# Production of bio-based paper coating made with the addition of eggshell powder

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**Abstract.** A chitosan based coating was prepared where eggshell powder was added. Eggshell is a product that appears in large numbers in everyday life, so it has great potential as waste, which can be used to turn it into a valuable material. Cellulose sheets were made from secondary fiber, and after coated with the chitosan based solution to investigate the properties of the sheets. The results of the treated handsheets were compared with the results of the control sheet. The control sheets were compared with 4 different type of paper: coatings of chitosan with 5wt% and 10wt% eggshell powder, only chitosan coating, and paper where eggshell powder was added to the paper pulp. The use of the eggshell powder as an additive in the coating would be a promising material, because it can improve in a large extent the water resistance and the air barrier properties of the paper.

## 1 Introduction

The raw material of paper is cellulose, which is the most common natural polymer on earth. Cellulose is a renewable material, the sources of which can be the wood, annual plants, marine animals, algae, fungi [1]. In other words, sustainable raw materials are used for the production of paper products. Paper and cardboard products are biodegradable, thus not polluting the environment, but it can also be reused, i.e. a product that fits into the model of the circular economy, which is mostly used in the packaging sector as an environmental friendly alternative. In addition to these favorable properties, fiber-based products have weak barrier properties against water, oil and oxygen. Polymers, aluminum foils, and waxes are used to create coatings on the paper, which can be used to improve poor barrier properties [2-5]. These coatings often adversely affect recyclability and biodegradability because they are fossil-based, synthetic materials [6].

In recent decades, sustainable biopolymers have been extensively researched as an alternative to fossil-based plastics. Among the biopolymers, polysaccharides, proteins, lipids and polyesters can also be used to produce films and coatings [7]. A lot of emphasis was placed on chitosan research because of its favorable properties: excellent film-forming properties, non-toxic, biodegradable, antibacterial and it's naturally occuring [8, 9]. The production of chitosan requires chitin, which can be found in shrimps, crabs and the shells of insects. The waste product of the seafood industry can be used to produce chitosan. Chitosan is produced by deacetylating chitin with sodium hydroxide [8, 10]. Chitosan is semi-

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crystalline in the solid phase, and its dissolution requires a dilute organic acid medium [11]. The barrier properties such as oxygen and water vapour permeability and mechanical properties of chitosan are weak [10, 12].

Eggshell is a by-product that appears in the food processing and manufacturing sectors in large numbers in everyday life. Since eggs are often used in households, restaurants, or industry. The eggshell and its membrane are largely composed of inorganic components and contain only a small proportion of organic components. 95% is calcium carbonate, while 5% contains collagen, sulfated polysaccharides and other proteins [13, 14]. Between 2019 and 2021, egg production in Hungary averaged 2,550 million eggs based on statistics [15]. Most of the eggshell waste ends up in landfills without pretreatment [16]. Eggshells are non-hazardous waste in the environment, however, the organic protein matrix in them attracts rats and worms, which can lead to public health problems [17]. In the past decade, many studies have focused on how eggshells or eggshell membrane can be used as a value-added product in different fields e.g. ceramic wall tile, alginate, cornstarch and chitosan based biodegradable or edible film [14, 17-20].

The aim of the research is to create a coating for paper industry products that does not prevent the biological degradation of the paper. For this a chitosan-based coating was prepared. By adding ground eggshell to chitosan, we investigated whether it improves the weak mechanical and barrier properties of chitosan. We also investigated how much the paper's properties are affected by the applied coating. Although chitosan films and coatings are examined in many researches, its composites with eggshell as a paper coating material are not included in the reviewed publications.

# 2 Materials and methods

## 2.1 Materials

The eggshells were collected from local households in Sopron, Hungary. Chitosan (medium molecular weight) was procured from Sigma-Aldrich. Acetic acid was purchased from Molar Chemicals Ltd., Hungary. Deionized water was used for making the solution.

## 2.2 Preparation of eggshell powder

After collection, the eggshells were washed several times with tap water. Then with deionized water to remove impurities. After that, the eggshells were dried for 8 hours at 50°C in a hot air oven. The eggshell was blended into fine particles using a Planetary Ball Mills during 2 minutes and 400 rpm with 10 mm diameter balls (Retsch, PM 100).

## 2.3 Preparation of coating material

Chitosan solution of 1 wt% was prepared by dissolving chitosan powder in 1 mg/mL acetic acid solution for 24 h on a magnetic stirrer at room temperature (21 ± 2 °C). Then 5 wt% and 10 wt% of eggshell powder was added to the chitosan solution and gently stirring for 20 h. Later it was kept in a closed container in the fridge.

