THERMAL STABILITY OF PACKAGING PAPERS TREATED OF SILVER WATER

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Abstract: Paper aging depends on the type and chemical composition of the fiber raw materials, the chemical additives used, such as dyes, fillers, sizing additives, pH and others as storage conditions of the paper (relative humidity and temperature) and the degree of exposure of temperature, light and some microbiological factors. The durability of paper is its ability to retain certain physic-mechanical, optical and chemical properties unchanged over time. In this context and in line with the increased consumption of coated or treated printing and packaging papers, the aging resistance of treated or coated paper is of a great scientific, research and applied interest. This research work inherently involves preparation and properties evaluation of thermal stability of packaging papers treated of silver 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 silver water – 1, 2 and 3 ml) together with the structural-dimensional and strength properties of the laboratory obtained paper samples. The degree of colour changes in the CIELab colour space have been studied, bearing in mind that the changes in colour characteristics define the stability over time and even more – the influence of the silver water treatment. As a result of the studies carried out it was found out that paper do not change significantly during 72h of accelerated thermal ageing, but it is not recommended to be used more than 2 ml of silver water, as silver ions probably 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. In addition, the surface of the treated paper samples is more even compared to the untreated due to the calendering effect of the manufacturing process.

Key words: ageing stability, thermal stability, packaging paper, silver water

1. INTRODUCTION

The bactericidal effects of silver (Ag) have been recognized many years ago. In ancient times, it was used in water and food containers to prevent putrefaction. Years ago in Mexico, water and milk were kept in silver containers. Silver was also mentioned in the Roman pharmacopoeia of 69 b.c. In 1884, silver nitrate drops were introduced as a prophylactic treatment for the eyes of new-born, and this became a common practice in many countries throughout the world. 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 (Silvestry-Rodriguez et al., 2007).
Enhanced manufacturing methods and technologies have led to more widespread employment of nanomaterials in newly developed and commercially available products. Silver could be incorporated to polymers (Gordon et al., 2010; Schierholz et al., 1999; Sun et al., 2004) for the production of consumer products such as washing machines, refrigerators and ice machines that have silver. Silver has been added to plastics to produce items such as public telephones and public toilets (in Japan), toys, and infant pacifiers (Xiao et al., 2017). Silver is added to inorganic composite with immobilized slow-release silver effect. Synthetic fabrics with silver are popular in items such as sportswear, sleeping bags, bedsheet, and dishcloths (Wang et al., 2007). These fabrics are believed to reduce the level of bacterial contamination and thus odor.
Some inorganic ceramics (e.g., zirconium phosphate, zeolite) are also combined with silver (Wang et al., 2021) thus are able to trap metal ions and may then be added to other materials (e.g., paints, plastics, waxes, polyesters) to confer antimicrobial properties (Asafa et al., 2021; Kurnyta et al., 2021; Ma et al., 2016).

Among these materials, silver nanoparticles are increasingly being used as a comprehensive antimicrobial agent in clothing, food storage containers, pharmaceuticals, cosmetics, electronics, and optical devices. The silver nanoparticles are readily released from these products during use, particularly washing and thus it is likely that these materials will eventually be introduced into the environment (Li & Lenhart, 2012). The toxicity of silver nanoparticles is primarily related to the released ionic silver produced as the silver nanoparticles oxidize and dissolve. The known toxicity of silver and silver nanoparticles necessitates their use and fate in the environment be closely scrutinized to avoid compromising environmental or human health (Gorka et al., 2015; Strużyńska, Dąbrowska-Bouta & Sulkowski 2022).

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 & Gniewosz, 2020) or as a coating (Gottesman et al., 2011; Srichiangsa et al., 2022; Tsai et al., 2017; Wang et al., 2014). Packaging materials with nanoparticles of silver or coated silver containing coatings allow creating effective and safe antimicrobial packaging. Therefore, 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 produces papers, which was also achieved and results are in process of publication.

