

# Biopolymers based paper coating with promoted grease resistivity, biodegradable and mechanical properties

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The dominance of plastics in the packaging market is due to their low weight and thickness, which save transportation costs. However, their non-biodegradability poses a significant threat to the environment. Paper, on the other hand, is considered as a safer alternative due to its natural composition and biodegradability. The porous structure of paper limits its application in packaging, and its poor water resistance further restricts its use in humid environments. Therefore, lamination is a method useful tool to improve the barrier properties of paper. Additionally, the researchers are focusing on developing biodegradable and water-based coatings with anti-fat properties as a green alternative to plastic packaging. The impact of a new grease-resistant coating composed of starch, gelatin and sodium alginate on the mechanical properties of paper was investigated through tensile, tearing, and bursting strength tests. Furthermore, the biodegradability test indicated that the paper samples coated with the new composition showed a 50% weight loss after one week of incubation in the soil, and after three weeks, they exhibited 100% weight loss, demonstrating their outstanding biodegradability.

Keywords: paper, grease resistance, lamination.

## **INTRODUCTION**

The most commonly used packaging materials are plastics. They are a distinctive type of polymer materials that can be formed by heat, time and pressure treatment. Their low density (thus low weight) and their thickness being lower than the ones of glass, metal and paper packages save a lot of cost in transportation, and thanks to that plastics have dominated the packaging market<sup>1</sup>. However, plastics are dangerous to the environment due to their non-biodegradability, consumption by animals and slow degradation that pollutes the ecosystem<sup>2</sup>. On the other hand, paper – being composed of natural materials like cellulose and lignin<sup>3</sup> – is much safer for both, environment and the consumers. All thanks to paper abundance, recyclability and biodegradability.

Barrier properties are crucial to packaging applications. Especially to protect moisture-sensitive items, such as food or electronic devices, but also as anti-fat bags. Unfortunately, porous structure of paper allows different molecules to migrate throughout the bulk framework which may damage the objects inside. That alone limits applications of paper in packaging industry. Furthermore, paper displays poor water resistance, due to the hydroxyl groups of cellulose, which further limits its applications in humid environment. Once large quantities of water molecules have been absorbed by paper its structure degrades rendering the packaging impractical. One of the methods of protecting paper is coating via lamination<sup>4</sup> and it may be performed by applying heat, pressure or adhesion. The lamination creates an outer layer onto paper that improves durability, appearance, barrier properties or other features depending on the type of used laminate. Currently, the most laminates are based on synthetic polymers and fossil-oil thanks to their abundance and low cost<sup>5, 6</sup>. Such polymer-coated paper packaging and cardboards are considered as a green alternative for plastic packaging, which is not entirely true, since such coating consists of non-degradable plastic that is also challenging to recycle and therefore demands special treatment. Hence, water-based coatings with anti-fat properties are the focus of researchers. However, there is a limited number of materials allowed to be used as laminates, since food packaging requires strict quality standards. Poly(lactic acid) (PLA)7-10 is, among, the most common biodegradable coatings. For instance, Hervy et al. prepared laminated composites of bacterial cellulose (BC) nanopaper reinforced with PLA<sup>11</sup>. The tensile moduli of the composites settled between ~12.6 and 13.5 GPa, indifferent to the number of BC sheets. On the other hand, the tensile strength decreased with the increment of BC sheets. Sundar et al. investigated barrier properties of microporous Kraft paper coated with different amounts of PLA<sup>12</sup>. Many properties, such as coating weight, moisture blocking, bursting and tensile strength, air porosity and surface roughness defined 9 g/m<sup>2</sup> PLA-coated Kraft paper as superior packaging material. Unfortunately, PLA is not thermally stable and deteriorates during processing. Another class of materials favorable for packaging paper coatings are based on polysaccharides, mainly cellulose<sup>13</sup>, chitosan<sup>14</sup>, starch<sup>15</sup> and their derivatives. They are not only biodegradable but also non-toxic, display good compatibility with paper, have great barrier properties against aromas, lipids and gases but also increase mechanical strength<sup>16-18</sup>. Yook et al. prepared numerous types of linerboard and wood-free papers coated with different types of cellulose nanofibrils<sup>19</sup>. The CM-CNF (carboxymethylated cellulose nanofibril) coating displayed

excellent barrier properties and AKD-CNF (alkyl ketene dimer-added cellulose nanofibril) coating enhanced water vapor barrier ability and water resistance. The main flaw of polysaccharides, however, is their high sensitivity to moisture, hence it is crucial to modify these materials when applied in packaging industry.