## 2.4 Preparation of samples

To prepare the cellulose sheets, secondary fiber was used and prepared 0.6 wt% suspension in a disintegrator with tap water. 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. 5 different type of paper was made: control paper which contains only secondary fiber (C) paper with coating of chitosan with 5 wt% eggshell powder (E1), paper with coating of chitosan with 10 wt% eggshell powder (E2), paper which only coated with chitosan (CH), and paper where eggshell powder (10 wt% for dry basis of fiber) was added to the paper pulp (PEGS).

For coating a brush was used where 4 g of coating was applied to the surface. Then it was dried on a Rapid-Köthen sheet former's dryer under vacuum at 90°C for 1 minutes. The finished sheets were kept in a sealed bag at room temperature, protected from light, until the tests started.

### 2.5 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.

### 2.6 Thickness, grammage

The thickness of the sheets was measured according to MSZ ISO 534 with a digital micrometer (Lorentzen & Wettre) to an accuracy of 100 µm. 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.

### 2.7 Examination of paper properties

The air permeability test was performed according to ISO 5636-5 using a Gurley densometer (Lorentzen & Wettre). The tensile test was performed according to MSZ ISO 1924 standard on an Alwetron TH1 equipment (Lorentzen & Wettre). For the test the samples were cut out of the sheet in the size of 15 x 100 mm). The values which given are averages, with standard deviations, according to standard measurements.

### 2.8 Water resistance

To study the water resistance of the samples a Cobb test and a microscopy test were performed. The test was performed during 30 seconds, where 20 seconds was the wetting process and 10 seconds was the drying process where samples was put between blotting paper. The absorption was expressed in $g/m^2$. The microscopics images was taken with a Tagarno FHD Prestige digital microscopy, where a water drop dropped at the surface of the sample then images was taken immediately at the dropping time and after one minute, in that cases where were sense to take images after one minute.

### 2.9 Scanning electron microscopy (SEM)

The SEM images of the samples and the coated surface were taken with a Hitachi S-3400 N scanning electron microscope (Tokyo, Japan) with an accelerating voltage of 10 kV. The magnification was 100 and 300.

### 2.10 Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra were collected with a Jasco FT/IR 6300 spectrophotometer (Tokyo, Japan) equipped with an ATR PRO 470-H. The spectra were recorded in the range of 4000 to 1000 cm−1 in the transmission mode with 40 scans per samples.

### 2.11 Statistical analysis

The one-way analysis of variance (ANOVA) and Tukey's multiple range test were used to compare the differences between the mean values of the tested samples. Differences below the significance level of 0.05 were considered statistically significant.

## 3 Results and discussion

### 3.1 Thickness, grammage

The mean values and standard deviations of thickness and grammage are shown in Table 1. It shows clearly that the control sheet is the thinner, and the treated sheets are thicker, because it contains an extra layer on the surface or extra additive in the structure. The treated sheets showed significant difference in all cases compared to the control sheet. However, compared the treated sheets to each other only between the E1 and E2 and between the E2 and CH there are significant difference.

**Table 1.** Thickness and grammage of the tested sheets.

| | Control | E1 | E2 | CH | PEGS |
|---|---|---|---|---|---|
| Thickness (μm) | 195±4 $^{a}$ | 213±7 $^{b}$ | 223±8 $^{c}$ | 215±7 $^{b\,c}$ | 207±6 $^{b}$ |
| Grammage (g/m$^2$) | 88±4 $^{a}$ | 97±3 $^{b}$ | 103±4 $^{b\,c}$ | 86±4 $^{a\,d}$ | 91±7 $^{a\,e}$ |

Values with different letters in the same columns indicate significant differences ($p < 0.05$).

### 3.2 Air permeability and tensile test

Table 2. shows the results of the air permeability test of the samples, where there is no significant difference between the control, the E1, the chitosan coated and the eggshell powder contained paper. E1 and E2 shows better airtight properties, however only the E2 results shows significant difference compared to the other results. The time required to penetrate 100 cm$^3$ of air increased by 27 times more at E1, and by 175 times more at E2 compared to the control sheets. In case of E2 outstanding improvement can be observed. Consequently, we can say only the chitosan coating cannot improve the air barrier properties, but when eggshell powder was added to the chitosan it can improve the air barrier properties. In addition, by increasing the eggshell powder, the time required for penetration also increases.