2. MATERIALS AND METHODS

The cellulose mixtures for paper samples were prepared from a bleached kraft woodfree pulp samples from softwood (delivered by SCA, Sweden) and hardwood tree species (delivered by Svilosa AD, Bulgaria) in ratio 80:20 percentage. The used kraft cellulose were refined by laboratory Valley beater method, acc. ISO 5264-1:1979. The celluloses were refined separately and the Schopper Riegler Value as degree SR (ISO 5267-1/AC:2004) of the obtained pulp mixture was 30 °SR.

The analyses have been conducted with one sample of only pulp, base paper and three paper samples treated with 1, 2 and 3 ml silver water. The wet-end chemical additives have been added to the obtained base paper, in the following sequence: alkylketendimer (AKD) sizing agent – 1 % of o.d.f (Kemira® Fennosize KD 157Y) 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)). The 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.

2.1 Microscopic analysis

The microscopic analysis of cellulose and paper materials, is a specific analysis generally used to determine the fiber composition of the paper and to study the structure and size of the source fibres. Small amount of test fibres (pre-milled mechanically) is placed in a porcelain pounder with a few drops of 1 % NaOH. This is followed by rinsing the sample several times with distilled water on a fine, metal mesh. Three samples of fibres have to be placed on a glass slide, well distributed. A drop of Herzberg’s reagent (Cl-Zn-J) according to ISO 9184-3:1990 is dropped on each of the samples and again very carefully the fibres should be distributed. Finally, the samples are dried at about 60°C. After cooling down to room temperature, each sample is covered with a thin glass slide, so the fibre samples are evenly distributed, free of accumulations and air bubbles. Stained fibre samples were observed with microscope VisiScope® TL254T1 (VWR, Italy) at 100x magnification. Objective: 10x/0.25 E-PLAN, Eyepiece: WF10x/20mm.

2.2 The papermaking processes

The papermaking process was simulated by using laboratory paper-sheet machine. All samples were prepared on paper laboratory machine (Rapid-Kothen, Germany) acc. ISO 5269-2:2005, with a grammage
of 50 g/m², with drying conditions of – 95°C and duration of 7 minutes. After the silver water treatment, paper samples have been again dried for 5 minutes at the same drying conditions.

2.3 Grammage, thickness, density, porosity, smoothness

Grammage of all samples was determined in accordance with the ISO 536 standard. Density and porosity were calculated form grammage and thickness, as described in the standard method ISO 534. Smoothness was determined by Bekk method according to standard ISO 5627/A1:2004.

2.4 Tensile strength, TEA Index, elongation and tear resistance

Tensile strength, TEA Index and elongation at break of papers were determined on a tensile testing machine Zwick/Roell according to ISO 1924-1/2:2000. The samples were analyzed in the standard atmosphere at 23°C of temperature and 50 % of relative humidity. The tested speed was 20 mm/min. Paper stripes of 18 cm in length and 1.5 cm in width were used and a minimum of ten probes for each sample was tested. During the sample stretching, several load and elongation data per second were recorded until the break of a sample occurred. After the measurement and determination of tensile strength, the tensile index was calculated. The tensile index is tensile strength divided by grammage, the unit being Nm/g.

Tear resistance is the force, required to tear the sample after a cut was already made. The test was performed with an Elmendorf tester and proceeded as described in standard ISO 1974:2012. For each paper sheet, two parallels were measured. All samples were tested at 23°C and 50 % RH. When tear resistance is normalized with respect to grammage, then the tear index can be calculated and the unit is mNm²/g

2.5 TGA analysis

TGA analysis was performed on TGA analyzer TGA Q5000. Samples (see Table 1) 5 x 5 mm were cut into squares and put into the sample dish. The method was dynamic TGA, meaning that the temperature continued to increase over time as mass was recorded. The temperature measuring range was between 10°C and 600°C. Heating range was 10°C/min. On graphs two curves are presented, where the first one (green presents the curve of measurement) and the blue one present the 1st derivative of the curve, at which the start and end of the 2nd stage of the weight loss can be determined.

