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FAIPARI MÉRNÖKI ÉS
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KAR

AZ ALKALMAZOTT MŰVÉSZET LÉTMÓDJAI ÉS A KREATÍV IPAR KIHÍVÁSAI NAPJAINKBAN

Faipari Mérnöki és Kreatívipari Kar Tudományos Kiadványa

Szerkesztette: Márfai Molnár László és Pásztory Zoltán

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Foregin languages section

The effect of natural-based additive on paper

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Abstract
In the present research, the effect of Plantago psyllium seed husk was investigated in the case of sheets made of secondary fiber. Seed husk has a high hemicellulose content, which shows good compatibility with cellulose. After the addition of the additive, the sheets formed after different absorption times. We examined the mechanical properties and air permeability of the papers. Based on the results, the presence of the additive showed a significant improvement, so the seed husk can be an environmentally friendly solution to improve the properties of the secondary fiber sheets.

Keywords: natural-based additive, Plantago psyllium seed husk, biodegradable additive, cellulose, hemicellulose

Introduction

Today an important task is to utilize the raw materials provided by nature from a sustainable source and in a sustainable way, fitting into the process of the circular economy. It is necessary to develop and produce products whose raw materials come from renewable sources and can be recycled at the end of their life cycle, (even through organic recovery). Cellulose and its products fulfil these requirements. Cellulose is the most abundant natural polymer that occurs in a number of annually renewable sources. The largest user of pulp is the paper industry where the fibers recoverable from used paper can be recycled up to 3 to 6 times, depending on their origin and quality (Adu et al., 2018; Dexter et al., 2019) and the paper product can be produced again. When the quality of the fibers no longer appropriate for recycling, then paper products can be utilized by composting.

Paper made from recycled secondary fibers has weaker properties due to fiber fibrillation and reduced fiber interactions (Scott and Abubakr, 1994). This can also be observed in the strength properties of the paper. In order to eliminate these effects, various strength enhancing additives can be added to the fiber. These additives, which are also used for primary fibers, are usually water soluble polymers and in most cases are synthetic based, (such as polyvinyl alcohol), (Vishtal and Retulainen, 2014) except for natural-based cationic starch and carboxymethylcellulose (Hamzeh et al., 2013; Rasa and Resalati, 2014). Examples of the use of other natural-based materials have been reported in the literature, such as chitosan (Ashori et al., 2006), agar (Vishtal and Retulainen, 2014), carrageenan (Liu et al., 2017) or hemicelluloses (Deutschle et al., 2014; Köhnke et al., 2011; Silva et al., 2011). After cellulose, hemicellulose is the second most abundant naturally occurring polysaccharide, which can be extracted from various plants. Numerous studies report on how hemicelluloses affect the improvement of mechanical properties of paper (Köhnke et al., 2011; Köhnke et al., 2008; Köhnke and Gatenholm, 2007; Silva et al., 2011). Köhnke et al. (2008) observed that the amount of xylan bound on the surface of cellulose fibers increases over time and then shows stagnation. Köhnke et al. (2011) also found that amount of xylan absorbed which is time dependent has an effect on the tensile index, which first shows an increase and then reached a maximum value. Halász et al. (2020) in a previous research was investigated that the sheets made from primary fiber modified with Plantago psyllium seed husk flour, had a significant improvement its mechanical properties.

The great advantage of using hemicelluloses is that they show extremely good compatibility with cellulose and improve the strength characteristics of the sheets formed from the fibers, however, their application is not widespread. The main reason is the cost of extracting and purifying hemicelluloses from the plant (Köhnke et al., 2008). The Plantago psyllium seed husk also contains large amounts of water-swellable and water-soluble film-forming hemicelluloses, such as heteropolysaccharides like arabinoxylan, which is the most abundant in the husk (Qaisrani et al., 2016; Yu et al., 2017). In the present research, we investigated whether unground seed husk added directly to the fiber can improve the mechanical properties of the sheet made of secondary fibers and how it can affect its permeability properties. Since the degree of swelling and solubility of hemicellulose may vary over time, the effect on the properties was investigated at different adsorption times.

Materials and methods

Materials

During the research, the secondary fiber was provided by the edge of the paper towel from manufacturing waste. The Plantago psyllium seed husk used to modify the fibers came from Bioorganic Kft. (99% pure).

Sheet forming

To prepare the cellulose sheets, a 0.5 wt% suspension of the secondary fiber was prepared in a disintegrator with tap water, followed by the addition of 5 wt% (on dry basis weight) of psyllium husk. After 10, 30, 60 and 120 minutes, we made handsheets from the fiber suspension. Sheet formation was performed on a Rapid-Köthen sheet former (Ernst Haage, D-45476). The wet sheets were dried in a sheet dryer under vacuum at 90 ° C for 3 minutes. Control cellulose sheets were prepared in the same way without the addition of psyllium husk. The finished sheets were kept in a sealed bag at room temperature, protected from light, until the tests started.

