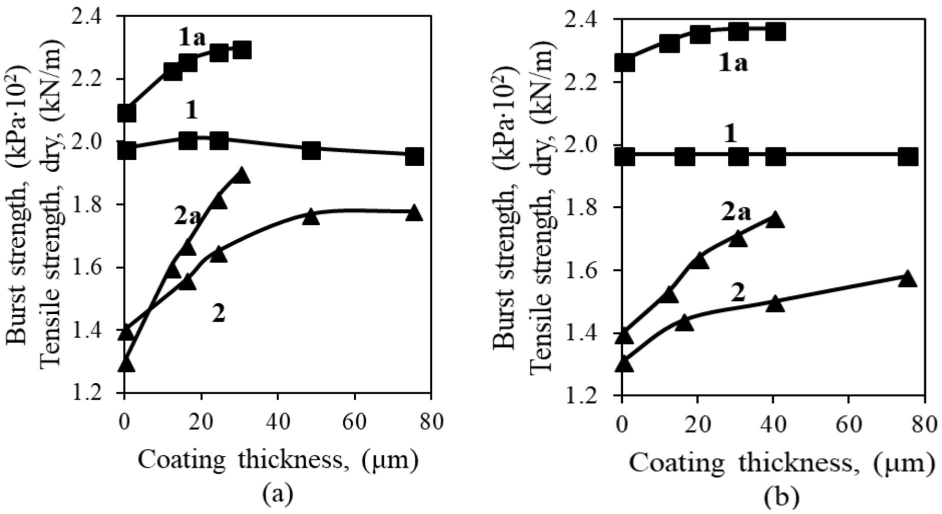

Figure 4. Tensile strength (1;1a) and burst strength (2;2a) versus thickness of coatings made from 6% non-extracted and extracted (a) birch (Fig. 4a) and pine (Fig.4b) bark nanoparticle gels.

Figure 5 demonstrates tensile strength and burst strength versus the concentration of non-extracted and extracted birch (5a) and pine (5b) bark nanoparticle gels (coating thickness in the suspension form was 100 μm). Tensile strength for paper sheets covered with coatings made from non-extracted and extracted bark nanoparticle gels practically does not change until 4-6 % and then decreases. Burst strength increases with increasing gel concentration until 6% and then also decreases (except for non-extracted pine bark). At a concentration of 6 %, burst strength increases in the case of non-extracted birch and pine bark by 25.0 and 15.0 %, respectively, and in the case of extracted bark by 44.6 and 28.6 %.

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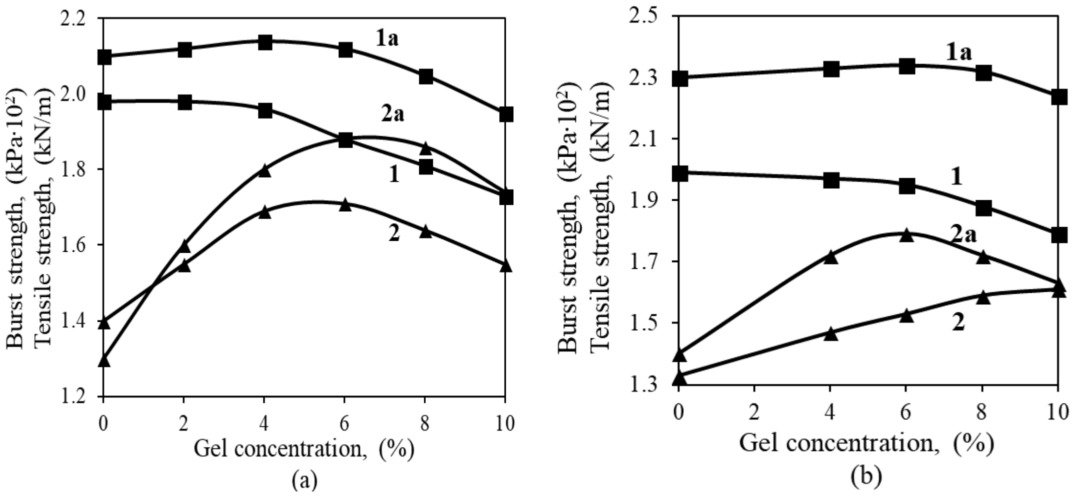

Figure 5. Tensile strength (1; 1a) and burst strength (2; 2a) versus the concentration of the nanoparticle gel made from non-extracted and extracted (a) birch (Fig. 5a) and pine (Fig. 5b) bark.