**Table 2.** Air permeability result of the samples.

| | Control | E1 | E2 | CH | PEGS |
|---|---|---|---|---|---|
| Air permeability (Gurley s) | 0.9±0.1 $^{a}$ | 24.7±14.2 $^{a}$ | 157.3±40.8 $^{b}$ | 1.6±0.3 $^{a}$ | 1.09±0.2 $^{a}$ |

Values with different letters in the same columns indicate significant difference ($p < 0.05$).

The results of the tensile test, so the tensile strength and the strain of the samples are shown in the Table 3. The best results in tensile strength was achieved with the pure chitosan coating. The addition of the eggshell powder decreased the strength of the paper, and it weakens further by increasing the amount of eggshell powder. However, the addition of the eggshell powder in 5 wt% was increased the strain. Except for the PEGS sheet, all results proved significantly different compared to the control sheet in the results of the tensile test and also in the strain results.

**Table 3.** Results of the tensile test.

| | Control | E1 | E2 | CH | PEGS |
|---|---|---|---|---|---|
| Tensile strength (kN/m) | 0.8±0.1 [a] | 1.6±0.2 [b] | 1.2±0.1 [c] | 1.7±0.1 [b] | 0.8±0.3 [a] |
| Strain (%) | 0.9±0.2 [a] | 2.0±0.3 [b] | 1.3±0.3 [c] | 1.7±0.3 [d] | 1.1±0.2 [a c] |

Values with different letters in the same columns indicate significant difference ($p < 0.05$).

## 3.3 Water resistance

### *3.3.1 Cobb test*

The results of the water absorption test shows huge differences. Figure 1. shows the control (a), the E1 (b), E2 (c) and the CH (d) sheets after wetting. No picture from PEGS sheet because it shows totally the same than the control sheet. On the control sheet (Fig. 1. a) we can observe that almost the whole paper was wet, only some lighter parts can see which are the dry parts. The E1 sheet (Fig.1. b) shows better result, since the water surface is almost only visible in a circular shape (which is the shape of the Cobb tester, and on this circular surface water directly touches the paper). This means that the fibers in contact with water did not absorb as much water as in the case of the control, since the water did not spread over a larger surface than the surface in contact with the Cobb tester. In case of E2 sheet (Fig 1. c) we can see the best results, because even on the surface in contact with water, you can see lighter spots, which means that it has not absorbed as much water as the area around it. CH sheet (Fig. 1. d) shows better results than control, but it was able to absorb more water compared to eggshell powder-containing coatings. Therefore, the addition of the eggshell powder to the chitosan can improve the water resistance of the paper.

The mean values and standard deviations of the Cobb test are shown in Table 4. The results of the Cobb test shows that E1 and E2 sheets showed significant improvement compared to the control sheet, which we can clearly observe with the images. E1 and E2 compared to the PEGS sheet also show significant improvement, but other cases the statistical analysis did not show significant differences between the results.