Conditioning

Before the measurements, the sheets were conditioned according to MSZ EN 20187 at 23 °C and 50% relative humidity. The tests were performed in the same environment.

Thickness, grammage

The thickness of the sheets was measured to an accuracy of 100 µm according to MSZ ISO 534 with a digital micrometer (Lorentz & Wettre). The grammage was determined according to MSZ ISO 536. After weighing the mass (0.0001 g) on an analytical balance (Sartorius), the grammage was expressed in g/m^2. The values which were given are the averages with the standard deviations.

Examination of paper properties

The bursting strength (kPa) was measured according to MSZ ISO 2758 using a bursting tester (Lorentz & Wettre), and then the bursting index ($kPa \cdot m^2/g$) was determined from the quotient of the bursting strength and the grammage. The tensile force and stretch at break of the specimens cut out of the sheets (15 x 100 mm) were tested according to the MSZ ISO 1924 standard on an Instron 3345 tensile tester. The tensile index (Nm/g) was calculated from the quotient of the tensile force and the grammage. The tear resistance (mN) was measured according to the MSZ ISO 1974 (using a Lorentz & Wettre Elmendorf instrument), and then the tear index ($mN \cdot m^2/g$) was calculated by dividing the tear resistance with the grammage.

The air permeability test was performed according to ISO 5636-5 using a Gurley densometer (Lorentz & Wettre). The values which given are averages, with standard deviations, according to standard measurements.

Statistical calculation

Analysis of variance (ANOVA) and Tukey's multiple range test were used to compare the differences between the mean values. Differences below the significance level of 0.05 were considered statistically significant.

Results and discussion

Physical appearance of sheets, thickness and grammage

Figure 1 shows the control sheet and the sheets containing 5wt% Plantago psyllium seed husk, where we can observe parts of the shell homogeneously distributed in the fibers. After lighting the samples, a difference was seen as a function of the absorption time. After an absorption time of 10 minutes it can be observed the hemicellulose part, surrounding the fibrous shells, dried after swelling. These spots decrease more and more as a function of the adsorption time and then are barely detectable after absorption for 120 minutes. This is presumably due to the fact that as the time increased, the chains of hemicellulose expanded more and more and a continuous film matrix was formed between the fibers after drying.

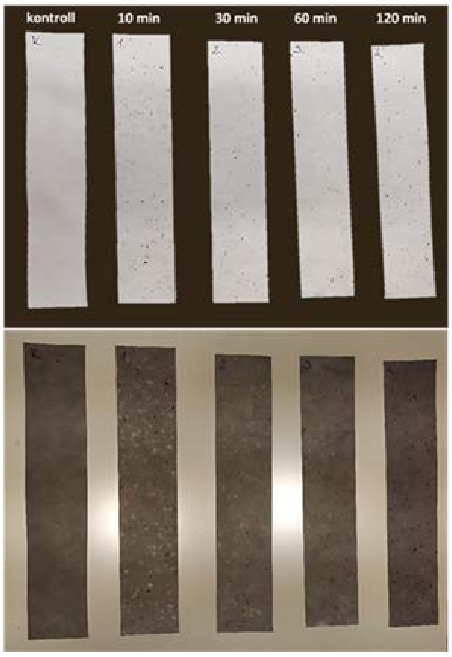

Figure 1: Control sheet and sheets containing 5 wt% seed husk (with adsorption times of 10, 30, 60 and 120 min).

The mean values and standard deviations of thickness and grammage are shown in Table 1. No significant differences were observed in the results of the thickness. After the adsorption time of 10 minutes, the average value of the grammage slightly increased, the difference didn't prove to be significant. With adsorption times of 30, 60 and 120 minutes, the difference is significant which is probably due to the retention effect of hemicellulose fiber from the kernel husk, which does not intensify further by increasing the adsorption time.

	Control	Sheets containing seed husk (5wt%)			
		10 min	30 min	60 min	120 min
Thickness (µm)	164±5 [a]	168±6 [a]	171±4 [a]	170±4 [a]	166±5 [a]
Grammage (g/m^2)	65±2 [a]	68±3 [a]	72±1 [b]	73±1 [b]	72±1 [b]

Values with different letters in the same columns indicate significant differences ($p < 0.05$).
Table 1: Thickness and grammage of control sheet and sheets containing seed husk as a function of adsorption time.

