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# Thermal stability of packaging papers treated of silver water

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## Introduction



Silver ions have the highest level of antimicrobial activity of all the heavy metals. Generally speaking, the observed antimicrobial efficacy of silver and its associated ions is through the strong binding with disulfide (S-S) and sulfhydryl (-SH) groups found in the proteins of microbial cell walls. Through this binding, normal metabolic processes are disrupted, leading to cell death. The antimicrobial metals silver (Ag), copper (Cu), and zinc (Zn) have thus found their way into a number of applications. The application of nanotechnology shows significant advantages for improving the quality of packaging materials (Barage et al, 2022). Innovation related to the use of nanotechnology in food packaging and quality control is the focus in the modern food industry. The silver nanoparticles can be relatively uniformly distributed in a matrix of other materials such as pulp, plastics, and others and thus be more effective at killing bacteria and fungi, either in stock preparation processes (Kraśniewska, Galus and Gniewosz, 2020) or as a coating (Gottesman et al, 2011); (Wang et al, 2014); (Tsai et al, 2017); (Srichiangsa et al, 2022). Packaging materials with nanoparticles of silver or coated silver containing coatings allow creating effective and safe antimicrobial packaging.

## Problem Description



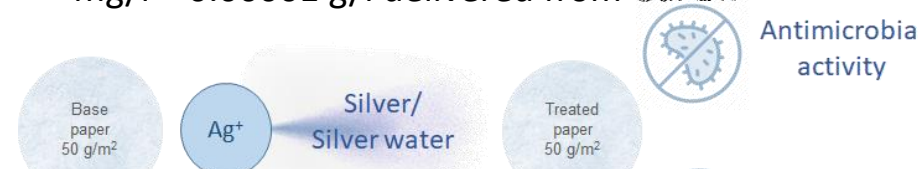
Studies on the thermal stability of the silver water treated cellulose paper and packaging could possess the desired knowledge if the silver-water treatment catalyses the paper aging or makes it more stable. This research shows the preparation, characterisation, TGA and accelerated thermal ageing analysis of packaging papers treated with silver water. The purpose of the research conducted was also to improve the antibacterial activity of the produced papers, which was also achieved and results are in process of publication.

## Methods



- Cellulose mixtures for paper samples;
- Wet-end chemical additives have been added to obtain base paper, in the following sequence: alkylketendimer (AKD) sizing agent – 1 % of o.d.f (Kemira® FennoSize KD 157YC) and cationic retention additive – 0.025 % of o.d.f. (modified polyacrylamide with molecular weight 11.106 g/mol and charge density +1.05 from Ciba Specialty Chemicals-Ciba® Percol® Co (Basel, Switzerland)).
- Base paper has been sprayed with the exact amount of Arcol silver water with concentration of C = 10 mg/l = 0.00001 g/l delivered from Gal ET.

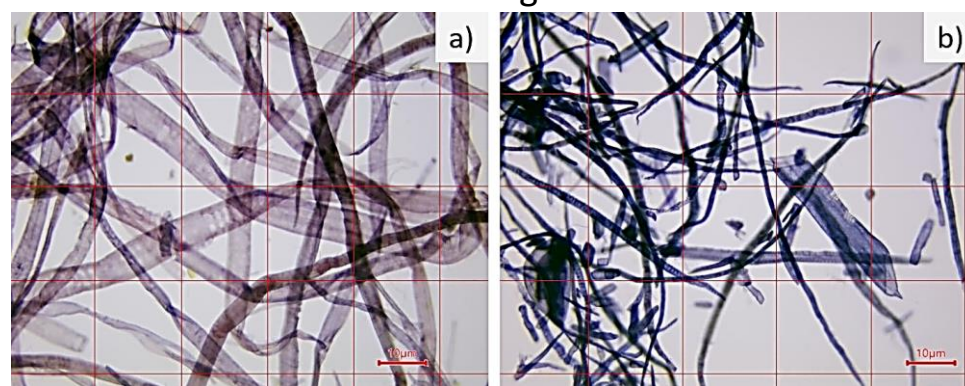
- Microscopic analysis of cellulose;
- Papermaking and Ag-water surface treatment;
- Grammage, thickness, density, porosity, smoothness
- Tensile strength, TEA Index, elongation and tear resistance of obtained paper samples;
- TGA analysis of all paper samples;
- 72h of thermal aging of paper samples.