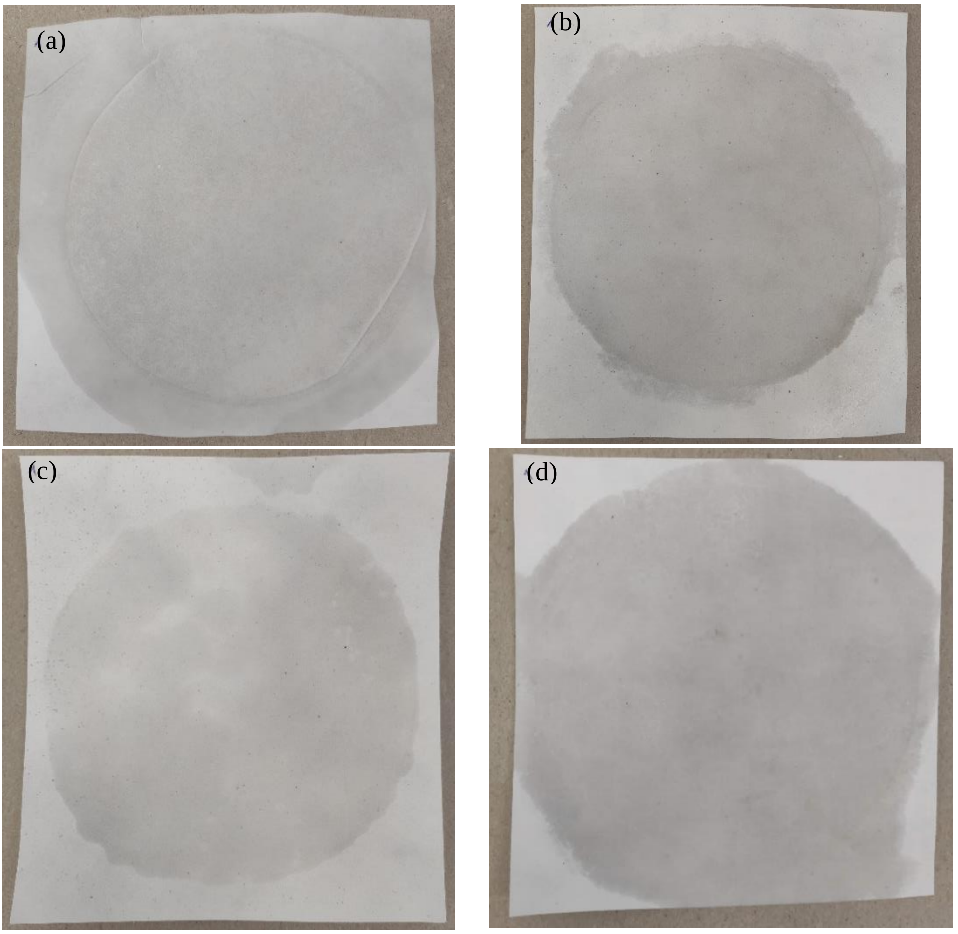



**Fig. 1.** The water absorption test of control (a); E1 (b); E2 (c) and CH (d).

**Table 4.** Results of the Cobb test.

| | Control | E1 | E2 | CH | PEGS |
|---|---|---|---|---|---|
| Absorbed water (g/m$^2$) | 284.9±7.9 $^{a}$ | 159.6±22.2 $^{b}$ | 137.6±36.3 $^{b\,c}$ | 208.6±21.2 $^{a\,b}$ | 247.5±31.9 $^{a}$ |

### *3.3.2 Microscopic images*

Figure 2. (a) shows the control paper where the dropped water drop spread over the surface of the paper, and the paper immediately absorbed the water. E1 sample (Fig. 2. b,c) and CH samples (Fig. 2. f, g) showed similar results, which were better results compared to the control sheet. After the drop, the water drop can be seen on the surface of the paper and not spreads out. Even after 1 minute, the water drop is still clearly visible on the surface, but at this point a darker spot can be seen around it, which means that absorption has begun, but much slower than with the control paper. E2 samples showed the best results from all the samples. After 1 minute the drop spread in a small amount compared to the initial state, but darker parts around the water drop cannot be visible, which means the fibers did not absorb much water. PEGS (Fig. 2. h) showed that the eggshell powder as an additive of the paper

pulp cannot improve the water resistance properties of the paper, because it showed the same results, then the control sheet.