Mechanical properties and air permeabilty

In general, the mechanical properties of sheets made from secondary fiber containing seed husk were improved compared to the control sheet (Table 2, Figure 3). The mechanical properties of the paper are determined by the strength and flexibility of the fibers and the interactions between the fibers. These interactions are primarily hydrogen bonds and van der Waals bonds. When seed husk was added to the fiber, we can presumably talk about van der Waals interactions between arabinoxylan and cellulose, but hydrogen bonds can also form between the two polysaccharides (Paananen et al., 2004). The improvement in mechanical properties is due to the bonds formed between the hemicellulose and the cellulose fiber. This improvement showed a dependence on absorption time. Increasing the absorption time increased the rate of improvement of the properties. As the duration of treatment increased, the binding of arabinoxylan to cellulose fibers increased.

	Control	Sheets containing seed husk (5wt%)			
		10 min	30 min	60 min	120 min
Burst index ($kPa \cdot m^2/g$)	1.5±0.1 [a]	2.0±0.1 [b]	2.3±0.3 [c]	2.6±0.1 [c]	3.0±0.1 [d]
Tensile index (Nm/g)	23.8±1.64 [a]	29.5±4.0 [b]	30.8±1.9 [b]	32.6±2.9 [b]	33.6±2.6 [b]

Stretch at break (%)	4.1±0.4 [a]	5.0±0.4 [a b]	5.4±0.3 [b]	6.0±0.5 [b c]	6.7±1.1 [c]
Tear index ($mN \cdot m^2/g$)	15.5±1.5 [a]	17.6±0.9 [b]	18.7±0.6 [b]	19.5±0.4 [b]	19.7±0.6 [b]
Air permeabilty (Gurley s)	2.4±0.3 [a]	5.4±0.6 [b]	7.1±0.3 [c]	7.7±0.3 [d]	7.9±0.1 [d]

Values with different letters in the same columns indicate signifcant diference ($p < 0.05$).
Table 2: Mechanical properties of control sheet and sheets containing seed husk as a function of absorption time

The presence of arabinoxylan improved the burst index to the greatest extent, where a 99% increase over the control sheet was observed at an absorption time of 120 minutes. The resistance of the sheets to bursting increased by 31% at 10 minutes, by 57% at 30 minutes, and by 74% at 60 minutes. The increase compared to the control sheet was found to be significant in all cases. There was no statistically significant difference between the bursting index of the 30 and 60 minute adsorption sheets. There was a significant difference after an absorption time of 120 minutes.

The highest value of tensile index was measured at the absorption time of 120 minutes, where the increase was 44%. Compared to the control sheet, the increases were 24, 19 and 42% with absorption time of 10, 30 and 60 minutes which was statistically significant. Although there is an increase in the tensile index with the absorption time, statistically evaluated, there is no significant difference between the values of the different times.

