

# UTILIZATION OF BIO-BASED POLYMERS AND DIMETHYLOL DIHYDROXYETHYLENE UREA IN COATING KRAFT PACKAGING PAPERS

MERYEM ONDARAL and EVREN ERSOY KALYONCU

*Karadeniz Technical University, Arsin Vocational School, Department of Material and Material Processing Technologies, Arsin/Trabzon, Turkey*

✉ *Corresponding author: M. Ondaral, mondaral@ktu.edu.tr*

*Received June 24, 2024*

The use of polymers in food packaging that do not harm human health and are biodegradable provides a reliable and environmentally friendly packaging option. In this study, the use of biodegradable polymers, such as guar gum (GG), whey protein isolate (WPI), and soy protein isolate (SPI), with the addition of dimethyloldihydroxyethyleneurea (DMDHEU) as a surface coating, on unbleached kraft food packaging papers was investigated. For this purpose, 3% SPI, 0.5% GG, 6.0% WPI, and four different amounts of DMDHEU (0%, 0.5%, 1.0%, and 1.5%) were used. Mechanical properties, including tensile strength, tear resistance, and burst strengths were determined; physical properties including Cobb and air permeability tests were conducted, and scanning electron microscope images of paper samples were analyzed for characterization. Improvements were obtained in the tensile strength of papers coated with all three of the biopolymers used without DMDHEU. The highest breaking resistance was obtained with GG. While the tear index value improved with GG and SPI, it decreased with WPI. Moderate decreases were observed in burst index values, with the lowest values obtained with WPI. It was determined that the water repellency of GG, SPI, and WPI-coated papers decreased, while air permeability resistance increased. SPI, GG, and WPI biopolymers are expected to serve as coating materials in packaging paper production.

**Keywords:** guar gum, soya protein isolate, whey protein isolate, Kraft paper, food packaging

## INTRODUCTION

Packaging materials help preserve food quality, freshness, and properties, ensure safe delivery, aid transportation and storage, and extend shelf life while reducing waste.<sup>1,2</sup>

Population growth and changes in consumption habits have further increased the demand for packaging materials. Paper, metal, glass, and plastic are commonly used in food packaging. Plastic is the most preferred food packaging material due to its high quality, ease of processing, and suitable properties. However, its widespread use also brings environmental and human health issues.<sup>3,4</sup> The EU's bioeconomy strategy aims to promote the use of environmentally friendly and recyclable materials, particularly in critical areas, such as packaging. This strategy seeks to facilitate the recycling of packaging materials, enhance environmental sustainability, and reduce waste by 2030.<sup>5</sup>

The long decomposition time of plastic packaging materials in nature, the difficulty and costliness of recycling, and the leakage of certain chemicals into food, causing health concerns, all contribute to the spread of waste into the environment. Therefore, being aware of potential problems, it will be possible to reduce environmental and health problems by using alternative environmentally friendly packaging materials.

Kraft paper is a preferred type of paper in food packaging production due to its durability, ease of production<sup>6,7</sup> and recyclability. However, the hydrophilic nature and porous structure of paper pose challenges in managing the absorption of water, oil, and gas, particularly in packaging applications. It is very important to regulate wetting and barrier properties, minimize fiber swelling, prevent spoilage of packaged products by maintaining the shape and mechanical integrity of the packaging.<sup>8</sup> In order to improve the barrier properties of paper packaging materials, various technologies and coating processes were developed in the late 19<sup>th</sup> century.<sup>9</sup> Oxygen, carbon dioxide, nitrogen, and water vapor directly affect the quality, spoilage, ripening and shelf life of food products.<sup>10</sup> Since paper is a porous material commonly used in food packaging, it allows the passage of moisture, water vapor, and gases. In the packaging industry, protecting products and preventing the permeability of gases, particularly

oxygen and carbon dioxide, is a major priority. Therefore, various studies have been conducted to reduce the permeability of paper packaging materials by coating the paper surface with a biopolymer film layer.<sup>11,12</sup>

The main components used for barrier properties in paper packaging materials are based on plastics,<sup>13</sup> glass<sup>14</sup> and metals.<sup>15</sup> Plastic, glass, or metal based coatings as barriers in paper based packaging complicates the recycling process. With the increasing environmental concerns in recent years, more environmentally friendly solutions have been sought in the packaging sector. Shifting from petroleum-based plastics to sustainable polymers is a practical alternative solution to reduce pollution from non-degradable materials.<sup>16,17</sup> Peng and colleagues<sup>18</sup> successfully removed the coating material from biopolymer coated papers using chemical methods, enabling the pulp to be reused in paper production.