Table 1: Sample names and compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Mass of the measured sample, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Only pulp</td>
<td>2.7380</td>
</tr>
<tr>
<td>1</td>
<td>Base paper</td>
<td>2.3680</td>
</tr>
<tr>
<td>2</td>
<td>Base paper+1 ml Ag water</td>
<td>1.8150</td>
</tr>
<tr>
<td>3</td>
<td>Base paper+2 ml Ag water</td>
<td>2.4090</td>
</tr>
<tr>
<td>4</td>
<td>Base paper+3 ml Ag water</td>
<td>2.0180</td>
</tr>
</tbody>
</table>

2.6 Thermal aging of papers

The accelerated thermal ageing of the investigated paper samples was conducted according to ISO 5630-1:2014 in closed chamber at 105°C and air circulation for standard humidity of 50 % with duration of 72 hours, because from the literature review is known that 72 h of thermal ageing corresponds to 25 years of natural ageing of paper. The colour coordinates L*, a*, b* from the CIE Lab colour space were measured before and after the thermal ageing by Konica Minolta Spectrophotometer CM-3630 from Frank – PTI, according to ISO 5631-2:2008.

3. RESULTS AND DISCUSSION

Paper as an anisotropic material has multifunctional properties, which are a result of the diversity of its fibrous composition, the presence of wet-end chemical additives, the technology of its production and additional coating, callandering or other finishing and ennobling processes. These properties should correspond to the application, and their degree should be consistent to the specifics of the end use.
As a packaging material for household application, the obtained paper samples have to have excellent surface and optical properties, sufficient strength, optimal barrier properties with respect to water and grease well-balance with its lower basic weight. Therefore, as a raw material was used virgin bleached kraft cellulose from soft and hardwood tree species. In order to establish the exact type of wood, a microscopic analysis have been carried out through a microscopic analysis illustrated in Fig. 1. From the analysis it was found out that the cellulose fibres from softwood tree are of bleached kraft coniferous cellulose from pine wood and bleached kraft deciduous cellulose from beech and poplar wood.

![Figure 1: Microphotograph of a fibre raw material: a) bleached sulfate softwood from pine wood; b) bleached sulfate hardwood from beech wood](image)

As the colour of the fibre staining, by the used Herzberg's reagent, determines the degree of delignification (bluish colour means lignin content up to 9 %, while yellowish over 9 %.) and furthermore the delignification determines the degree of inter-fibre bonds as strong hydrogen bonds in the obtained paper, we could assume that the strength properties of the examined paper samples could meet the requirements of the end users.

To determine the influence of chemical additives on the complex parameters of the papers, the correct and maximum detailed characterization of the paper structure is of essential importance. As an anisotropic material and on the basis of the used experimental methods determining the properties of the paper in different directions, the provenance of meaningful trends is a complex process, which starts with determining the basic weight, thickness, density, porosity and smoothness of the paper. The smoothness of the papers is of essential importance for the surface-coated papers. It is also an indicator of a change in the structure of the paper surface.

<table>
<thead>
<tr>
<th>Paper properties</th>
<th>Testing method</th>
<th>Only pulp</th>
<th>Base paper</th>
<th>Base paper +1 ml Silver water</th>
<th>Base paper +2 ml Silver water</th>
<th>Base paper +3 ml Silver water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grammage</td>
<td>ISO 536:2012</td>
<td>50.89</td>
<td>50.96</td>
<td>50.48</td>
<td>49.68</td>
<td>49.95</td>
</tr>
<tr>
<td>Thickness</td>
<td>ISO 534:2011</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Density</td>
<td>ISO 534:2011</td>
<td>63.61</td>
<td>63.73</td>
<td>63.12</td>
<td>70.97</td>
<td>71.35</td>
</tr>
<tr>
<td>Porosity</td>
<td>ISO 534:2011</td>
<td>% 95.76</td>
<td>95.75</td>
<td>96.46</td>
<td>95.27</td>
<td>95.24</td>
</tr>
</tbody>
</table>