In this work, we designed biopolymers composition based on starch, gelatin and sodium alginate to laminate. As prepared samples barrier properties were tested against grease, wax and oil (Scheme 1). Additionally, their mechanical properties were evaluated. The detailed experimental study allowed us to reveal the most promising composition, also in terms of its biodegradability. The results indicated that after three weeks of incubation in the soil, 100% decrease in weight of the sample was detected proving it full biodegradability. This finding opens new route to penetrate grease resistant paper with boosted mechanical performance and biodegradable response observed in a very short time. Due to also its low cost this composition shows practical application in paper packaging industry.

## EXPERIMENTAL PART

### Chemicals

25% solution of gelatin (Carrefour); sodium alginate was purchased from Biomus, (analytically pure). Raw paper was delivered by Arctic Paper Kostrzyn SA.

### Preparation of a starch solution (S)

In a round-bottomed flask with a capacity of 500 ml, 180 ml of distilled water and 20 g of starch were mixed together. Then, the flask was placed on a hot plate and a mechanical stirrer was mounted. The hot plate was heated to 90 °C, then cooled down to 65 °C, and the stirrer was set to 150 rpm. After the solution was cooled, 30 g of citric acid was added and left to mix for 2 hours at 65 °C while continuously stirring. This solution served as a coating composition. The composition of the coatings applied to the paper differed in gelatin content (1–5 ml).

## Lamination

Coatings of the paper were applied using the K Control Coater. An A4 sheet was mounted in the coater and a rod with a dimension of 14  $\mu$ m was attached. Using a pipette, 10 ml of a properly prepared mixture was taken from a plastic container and spread along the rod. Then, the coating was evenly distributed over the paper surface. The sheet was transferred to a dryer (50  $^{\circ}$ C). Scheme 1 presents an illustration of creating an anti-grease and biodegradable layer.

### Biodegradation

Selected paper samples were analyzed to determine their suitability for composting and biodegradation, following the standards PN-EN 13432. The tests were conducted using soil as the test environment, under aerobic conditions with a constant temperature and humidity level. Four square pieces ( $25 \times 25 \text{ mm}$ ) were cut from each sheet and weighed separately each week. Pots were filled with 6 cm of universal soil and cut sheet fragments were placed on top, followed by another 10 cm of soil. After each week, one fragment was excavated, cleaned, dried in a desiccator overnight, and weighed to determine mass loss.

## Characterization

To determine the morphology of paper sheets coated with coatings, a scanning electron microscope (SEM) was used (SEM, VEGA3 TESCAN). The quality of the coating of cellulose fibers and the amount of cracks were presented. Raman spectroscopy (InVia Renishaw) with microscope mode was used to explore the bonding in cellulose pulp and coating using a laser with a wavelength of 785 nm.

## Mechanical properties evaluation

Mechanical properties of paper with coatings were investigated. For comparative purposes, non-coating paper sheets were also tested and used as a reference sample. The tests were performed in an air-conditioned room with a temperature of 23 °C and humidity level of 50%. The tested paper strips had a width and length of 15 and 100 mm, respectively. Tensile strength measurements were carried out using an automatic tensile tester (Messmer Büchel, K465, Veenendaal, Netherlands), in accordance with ISO 1974, on a sample consisting of 4 paper sheets. The bursting strength of the paper was tested using a bursting strength tester (Messmer Büchel), in accordance with ISO 2758, on paper samples with dimensions of over 70 mm  $\times$  70 mm.



Scheme 1. Simplified scheme for creating an anti-grease and biodegradable layer

#### Greases, oils, and waxes test (TAPPI UM 667)

After coating, a grease resistance test was conducted in accordance with TAPPI UM 557 (1 – no resistance to grease, 12 – grease resistance) standard. This test determines the resistance of paper and cardboard to the effects of greases, oils, and waxes. The samples were tested using a series of numbered reagents that differed in the concentration of castor oil, toluene, and n-heptane.