The use of biodegradable, bio-based materials that do not pose a threat to the environment or human health<sup>19,20</sup> can be considered for eco-friendly packaging materials.<sup>21,22,23</sup> Food packaging made from biodegradable materials, typically sourced from natural resources, does not pose any issues with food contact. The use of these materials, which do not harm human health, provides consumers with a safe usage option due to their ability to biodegrade and be recycled. One of the main categories of biodegradable polymers consists of polysaccharides, proteins, and lipids obtained from renewable resources. Biodegradable polysaccharide and protein-based materials are gaining increasing attention in the packaging industry. Examples of polysaccharide-based biopolymers include starch, cellulose, guar gum, chitin, and chitosan,<sup>24,25,26</sup> while protein-based polymers include wheat gluten, soy, whey,<sup>12,27</sup> gelatin, and casein.<sup>24,28,29,30</sup>

The positive attributes of polysaccharide-based biodegradable biopolymers include the ability to form films, compatibility with paper as a raw material, the ability to create barriers to various gases, and the potential to enhance the mechanical strength properties of papers.<sup>9,30</sup> The improvement of optical properties, provision of superior oil barrier, formation of high levels of oxygen and organic vapor barriers at low and medium humidity levels, and attainment of robust mechanical properties are advantageous features achieved through the utilization of protein-based biodegradable biopolymers in packaging materials.<sup>31,30</sup>

Guar gum (GG) is a polysaccharide derived from the seeds of the guar plant, consisting of long polymeric chains and classified as a high molecular weight galactomannan.<sup>32</sup> This natural hydrocolloid is water-soluble, forming thick solutions even at low concentrations.<sup>33</sup> Due to its high water absorption capacity, guar gum is widely used as a food additive and finds applications not only in the food industry, but also in pharmaceuticals, textiles, and the paper industry.<sup>33,34</sup> In the paper industry, guar gum exhibits properties similar to hemicelluloses, enhancing strength, hydration, adhesion, and reducing porosity.<sup>33</sup>

Whey protein isolate (WPI), which falls under the protein group, is obtained through specific filtration methods during industrial cheese production.<sup>35,36</sup> WPI is used as a film-forming and coating agent due to its properties.<sup>37</sup>

Soy protein isolate (SPI), containing approximately 90% protein, is obtained through alkaline extraction of defatted soybean flour followed by precipitation at an acidic pH.<sup>38</sup> SPI exhibits significant technological properties, such as solubility, gel formation, emulsification, dispersibility, high viscosity, and resistance to challenging processing conditions.<sup>39</sup> Furthermore, due to its high viscosity, plasticity, elasticity, and excellent mechanical properties, it is widely used in film-forming materials.<sup>40</sup> Studies have also demonstrated that SPI offers exceptional oxygen barrier properties.<sup>41,42,43</sup>

Dimethyloldihydroxyethylene urea (DMDHEU), which can react with the hydroxyl groups of lignin and hemicelluloses and which can cross-link with each other,<sup>44,45</sup> is frequently utilized as a wrinkle-resistance additive in cotton fabrics within the textile industry.<sup>46</sup> It has also been applied in wood modification processes<sup>47,48,49</sup> and the paper industry.<sup>50</sup>

The aim of this study is to investigate the effect of surface coating with GG, WPI, and SPI containing DMDHEU additive on the mechanical and physical strength of kraft packaging paper.

## **EXPERIMENTAL**

### **Materials**

In the study, commercially obtained unbleached softwood kraft cellulose fiber was used as raw material for paper handsheet production. Commercially available whey protein isolate (Alfasol, Turkey), guar gum (E412,

Alfasol, India), soy protein isolate (90% protein, Alfasol, India), dimethylol dihydroxyethylene urea and glycerol were used for preparing biopolymer solutions.

### **Pulp and handsheet test paper preparation**

For the pulping process, commercially obtained unbleached kraft sheets were torn into small pieces and then softened by soaking in water and pulped in a laboratory type disintegrator at 3000 rpm $\pm$ 25 speed for 10 minutes to release the fibers.

10 paper sheets were prepared on a Rapid Köthen Test Paper machine with a diameter of 20 cm, according to TAPPI standard T 205 sp-12.<sup>51</sup> The handsheets were conditioned for 24 hours in a climate-controlled room at 23 °C  $\pm$  1 °C and 50%  $\pm$  2% relative humidity, following TAPPI standard T 402 om-93<sup>52</sup> before testing their physical properties.

### **Preparation of solutions utilized in surface coating and application to test papers**

Guar gum, whey protein, and soy protein isolate biopolymers were used to prepare the solutions to be used in the method of coating on the surface of kraft papers. The biopolymer ratios used for the preparation of the solutions were 0.5% for guar gum, 3% for soy protein isolate, and 6% for whey protein isolate, as discussed in previous studies.<sup>53-55</sup> To achieve uniform distribution of the solutions during their application to the papers and to enhance the flexibility of the resulting papers, 0.8% glycerol was added. To impart water repellency to the papers, the chemical DMDHEU was incorporated into the solutions at concentrations of 0.5%, 1%, and 1.5%. The water used for preparing the solutions was added slowly. To ensure a homogeneous distribution, each prepared solution was heated to 100 °C and stirred at 850 rpm for 30 minutes. The spreading method was used to apply the solution to the test papers. Following the rolling process applied to the surface to ensure better adhesion and remove excess solution, the papers were dried in the drying section of the Rapid Köthen Test machine. The samples were conditioned before analysis and measurements.