From the data on the structural-dimensional properties (Table 2) of the base paper and the silver water-treated papers, it is found out that the addition of sizing agent and retention additive does not affect the smoothness of the paper. Regarding the samples treated with silver water, an increase in the smoothness of the papers was observed, and as the amount of silver water increased, the effect decreased. As expected, the thickness of the samples had mostly the same values with a slight decrease at paper samples treated with 2 and 3 ml silver water. These results are based on the additional moistening of the paper bases with a silver water solution and their subsequent drying on a sheet-making apparatus at 96°C for 5 minutes. During this additional drying process, the effect of temperature and the pressure of the...
vacuum created by the apparatus have the effect of calendering onto paper, which is also confirmed by the data on the density and porosity indicators of the investigated papers. From the data in Table 2, it can be seen also that as the amount of silver water increases from 1 to 3 milliliters, the density increases and the porosity decreases.

Strength properties of paper are a permanent indicator of all papers, describing the ability of the paper to tolerate processing and determine the level of loading of the products produced from the paper. To describe the strength of the paper, the tensile index, the tensile energy absorption index, the elongation and the tear index of the investigated paper samples are defined and the results are presented in Table 3.

Table 3: Strength properties of base and treated paper samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Tensile Index, Nm/g</th>
<th>TEA Index, mJ/g</th>
<th>Elongation, %</th>
<th>Tear Index, mN.m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Only pulp</td>
<td>63</td>
<td>1070</td>
<td>2.4</td>
<td>1.1004</td>
</tr>
<tr>
<td>1</td>
<td>Base paper</td>
<td>69.5</td>
<td>1430</td>
<td>2.9</td>
<td>1.0989</td>
</tr>
<tr>
<td>2</td>
<td>Base paper+1 ml Silver water</td>
<td>66.6</td>
<td>1220</td>
<td>2.7</td>
<td>1.1094</td>
</tr>
<tr>
<td>3</td>
<td>Base paper+2 ml Silver water</td>
<td>64.7</td>
<td>1140</td>
<td>2.6</td>
<td>1.0881</td>
</tr>
<tr>
<td>4</td>
<td>Base paper+3 ml Silver water</td>
<td>63.6</td>
<td>1090</td>
<td>2.5</td>
<td>1.0889</td>
</tr>
</tbody>
</table>

From the strength properties data in Table 3 could be seen that with the greatest change compared to the indicators of the base paper are three indicators - tensile index (Tensile Index, Nm/g), the index of tensile work (TEA Index, mJ/g) and the elongation (Elongation, %) of the papers treated with silver water. In these three parameters, the treatment with silver water has a negative effect, but the reduction remains to the level of the strength of the paper samples with a composition of only cellulose. However, the strength of the paper after treatment does not cause further deterioration and the ability of the cellulose fibres to bond with each other is preserved. As the consumption of silver water increases from 1 to 3 ml, the values of the strength indicators, although within the error of the analysis, decrease. This effect is due to the irreversible destruction of the already formed hydrogen bonds between the cellulose fibres in the paper base, and the subsequent drying after spraying with silver water cannot compensate for the loss of the initially formed hydrogen bonds. Therefore, any additional processing of the paper should be carried out before the complete drying of the paper web, and if it cannot be avoided, the decrease in the strength indicators of the paper should be foreseen. In industrial paper production this reduction could be prevent. The main purpose of silver water treatment is to achieve antibacterial activity, in order to obtain a special type of paper, with application in packaging production in important sectors such as household, food packaging, medical and pharmaceutical products.

The results from the TGA analysis of the single sample analysis are presented in figures from 2 to 5. Figures show the weight loss of the samples as the function of the temperature. From figures could be observed that all samples have 3 stages of weight loss. First stage at sample 0 and 1 of weight loss is between 10°C and 100°C, where at the first part water, moisture evaporation occurs. Then at the second stage, the samples 0 and 1 (Figure 2 and 3) have similar weight loss at temperatures between 256°C and 411°C, with decreased mass of 77.91 % (Sample 0) and 79.52 % (Sample 1). The 3rd stage at both samples (after 411°C) presents the final degradation of the paper.