## Results



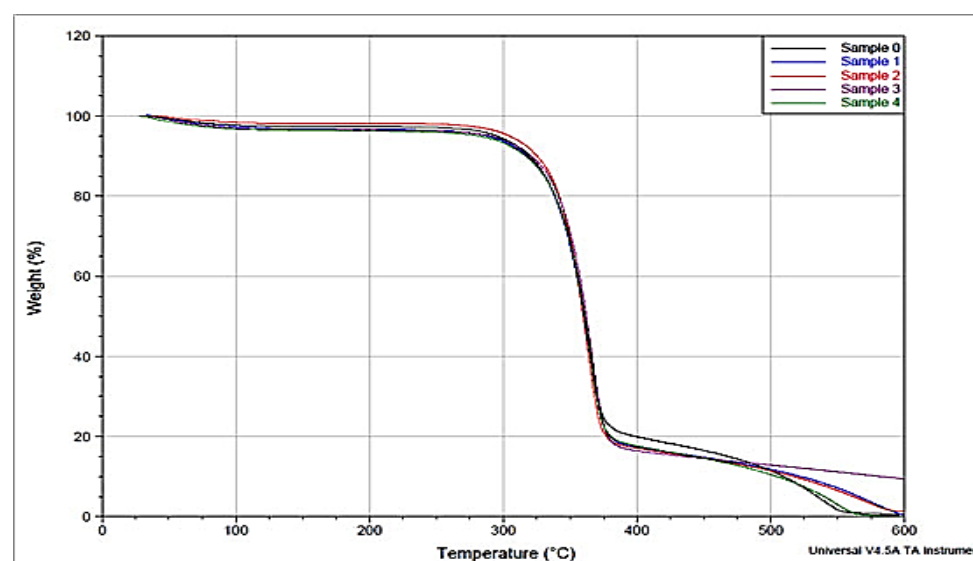
This research work inherently involves preparation and properties evaluation of thermal stability of packaging papers treated of Ag-water. In order to examine this process for woodfree packaging paper, accelerated thermal aging for 72h at temperature of 105°C and dynamic thermogravimetric analysis (TGA) was carried out of a pulp sample and four paper samples (three of them treated with Ag-water – 1, 2 and 3 ml) together with the structural-dimensional and strength properties of the laboratory obtained paper samples. The degree of color changes in the CIELab color space have been studied, bearing in mind that the changes in color characteristics define the stability over time and even more – the influence of the Ag-water treatment.



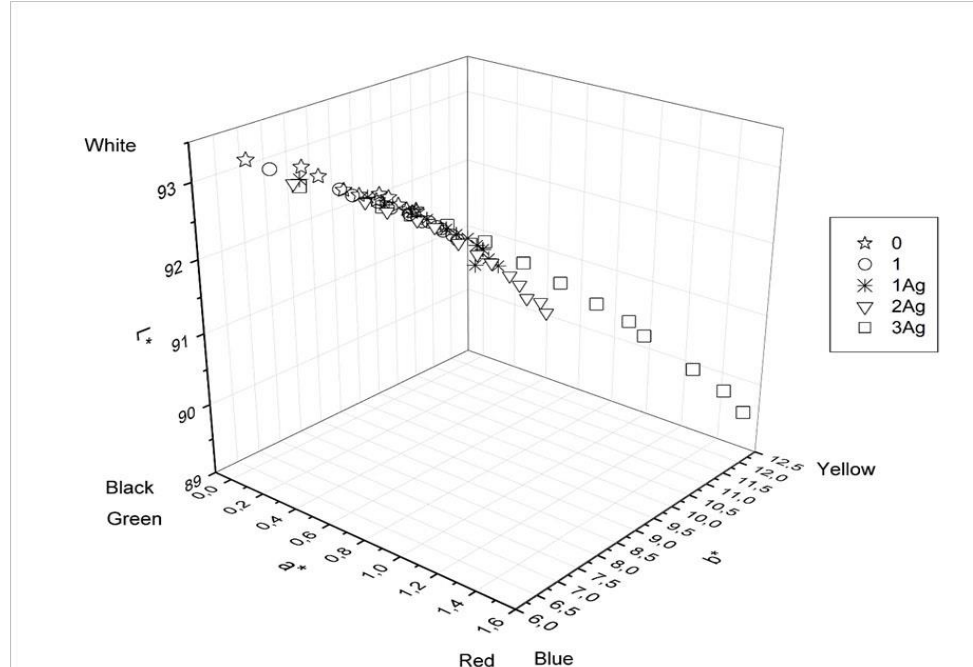
**Figure 1** Microphotograph a) bleached sulfate softwood from pine wood; b) bleached sulfate hardwood from beech wood