### **Paper characterization**

#### ***Physical and mechanical properties of test papers***

The tensile strength of the test papers was determined with the Karl-Frank-800 Pendulum Type Tensile Tester, burst strength – with the Mullen Burst Tester, and tear strength – with the Elmendorf 1650 Tear Tester, according to TAPPI standards T494 om-13(2013),<sup>56</sup> T403 om-15 (2010),<sup>57</sup> and T414 om-21 (2021),<sup>58</sup> respectively. Six different test paper sheets were used for each measurement. The water absorption (g/m<sup>2</sup>) capacity of the papers was determined in accordance with TAPPI standard T441om-20 (2020)<sup>59</sup> with a Cobb sizing tester. The results were reported as an average of 5 measurements per each sample. To measure the air resistance (s/100 mL) of the paper samples (felt side), a Gurley porosimeter was used in accordance with TAPPI standard T460 om-21 (2021).<sup>60</sup>

#### ***Scanning electron microscopy (SEM) imaging***

A Zeiss Evo LS-10 scanning electron microscope was used to study the biopolymer coated papers and the filler interaction of the samples at Karadeniz Technical University, Central Research Laboratory.

## **RESULTS AND DISCUSSION**

### **Mechanical properties**

Changes in the mechanical properties of test papers are shown in Table 1. The application of crosslinking agents can reinforce the bonds between fibers, thereby improving the mechanical properties of the paper.<sup>61</sup> Glycerol is widely recognized as an effective plasticizer for protein-based materials due to its ability to increase intermolecular distances and reduce intermolecular hydrogen bonding. By enhancing flexibility and film-forming properties, glycerol contributes to improved mechanical properties of papers.<sup>30,62</sup> Therefore, during the preparation of biopolymer solutions, the primary goal was to enhance the flexibility of the films and coated papers by reducing their brittle structure and imparting elastic properties. To achieve this, glycerol (0.8%) was added to all test paper solutions, except for the control.

The effect of surface coating on the tensile strength properties of all papers are shown in Figure 1. The surface coating process of paper has a significant impact on tensile strength.<sup>6</sup> Surface coating treatments performed with SPI, GG, and WPI without DMDHEU additives showed a notable increase in the tensile strength of the papers compared to the control sample. This increase was approximately 3 times for SPI and 4 times for GG relative to the control test paper.

In the control samples, a slight increase in tensile strength was observed as the DMDHEU content increased. In contrast, papers coated with biodegradable biopolymers exhibited a moderate decrease in

tensile strength with increasing DMDHEU content. Notably, the tensile strength of paper surfaces coated with SPI decreased more significantly than the others when 1.0% and 1.5% DMDHEU were added. Specifically, increasing the DMDHEU content from 0% to 1.5% led to a 15.83% reduction in tensile strength for GG-coated papers and a 30.80% reduction for SPI-coated papers.

Despite the reduction, the tensile strength of papers coated with SPI biopolymer was still higher than that of the control sample, a trend similarly observed for GG-coated papers. Figure 1 highlights that at 0% DMDHEU content, both SPI and GG biopolymers significantly enhanced the tensile strength of the paper compared to the control sample. Among the biopolymers, GG demonstrated superior tensile strength. These results indicate that SPI and GG biopolymers deliver promising outcomes, making them particularly advantageous for use in packaging paper applications.

In the study by Sudheer *et al.*,<sup>63</sup> it was noted that the use of GG as a filler material in cross-linked polymeric structures effectively enhanced the properties of the polymeric network. This is consistent with the observation that GG provides higher tensile strength compared to SPI and WPI as DMDHEU content increases.