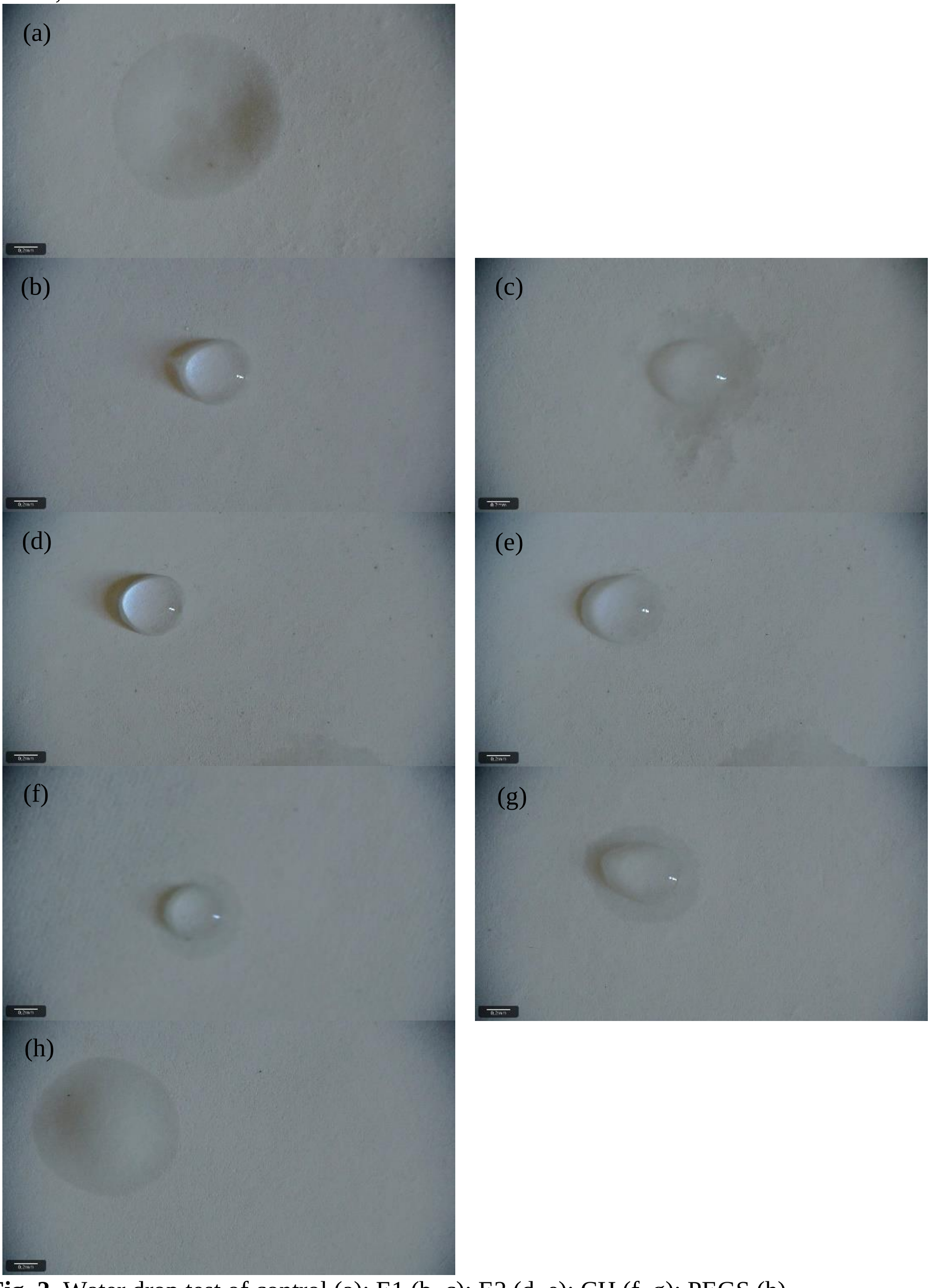
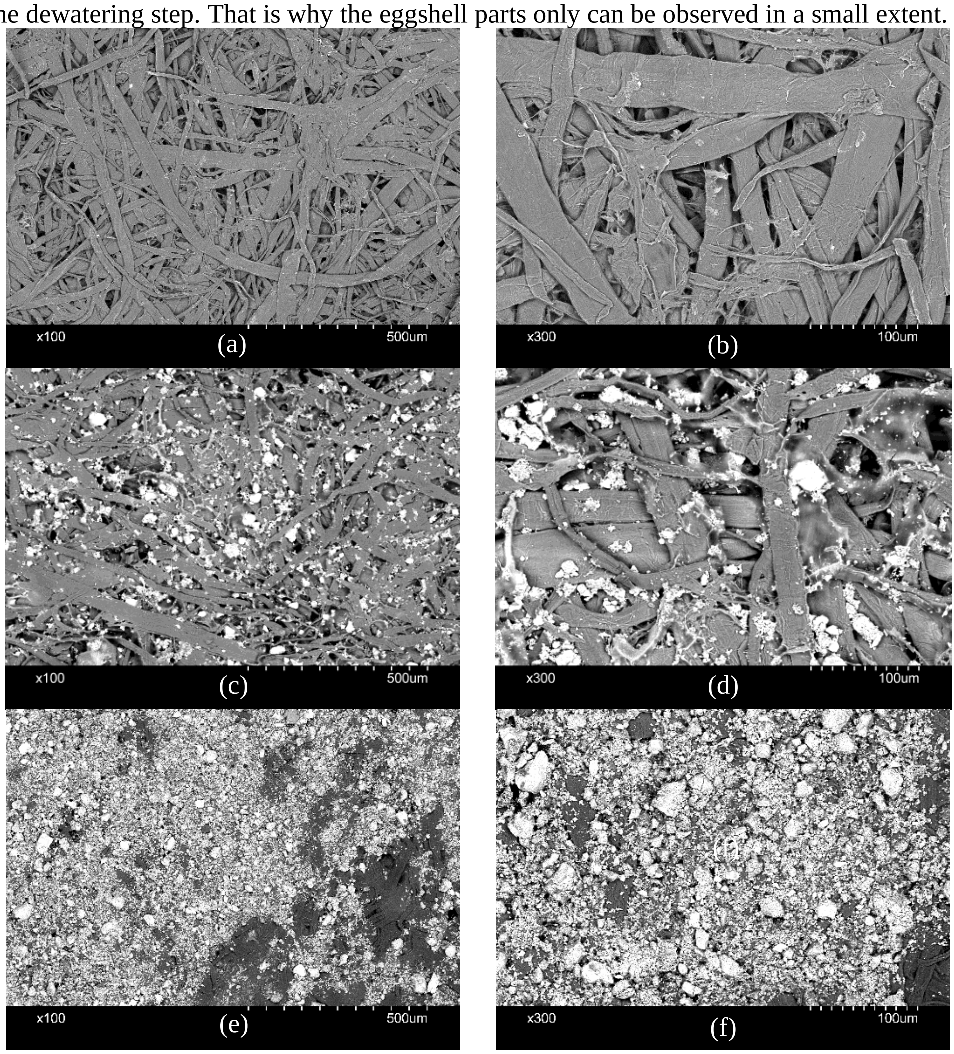