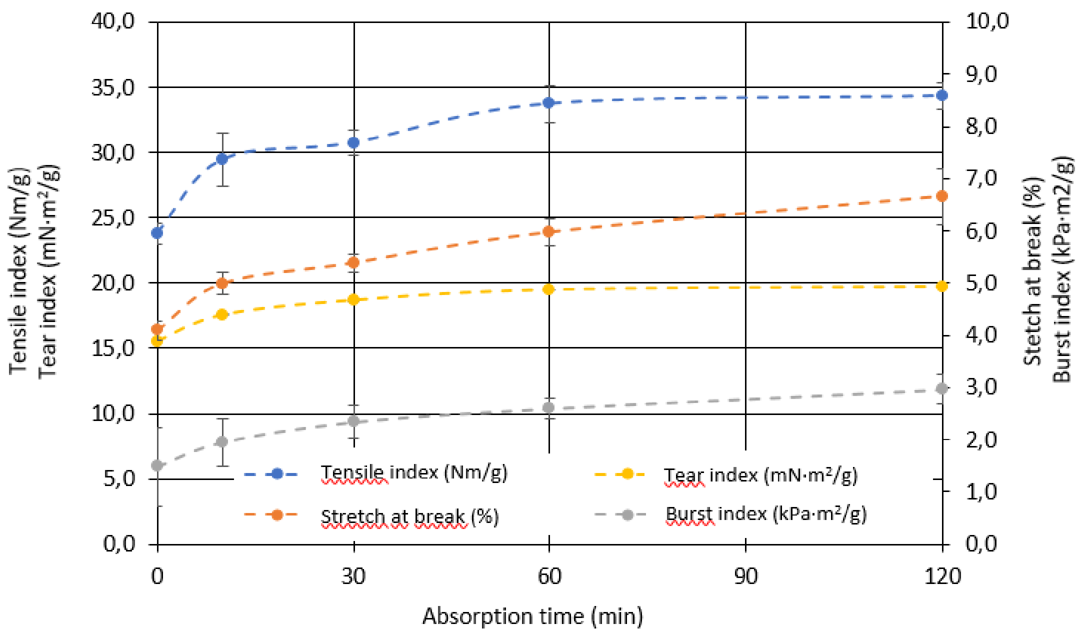

Figure 3: Change of mechanical properties as a function of absorption time

Compared to the tear index of the control sheet, the presence of 5wt% psyllium husk already caused an improvement. It increased the tear resistance by 13, 20, 25 and 27% for treatment times of 10, 30, 60 and 120 minutes. However, based on statistical analysis there is no significant difference between each treated sample sheets.

An outstanding improvement of air permeability was observed due to the increase of the seed husk and the adsorption time (Table 2, Figure 4). The time required to penetrate 100 cm^3 of air increased by 127% after 10 minutes of treatment, by 197% at 30 minutes, by 223% at 60 minutes and by 229% at 120 minutes compared to the sheet containing only secondary fibers. The improvement was significant except for the difference between the sheets with an adsorption time of 60 minutes and the sheets with an adsorption time of 120 minutes. The air permeability presumably reached its maximum at the absorption time of 60 minutes. The pore-filling effect of the seed husk, stops the increase of the air-barrier property.

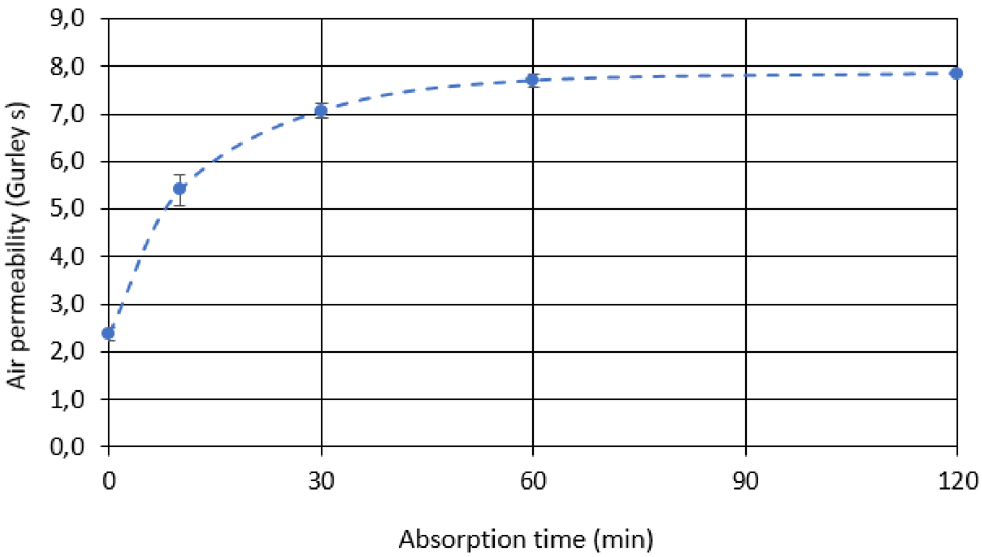

Figure 4: Change in air permeability as a function of absorption time

Conclusions

According to the results of the research, the tensile, burst and tear index of the secondary fiber sheet used in the research can be increased by adding 5wt% of Plantago psyllium seed husk to a fiber suspension. With an absorption time of 10 minutes, the increase in values was significant, but increasing the absorption time further enhanced the rate of improvement.

Comparing the sheets after 60 and 120 minutes of absorption, there was no further significant improvement except for the burst index. Based on this, it can be concluded that (with the parameters of the present research), the maximum improvement in mechanical properties and air permeability can be achieved with an absorption time of 60 minutes. Sheets made after 60 minutes of absorption showed an increase in tensile index of 42%, bursting index of 74%, a tear index of 25% and an air tightness of 223% compared to the control sheet. Based on the results, the Plantago psyllium seed husk,, is a promising plant raw material for improving the mechanical properties of secondary fibers due to the arabinoxylan it contains, even if added directly to the suspension without a prior hemicellulose separation operation.