## **RESULTS AND DISCUSSION**

In the first step of our study, the anti-grease composition of coating was evaluated to reveal the most practically promising formulation. Table 1. shows the types of coatings applied to paper sheets, as well as the values of grease resistance in accordance with the standard TAPPI UM 557 (1 – no resistance to grease, 12 – grease resistance). Starch (S), gelatin (G), and sodium alginate (A) were mixed in plastic containers. Approximately, 10 ml of the mixture was taken from each container and applied and coated to a paper sheet. The sample composed of 1 g starch + 1.25 g gelatin + 0.4 g sodium alginate (in 10 ml distilled water) showed the best grease resistance.

SEM microscopy was used to determine the morphology of the coated paper sheets exhibiting the best antigrease response. Figures 1(a-b) show the paper covered with a coating composed of 1 g starch + 1.25 g gelatin + 0.4 g sodium alginate. The images clearly show the

 
 Table 1. Grease resistance of different types of coatings applied to paper sheets

Sample name	grease resistance		
papier without coating	0		
10% S	3		
25% G	5		
1g S + 0.25g G + 0,4g A	0		
1g S + 0.5 g G + 0,4g A	4		
1g S + 0.75 g G + 0,4g A	7		
1g S + 1g G + 0,4g A	8		
1g S + 1.25ml g G + 0,4g A	12		

difference between uncoated and coated paper sheets. The fibers were smoothed by the coating mixture by filling the fiber pores.



Figure 2. XRD pattern (a) and TGA profile (b) of paper sheets



Figure 1. (a-b) SEM images of paper sheets with coating (1 g starch + 1.25 g gelatin + 0,4 g sodium alginate)

The crystallinity of the obtained samples was determined by X-ray diffraction (Figure 2a). All samples exhibited two strong, broad peaks at 16.3 and 22.2°, as well as one less intense and sharp reflection at 34.4°. These signals are characteristic of 110, 200, and 004 planes assigned to the typical cellulose-I structure<sup>20</sup>. One additional weak signal attributed to starch (19,76°) was observed on the paper sheets. Due to the small amount of starch content on the surface of the paper, its signal was weak. This characteristic peak corresponds to B-type starch<sup>21, 22</sup>. The TGA measurements in Figure 2b enable to reveal the quality of coated paper sheets. The test was carried out in an air atmosphere at a heating rate 10 °C. Based on the obtained thermograms, two main weight losses were determined. In the first one the initial weight loss at about 100 °C was due to water evaporation, and the second weight loss occurred at 260 °C-450 °C, which is associated with protein and peptide chain breakage. Additionally, the thermal degradation process of composite was continuously delayed by addition of starch, gelatin and sodium alginate.



Figure 3. Raman spectroscopy of paper sheets

Figure 3 presents the Raman spectra of pristine and coated paper. The Raman spectrum exhibits several prominent bands, including the stretching vibrations of symmetric and asymmetric COC glycosidic ring breathing and skeletal stretching. These bands are the most intense and occur at 1099 cm<sup>-1</sup> for the asymmetric band and 1125 cm<sup>-1</sup> for the symmetric band. Other characteristic vibrations of cellulose include CCC ring deformation bending at 331 and 381 cm<sup>-1</sup>, CCC and CCO ring deformation and skeletal bending at 438 and 460 cm<sup>-1</sup>, COC glycoside linkage and CCC ring deformation bending at 520 cm<sup>-1</sup>, and HCC and HCO skeletal rotating at 901 and 1001 cm<sup>-1</sup>. The stretching vibrations of CC and CO

Table 2. Mechanical properties of the paper sheets

of the glycosidic ring occur at 1156 cm<sup>-1</sup>. Additionally, a cluster of bands in the region between 1200 and 1500 cm<sup>-1</sup> corresponds to the twisting of CH<sub>2</sub> at 1297 cm<sup>-1</sup>, wagging of CH<sub>2</sub> at 1341 cm<sup>-1</sup>, bending of CH<sub>2</sub> at 1384 cm<sup>-1</sup>, and scissors bending of CH<sub>2</sub> at 1484 cm<sup>-1 23</sup>. This cluster also includes bending vibrations of alcohol COH that overlap with other bands. Finally, stretching bands of CH vibrations are present in the spectrum at 2903 cm<sup>-1</sup>.