**Fig. 2.** Water drop test of control (a); E1 (b, c); E2 (d, e); CH (f, g); PEGS (h).

### 3.4 SEM analysis

The surface structure of the paper and the coating was studied using a scanning electron microscopy. Figure 3 shows the SEM images with magnification of 100× and 300×. In the control picture (Fig. 3. a, b) only the fibers can be observed. These are long fibers, where the length at least 0.5 mm, but there are some fibrils, which are thinner broken fibers.

Picture of the E1 (Fig. 3. c, d) clearly shows the eggshell parts on the surface of the paper. In 300× magnification we can see obscure parts which can be the small parts of the protein-rich membrane layer. In the picture of E2 (Fig. 3. e, f) can be observed much more eggshell parts because of this coating contained the eggshell particles in the largest proportion. The coating covers the surface well, however we can see parts where is no coverage, so we can see the fibers. It can be concluded that the coating process was not totally perfect. The chitosan coating (Fig 3. g, h) shows nothing visible. It is quite similar to the control paper. The Figure 3. (i, j) shows the PEGS sheet. In the 100× magnification a large white spot is observed, which is believed to be clumped eggshell powder that has not been properly mixed into the pulp. Since the eggshell was added at the beginning of the papermaking process, it can be assumed that a part of the eggshell powder was removed along with the water during the dewatering step. That is why the eggshell parts only can be observed in a small extent.