In a wet state, tensile strength decreases with increasing coating thickness (Figure 6) and gel concentration. This is probably connected with the greater hydrophilicity of the bark nanoparticle coatings in comparison with paper sheets.

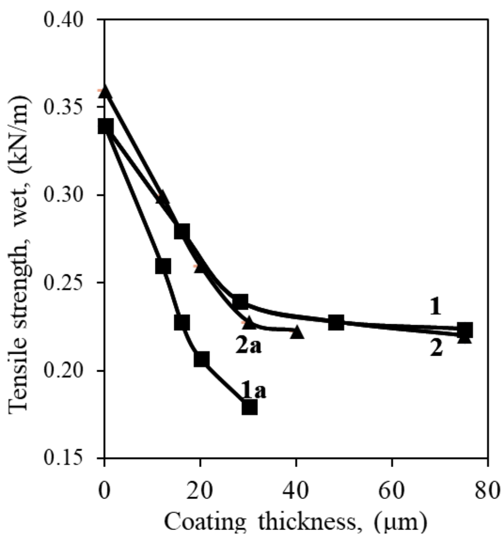

Figure 6. Tensile strength in a wet state versus thickness of coatings made from 6% non-extracted and extracted (a) birch (1) and pine (2) bark nanoparticle gels.

The coatings increase the stretch of paper sheets. Figure 7 demonstrates the stretch of the paper sheets covered with bark nanoparticle gel coatings versus coating thickness. Also, in this case, the nanoparticle coatings made from extracted bark increase the stretch of paper sheets to a greater extent. At a coating thickness of 30 µm, the coatings from non-extracted birch and pine bark 6% nanoparticle gels increase the stretch of paper sheets by 31.6 and 25.8 %, respectively, and from extracted bark by 79.2 and 37.5 %.

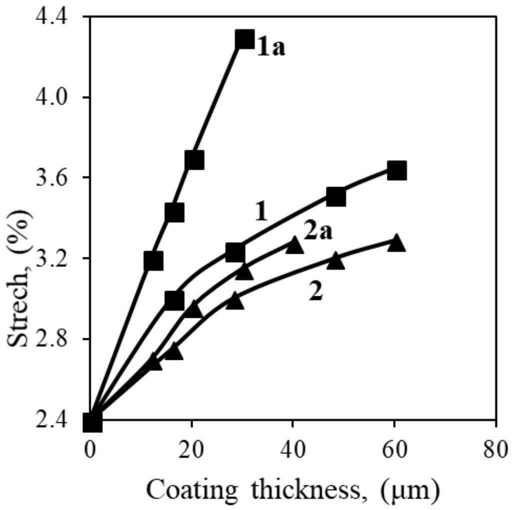

Figure 7. Stretch versus thickness of coatings made from 6% non-extracted and extracted (a) birch (1) and pine (2) bark nanoparticle gels.

4. Conclusion
Coatings were obtained from non-extracted and extracted hardwood and softwood bark nanoparticle gels, which were covered on both sides of paper sheets.

It was established that nanoparticle coatings improve the Gurley air resistance and mechanical properties (tensile strength in a dry state, burst strength) of paper sheets and increase their stretch. The effect of coatings depends on the coating thickness and gel concentration.

The greater effect of coatings, produced from extracted bark nanoparticle gels, can be explained by the fact that extractive substances hinder the bond formation between the cellulose fibres and nanoparticles.

For reinforcing of paper, the coatings from extracted bark nanoparticle gels can be used.

5. Acknowledgements
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