![Figure 2: TGA of Sample 0 – only pulp](image)
Figures 4 to 6 show samples with added Ag-water. 3 stages are also here detected. 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. From the analysis it is also determined that 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.
When comparing the weight losses of the treated samples examined, it was found out that, 2 ml of silver water increased the burn-up temperature of the paper by approximately 15°C. A comparative view of the weight loss of all the investigated samples (only pulp, base paper, Base paper + (1, 2, 3 ml) Ag – water) during TGA analysis is presented in figure 7. The pattern of thermal destruction of the investigated samples is not different, both for the cellulose sample and for the paper base and the papers treated with silver water. Undoubtedly makes an impression the different behavior of the sample with 3 ml of silver water (green line) which burns faster and is characterized with weight of 25 % in the range of 375°C. Due to the character of the application of the investigated paper, the change of the colour characteristics of the obtained papers over time, determined by accelerated thermal aging at 105°C for 72h, is also of interest.

The process of natural ageing of paper is too slow to permit observing changes in a reasonable period. Thus, different methods of accelerate ageing of paper under dry heat and light exposure have often been used. Accelerated ageing of paper is carried out for three major purposes. The first is to establish in a conveniently short time the relative ranking of materials, or physical combination of materials, with respect of their chemical stability or physical durability. The second is to estimate or predict potential long-term serviceability of material systems under expected conditions of use, and the third is to elucidate the chemical reactions involved (the degradation mechanism) and the physical consequences thereof. The hydrolytic degradation has been looked as the most important reason for the loss of strength properties of the paper and the lignin content as the most important factor for ageing. In the present study, the raw material was bleached pulp (lignin content is lower than 9 %), so that it cannot be of an essential factor for the colour change during thermal ageing, while the silver added as silver water could cause decrease of the thermal stability due to its catalytic action.
The L* axis in the CIE L*a*b* colour space represents lightness, brightness and the brilliance of the paper. This is vertical; from 0, which has no lightness (i.e., absolute black), at the bottom; through 50 in the middle, to 100, which is maximum lightness (i.e., absolute white) at the top. Just like CIELab, the lighter the colour, the higher the value. The lightness of the paper samples without and with silver water are presented in figure 8.

The colour coordinate - L*, which expresses the lightness, brightness and the brilliance of the paper, decreases with the silver water treatment. The colour parameter variation with time is comparatively low, being most sensitive during the first 24 hours. The differences between samples of cellulose (sample 0) and base paper (sample 1) are small – nearly to the error of the analysis. With increasing the consumption of the silver water and the duration of the thermal ageing, the colour of the paper samples is getting darker and the colour difference is getting bigger. At 3 ml silver water treatment the lightness of the paper samples significantly decrease starting at 91.76 around 24 hour of the ageing with continuous tendency till the end at 72 hours of accelerated thermal ageing at 89.66.

Figure 9 shows the results for the optical properties of the investigated paper samples (colour coordinates L*, a* and b*) with and without silver water treatment before and after 72 hours in each 6 hours of accelerated thermal ageing.
From the colour coordinates measurements, presented in figure 9 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 colour. For the other tree examined paper samples treated with 1, 2 and 3 ml silver water the colour amending occurs after the 36 hours of aging. The values of the colour 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 millilitres of silver water. Therefore, colloidal silver on the paper surface accelerates the aging by catalyzing the oxidation and hydrolysis of cellulose fibres. This is also confirmed by the observed decrease in the strength indicators, evidencing the destruction of hydrogen bonds between the cellulose fibres in the paper.

4. CONCLUSIONS

Coating and surface treatment of paper with multifunctional chemicals or additives has been proven excellent methods for improving its properties and for advancing the spectrum of its application. From the research carried out with paper samples of bleached softwood and hardwood pulp (80:20) treated with silver water was found out that treated papers has excellent thermal stability, as the colour coordinates do not change significantly during 72h of accelerated thermal ageing. 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 behaviour 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.

5. ACKNOWLEDGMENT

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6. REFERENCES


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