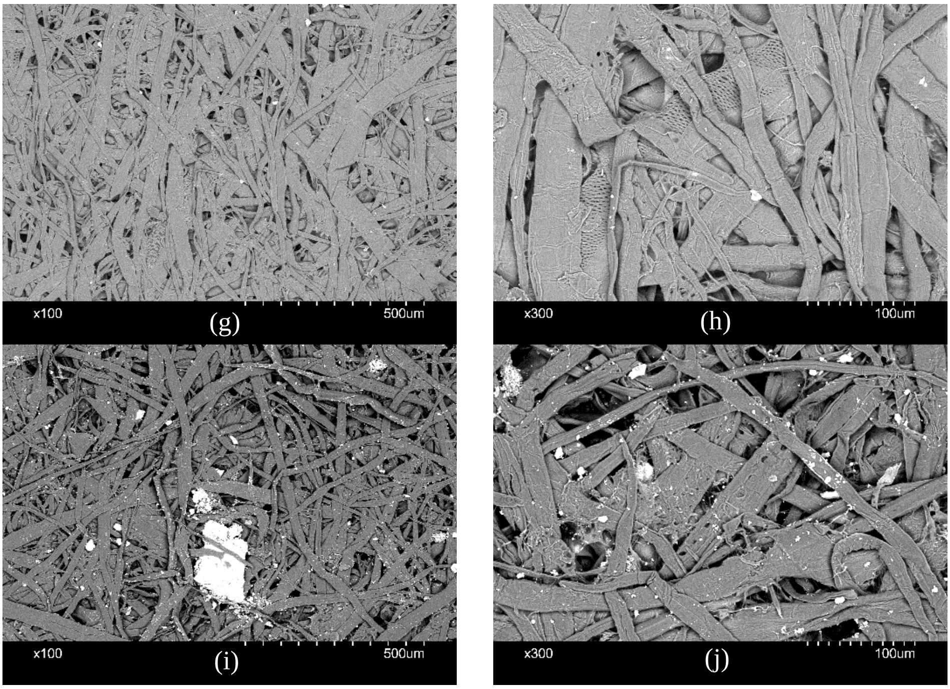



**Fig. 3.** SEM images of control (a,b); E1 (c,d); E2 (e,f); CH (g,h); PEGS (i,j).

### 3.5 FTIR analysis

With the use of infrared spectroscopy the intermolecular interaction of the control and treated samples were examined. Figure 4. showed the FTIR spectra of the samples. At 3330 $cm^{-1}$ a broad and strong band can be observed with all samples which is assigned to the O—H stretching vibration of H-bonded hydroxyl groups. The stretching vibration of C—H can be observed at the adsorption of 2896 $cm^{-1}$. The peak at 1622 $cm^{-1}$ is due to the vibration of the adsorbed $H_2O$ molecules. C—H bending of $CH_2$ can be seen at 1427 and 1315 $cm^{-1}$. The peak at 1368 $cm^{-1}$ is the C—H bending vibration of CH. The band at 1160 $cm^{-1}$ is due to the C—O—C stretching vibrations of β-(1,4)-glycosidic bonds. The in-plane ring C—O—C stretching vibration can be observed at 1160 $cm^{-1}$. Two strong peaks can be observed at 1053 and 1029 $cm^{-1}$correspond to the C—O stretching vibration at CH—OH and CH2—OH [21-24].

The spectra shapes are similar in all cases, however there are some differences in the peak positions of the different samples. In one case, we can observe a different peak compared to the control and PEGS sheet. Around 1550 $cm^{-1}$ there is a peak in the case of the chitosan contained samples, which can be the N—H [25].

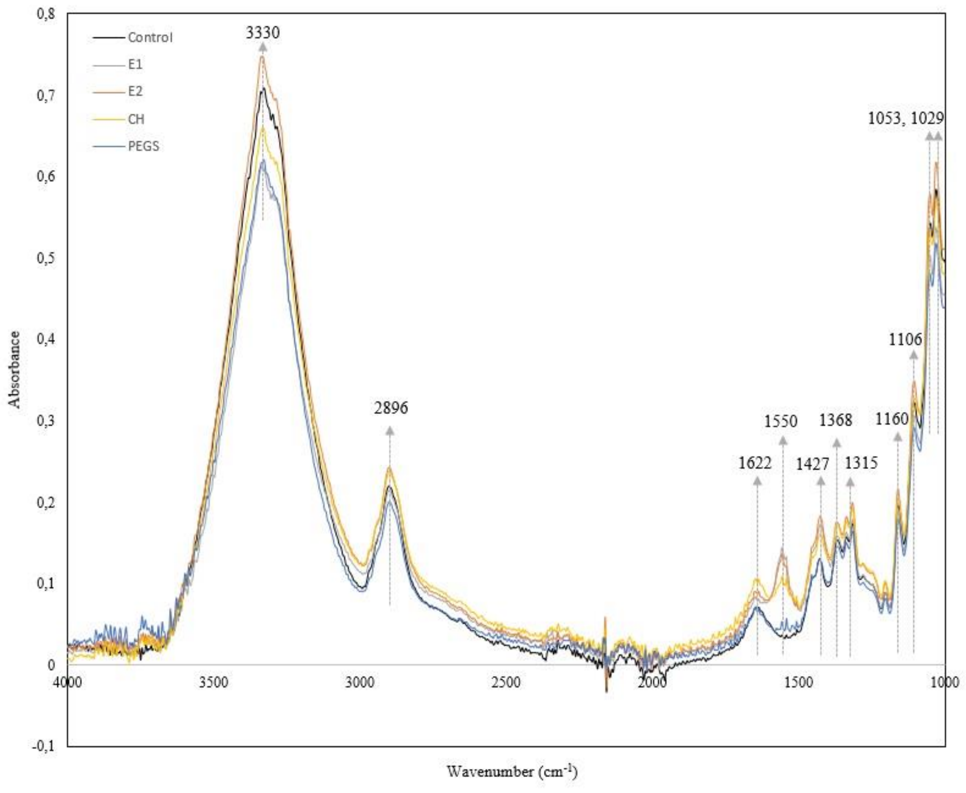



**Fig. 4.** Absorption spectra of the samples.

## 4 Conclusion

The results of the research showed that the air barrier property of the secondary fiber sheet can be improved to be coated with the eggshell powder contained chitosan film. However, the paper which contained in the chitosan coating 5 wt% eggshell powder showed an improvement compared to the control film but it was not significant. In the case of 10 wt% eggshell powder the improvement was significant compared to the other tested samples. According to the results of the tensile test the E1, E2 and CH sheets showed improvement compared to the control and PEGS sheets. The best outcomes showed by the E1 and CH sheets. The Cobb test showed that the water resistance of all the treated paper improved compared to the control sheet. In the water resistance, the significant improvement was achieved in the case of E1 and E2 sheets compared to the control and PEGS sheets. During the water drop test, the microscopic pictures showed that the highest improvement was achieved the E2 sheet, after followed the E1 and CH, which showed similar results. However, the PEGS sheet showed totally the same than the control sheet. The SEM images clearly showed that the most closed surface was achieved with the 10 wt% eggshell powder contained chitosan solution, which is explain the improved airtight and water resistance properties. The absorption spectra of the FTIR were similar in all cases, we can observe some differences only in the peak positions of the different samples. It can be concluded that the eggshell contained chitosan coating can improve the air barrier and water resistance properties of the paper compared to the chitosan-coated paper. However, the addition of the eggshell powder was not able to improve the tensile properties of the samples.