**Table 1** Strength properties of base and treated paper samples

No	Composition	Tensile Index, Nm/g	TEA Index, mJ/g	Elongation, %	Tear Index, mN.m <sup>2</sup> /g
0	Only pulp	63	1070	2.4	1.1004
1	Base paper	69.5	1430	2.9	1.0989
2	Base paper+1 ml Silver water	66.6	1220	2.7	1.1094
3	Base paper+2 ml Silver water	64.7	1140	2.6	1.0881
4	Base paper+3 ml Silver water	63.6	1090	2.5	1.0889



**Figure 2** Weight loss at TGA analysis of all paper samples



**Figure 3** Color coordinates L\*, a\* and b\* of paper samples during 72 hours of accelerated thermal ageing

## Discussion /Conclusion



All samples have 3 stages of weight loss. It is observed that with the increase of the amount of Ag-water, the 2nd stage of weight loss is decreasing. At 1 ml Ag-water, the start of the 2nd stage begins at 267.12°C and with the 3ml of Ag-water, the stage begins at 253°C. The less the amount of Ag-water was in the sample, the highest weight loss was detected. This confirms that the third stage presents further degradation of the paper (after 400°C) and that certain amount of Ag is probably still present.

From the color coordinates measurements, presented in figure 3 it is clearly visible that the cellulose (sample 0) and base paper (sample 1) are most stable and there is no drastically amending of the color. For the other tree examined paper samples treated with 1, 2 and 3 ml silver water the color amending occurs after the 36 hours of aging. The values of the color parameters decreases, which means that the paper is getting darker and yellowish. This change is significant and with a larger step for the paper samples treated with 3 milliliters of silver water. Therefore, colloidal silver on the paper surface accelerates the aging by catalyzing the oxidation and hydrolysis of cellulose fibers. This is also confirmed by the observed decrease in the strength indicators, evidencing the destruction of hydrogen bonds between the cellulose fibers in the paper. Research has also shown that it is not recommended to be used more than 2 ml of silver water, as silver ions catalyze the aging process and the paper darkens and turns yellow in a greater degree. The change of the weight of the paper samples as a function of temperature was monitored by TGA. When comparing the weight losses, it was found out that for the paper sample treated with 2 ml of silver water the temperature of complete burning of the sample increased by 2.28°C. It moreover makes an impression the different behavior of the sample with 3 ml of silver water which burns faster and is characterized with weight of 25 % in the range of 375°C. In addition, the surface of the treated paper samples is more even compared to the untreated due to the callandering effect of the manufacturing process.

## REFERENCES

- Barage, S., Lakkakula, J., Sharma, A., Roy, A., Alghamdi, S., Almeahadi, M., Hossain, M., Allahyani, M. and Abdulaziz, O. (2022) Nanomaterial in Food Packaging: A Comprehensive Review. *Journal of Nanomaterials*, 2022. doi: 10.1155/2022/6053922
- Kraśniewska, K., Galus, S. and Gniewosz, M. (2020) Biopolymers-based materials containing silver nanoparticles as active packaging for food applications—a review. *International Journal of Molecular Sciences*. 21(3), p.698. doi: 10.3390/ijms21030698
- Gottesman, R., Shukla, S., Perkas, N., Solovoy, L.A., Nitzan, Y. and Gedanken, A. (2011) Sonochemical coating of paper by microbicidal silver nanoparticles. *Langmuir*. 27(2), pp.720-726. doi: 10.1021/la103401z
- Tsai, T.T., Huang, T.H., Chang, C.J., Yi-Ju Ho, N., Tseng, Y.T. and Chen, C.F. (2017) Antibacterial cellulose paper made with silver-coated gold nanoparticles. *Scientific reports*. 7(1), pp.1-10. doi: 10.1038/s41598-017-03357-w
- Wang, F., Sun, H., Guo, H., Sui, H., Wu, Q., Liu, X. and Huang, D. (2021) High performance piezoelectric nanogenerator with silver nanowires embedded in polymer matrix for mechanical energy harvesting. *Ceramics International*. 47(24), pp.35096-35104. doi: 10.1016/j.ceramint.2021.09.052
- Wang, H., Wang, J., Hong, J., Wei, Q., Gao, W. and Zhu, Z., (2007) Preparation and characterization of silver nanocomposite textile. *Journal of Coatings Technology and Research*. 4(1), pp.101-106.
- Srichiangsa, N., Ounkaew, A., Kasemsiri, P., Okhawilai, M., Hiziroglu, S., Theerakulpisut, S. and Chindaprasit, P. (2022) Facile fabrication of green synthesized silver-decorated magnetic particles for coating of bioactive packaging. *Cellulose*, pp.1-16. doi: 10.1007/s10570-022-04636-0

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