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Bibliography

A. Ashori, J. Harun, W.M. Zin, Yusoff M.N.M., 2006. Enhancing dry-strength properties of kenaf (Hibiscus cannabinus) paper through chitosan, *Polym. Plast. Technol. Eng.* 45., 125–129. DOI: https://doi.org/10.1080/03602550500373709

A. L. Deutschle, K. Römhild, F. Meister, R. Janzon, C. Riegert, B. Saake, 2014. *Effects of cationic xylan from annual plants on the mechanical properties of paper*, Carbohydr. Polym. 102., 627–635. DOI: https://doi.org/10.1016/j.carbpol.2013.12.016

A. Paananen, M. Österberg, M. Rutland, T. Tammelin, T. Saarinen, K. Tappura, P. Stenius, 2004. Interaction between cellulose and xylan: An atomic force microscope and quartz crystal microbalance study, *Hemicelluloses: Science and Technology, ACS Publications* 864., 269-290. DOI: https://doi.org/10.1021/bk-2004-0864.ch018

A. Vishtal, E. Retulainen, Improving the extensibility, wet web and dry strength of paper by addition of agar, 2014. Nord. *Pulp Pap. Res. J.* 29., 434–443. DOI: https://doi.org/10.3183/npprj-2014-29-03-p434-443

C. Adu, M. Jolly, V.K. Thakur, 2018. Exploring new horizons for paper recycling: A review of biomaterials and biorefinery feedstocks derived from wastepaper, *Curr. Opin. Green Sustain. Chem.* 13., 21–26. DOI: https://doi.org/10.1016/j.cogsc.2018.03.003

G.M. Scott, S., 1994. Abubakr, Fractionation of secondary fiber–A review, Prog. *Pap. Recycle* 3., 50–59.

K. Halász, Z. Kóczán, A. Tóth, Z. Pásztory, E. Preklet, 2020.The effect of Plantago psyllium seed husk flour on the properties of cellulose sheet, Nord. *Pulp Pap. Res*. J. 35(4) (2020) 621–630. DOI: https://doi.org/10.1515/npprj-2020-0037

L. Yu, G.E. Yakubov, W. Zeng, X. Xing, J. Stenson, V. Bulone, J.R. Stokes, 2017. Multi-layer mucilage of Plantago ovata seeds: Rheological differences arise from variations in arabinoxylan side chains, *Carbohydr. Polym*. 165., 132–141. DOI: https://doi.org/10.1016/j.carbpol.2017.02.038

M. Dexter, K. Rickman, C. Pan, C. Chang, R., 2019. Malhotra, Intense Pulsed Light unprinting for reducing life-cycle stages in recycling of coated printing paper, *J. Clean. Prod.* 232., 274–284. DOI: https://doi.org/10.1016/j.jclepro.2019.05.387

M. Rasa, H. Resalati, 2014. Effect of CMC, cationic starch and carboxymethylation treatments on OCC pulp properties, *World Sci. J.* 2., 34–47.

T. Köhnke, Å. Östlund, H. Brelid, 2011. Adsorption of arabinoxylan on cellulosic surfaces: influence of degree of substitution and substitution pattern on adsorption characteristics, *Biomacromolecules* 12., 2633–2641. DOI: https://doi.org/10.1021/bm200437m

T. Köhnke, C. Pujolras, J.P. Roubroeks, P. Gatenholm, 2008. The effect of barley husk arabinoxylan adsorption on the properties of cellulose fibres, *Cellulose* 15., 537-546. DOI: https://doi.org/10.1007/s10570-008-9209-5

T. Köhnke, P. Gatenholm, 2007. The effect of controlled glucuronoxylan adsorption on drying-induced strength loss of bleached softwood pulp, Nord. *Pulp Pap. Res. J.* 22. 508–515. DOI: https://doi.org/10.3183/npprj-2007-22-04-p508-515

T.B. Qaisrani, M.M Qaisrani, T.M. Qaisrani, 2016. Arabinoxylans from psyllium husk: A review, *J. Environ. Agri. Sci* 6. 33–39.

T.C.F. Silva, J.L. Colodette, L.A. Lucia, R.C. de Oliveira, F.N. Oliveira, L.H.M. Silva, 2011. Adsorption of chemically modified xylans on eucalyptus pulp and its effect on the pulp physical properties, *Ind. Eng. Chem. Res.* 50., 1138–1145. DOI: https://doi.org/10.1021/ie101960a

Y. Hamzeh, A. Ashori, Z. Khorasani, A. Abdulkhani, A. Abyaz, 2013. Pre-extraction of hemicelluloses from bagasse fibers: Effects of dry-strength additives on paper properties, *Ind. Crops Prod.* 43., 365–371. DOI: https://doi.org/10.1016/j.indcrop.2012.07.047

Z. Liu, X. Li, W. Xie, 2017. Carrageenan as a dry strength additive for papermaking, *PLoS One* 12(2), e0171326 DOI: https://doi.org/10.1371/journal.pone.0171326