To investigate the impact of a new grease-resistant coating on the mechanical properties of paper sheets, mechanical tests were conducted to evaluate their tensile strength, tearing strength, and bursting strength. Each test was performed on ten different paper sheet samples. The collected data were presented as a strength index, and the standard deviation of the values was also reported. Table 2 summarizes the test results, indicating changes in the mechanical characteristics of paper sheets laminated, as compared to pristine cellulose paper. Additionally, paper sheets coated with individual components were also tested for comparison. The tensile index value showed a significant increase of 8.5% over non-coated paper, while the same sample demonstrated an improvement of 27% in tearing index value compared to the reference. Additionally, the bursting index value explicitly increased by 32%. These results suggest that the appropriate components in the coating play a key role in determining the mechanical properties of paper. When uniformly distributed on the paper sheet's surface and strongly adhered to the fibers, the coating can lead to an enhancement of the mechanical properties of paper.

### **Biodegradation**

Figure 4 presents the results obtained with pristine paper and paper coated with the new composition (1 g starch + 1.25 g gelatin + 0.4 g sodium alginate). The measurements were conducted according to the standard protocol and lasted for four weeks. After the first week of incubation in the soil, the reference sample was already 80% degraded, while the paper sample with the new coating showed a 50% weight loss. After three weeks of incubation, both samples showed a 100% decrease in weight, indicating their biodegradability.

The coating mixture combines starch, gelatin, and sodium alginate to create a hydrocolloid-based barrier that resists grease penetration into laminated paper. Starch, gelatin, and sodium alginate are all biopolymers that form a gel-like network in water<sup>24</sup>. The gel-like structure provides a physical barrier that hinders grease molecules from moving into its bulk structure. Starch is a polysaccharide composed of glucose units linked by  $\alpha(1\rightarrow 4)$ glycosidic bonds, with occasional  $\alpha(1\rightarrow 6)$  glycosidic bonds that create branching<sup>25</sup>. Starch has excellent filmforming properties and forms a gel-like structure when heated with water. This gel-like structure reduces grease penetration into the paper by creating a physical barrier.

	Tensile index [Nm g <sup>-1</sup> ]	Tear index [mN m <sup>2</sup> g <sup>-1</sup> ]	Burst index [kPa m² g⁻¹]
Paper without coating (reference)	8.69±0.15	46.76±0.22	3.9±0.09
10% S	8.34±0.18	46.69±0.25	4.08±0.11
25% G	9.08±0.15	58.12±0.31	4.83±0.05
0.4 g A	8.54±0.12	56.25±0.20	4.45±0.08
1g starch + 1.25g gelatin + 0,4g sodium alginate	9.43±0.18	59.28±0.24	5.13±0.08



Figure 4. Biodegradation of paper samples

Gelatin is a protein derived from the partial hydrolysis of collagen, the primary protein component in connective tissue. Gelatin is a highly versatile protein that forms a gel-like matrix when mixed with water<sup>26</sup>. The gelatin matrix can strengthen the overall hydrocolloid-based structure and enhance the coating's adhesion to the paper surface. Gelatin's film-forming properties also improve laminated paper grease resistance. Sodium alginate is a natural polysaccharide extracted from brown seaweed. It is composed of repeating units of  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid, linked by 1 $\rightarrow$ 4 glycosidic bonds. Sodium alginate can form a gel-like matrix through the reaction of divalent cations, such as calcium, with carboxyl groups on the polymer chain<sup>27</sup>. The gel-like matrix created by sodium alginate can further reinforce the overall structure of the hydrocolloid-based barrier and increase its grease resistance. The synergistic effects of the three hydrocolloids in the coating mixture result in a highly effective barrier against grease penetration in laminated paper. The combination of starch, gelatin, and sodium alginate creates a strong, flexible, and cohesive film that adheres well to the paper surface. This film hinders grease molecules' penetration. The optimal combination of the three components was 1 g starch + 1.25 g gelatin + 0.4 g sodium alginate.

# CONCLUSION

In conclusion, the study revealed the impact of a mixture composed of starch, gelatin, 0.4 sodium alginate on biodegradability, grease- resistivity and mechanical properties of fabricated paper sheets. The results showed that the appropriate components in the coating play a crucial role in determining the mechanical properties of paper. The coating, which combines starch, gelatin, and sodium alginate in a different ratio, creates a hydrocolloid-based barrier that resists grease penetration into laminated paper. The synergistic effects of the three hydrocolloids in the coating result in a highly effective barrier against grease penetration in laminated paper. The optimal combination of the three components was 1 g starch + 1.25 g gelatin + 0.4 g sodium alginate. The study also demonstrated the biodegradability of paper coated with the new composition. These findings could have important implications for the development of low-cost, sustainable

and environmentally friendly packaging materials with improved mechanical properties and grease resistance.

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