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## References

1. L. Brinchi, F. Cotana, E. Fortunati, J.M. Kenny, Carbohydr. Polym. **94**, 154–169 (2013)
2. P.K. Kunam, D. Ramakanth, A. Konala, K. Gaikwad, Biomass Convers. Biorefin. 1-16 (2022)
3. A. Adibi, D. Valdesueiro, J. Mok, N. Behabtu, C. Lenges, L. Simon, T.H. Mekonnen, Carbohydr. Polym. **282,** 119121 (2022)
4. L. Dai, X. Xi, X. Li, Y. Du, Y. Lv, W. Wang, Y. Ni, Carbohydr. Polym. **271**, 118425 (2021)
5. D. Raheem, Emir. J. Food Agric. **25,** 177-188 (2012)
6. K. Khwaldia, E. Arab-Tehrany, S. Desobry, Compr. Rev. Food Sci. Food Saf. **9**, 82–91 (2010)
7. V. Rastogi, P. Samyn, Coatings **5**, 887–930 (2015)
8. A. Jiang, R. Patel, B. Padhan, S. Palimkar, P. Galgali, A. Adhikari, I. Varga, M. Patel, Polymers **15**, 2235 (2023)
9. H. Singhi, L. Kumar, P. Sarkar, K. Gaikwad, J. Food Meas. Charact. **17,** (2023)
10. T. Liu, J. Li, Q. Tang, P. Qiu, D. Gou, J. Zhao, Foods **11,** 1490 (2022)
11. M. Flórez, E. Guerra-Rodríguez, P. Cazón, M. Vázquez, Food Hydrocoll. **124**, 107328 (2022)
12. D. Hu, X. Liu, Y. Qin, J. Yan, J. Li, Q. Yang, Food Qual. Saf. **6**, (2022)
13. S.C. Onwubu, V. Anisa, S. Shalini, M.K. Krishnan, J. Appl. Biomater. Funct. Mater. **15**, 341-346 (2017)
14. V.M. Joseph, R. Kobun, R.A. Azhar, N. Huda, E.H. Kana, W.X.L. Felicia, M.N. Nur'Aqilah, N.F.A. Halid, J. Funct. Biomater. **13,** 67 (2022)
15. https://www.ksh.hu/stadat_files/mez/hu/mez0034.html [Viewed: 10.08.2023]
16. Y. Gao, C. Xu, Catal. Today **190,** 107–111 (2012)
17. M.N. Freire, J.N.F. Holanda, Ceramica **52**, 240–244 (2006)
18. R. Mohammadi, M.A. Mohammadifar, M. Rouhi, M. Kariminejad, A.M. Mortazavian, E. Sadeghi, S. Hasanvand,. Int. J. Biol. Macromol. **107**, 406–412 (2018)
19. B.C.W. Webb, S. Rafferty, A.J. Vreugdenhil, Polymers **14**, 383 (2022)
20. V. Villanueva, F. Valdes, R.N. Zuniga, M.G. Villamizar-Sarmiento, E. Soto-Bustamante, P. Romero-Hasler, A.L. Riveros, J. Tapia, J. Lisoni, F. Oyarzun-Ampuero, C. Valenzuela, Food Hydrocoll. **142** (2023)
21. Y. Yan, C. Wen, M. Jin, L. Duan, R. Zhang, C. Luo, J. Xiao, Z. Ye, B. Gao, P. Liu, Y. Tang, Chem. Res. Chin. Univ. **35**, 586–591 (2019)
22. Y. Ma, J. Wang, Y. Zhang, J. Therm. Anal. Calorim. **129**, 1225–1232 (2017)

23. X. Colom, F. Carrillo, F. Nogués, P. Garriga, Polym. Degrad. Stab. **80**, 543–549 (2003)
24. N. Abidi, L. Cabrales, C.H. Haigler, Carbohydr. Polym. **100**, 9–16. (2014)
25. J. Novaes, E.A.S. Filho, P.M.F. Bernardo, E.R. Yapuchura, Polímeros **30**, e2020015 (2020)