Table 1  
Effect of DMDHEU ratio on mechanical resistance of test papers

| Component | DMDHEU (%) | Tensile strength (Nm/g) | Burst index (kN/g) | Tearing strength (mNm <sup>2</sup> /g) |
|-----------|------------|-------------------------|--------------------|--|
| Control   | 0          | 6.11 (0.086)*           | 3.8 (0.053)        | 8.26 (2.027)                           |
|           | 0.5        | 10.6 (0.053)            | 3.46 (0.074)       | 6.19 (0.086)                           |
|           | 1          | 10.05 (0.081)           | 3.55 (0.073)       | 8.27 (0.296)                           |
|           | 1.5        | 9.86 (0.139)            | 3.69 (0.129)       | 7.06 (1.110)                           |
| 3% SPI    | 0          | 25.68 (0.048)           | 3.82 (0.116)       | 16.53 (0.884)                          |
|           | 0.5        | 24.91(0.040)            | 3.88 (0.060)       | 17.14 (1.079)                          |
|           | 1          | 20.1 (0.245)            | 3.57 (0.093)       | 16.8 (1.246)                           |
|           | 1.5        | 17.17 (0.178)           | 3.51 (0.114)       | 11.03 (0.282)                          |
| 0.5% GG   | 0          | 30.31 (0.082)           | 3.72 (0.045)       | 19.55 (1.755)                          |
|           | 0.5        | 26.34 (0.062)           | 3.6 (0.055)        | 16.65 (1.615)                          |
|           | 1          | 26.6 (0.016)            | 3.52 (0.055)       | 18.15 (1.323)                          |
|           | 1.5        | 25.51 (0.192)           | 3.70 (0.018)       | 17.58 (1.084)                          |
| 6.0% WPI  | 0          | 8.63 (0.705)            | 3.43 (0.120)       | 6.84 (1.756)                           |
|           | 0.5        | 8.16 (0.685)            | 3.41 (0.093)       | 5.25 (0.502)                           |
|           | 1          | 9.16 (0.797)            | 3.46 (0.072)       | 5.72 (0.753)                           |
|           | 1.5        | 7.56 (0.611)            | 3.53 (0.061)       | 5.70 (0.160)                           |

\*- Numbers in parentheses represent standard deviations

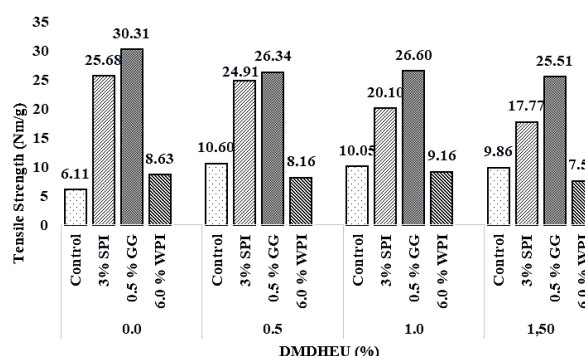


Figure 1: Tensile strength values of biopolymer coated papers

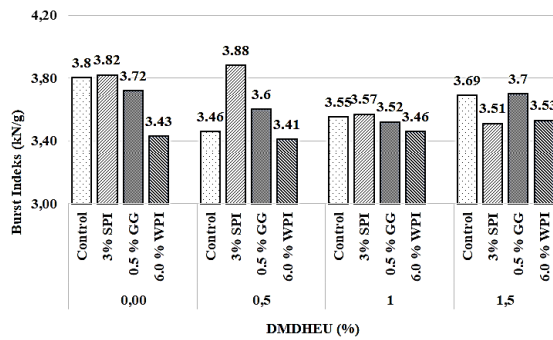


Figure 2: Burst resistance values of biopolymer coated papers

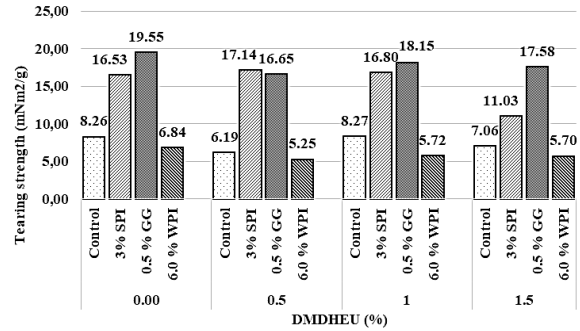


Figure 3: Tear resistance values of biopolymer coated papers

The compatibility of the biopolymer coating material applied to the paper with the fiber and its bonding capacity are also important in determining the breaking strength of the paper. It was thought that the decrease in the tensile strength values of the papers, despite the glycerol in the solution, was due to the fact that the DMDHEU chemical gave hardness to the paper<sup>64</sup> and caused the decrease in the tensile strength of DMDHEU-biopolymer coated papers.

Figure 2 shows the burst resistance values of the test papers. The SPI+0.5% DMDHEU biopolymer-coated paper displayed the highest value (3.88 kN/g), while the WPI+0.5% DMDHEU-coated paper had the lowest value (3.41 kN/g). For papers coated with biopolymer solutions without DMDHEU, the SPI-coated sample exhibited the highest burst resistance, which was closest to the control paper. However, other biopolymer-coated papers showed lower burst resistance values compared to the control sample.

It was found that the control paper, as well as papers coated with SPI, GG, and WPI, had higher burst index values when the DMDHEU ratio in the biopolymer was 0%. In contrast, lower burst index values were observed at 0.5%, 1.0%, and 1.5% DMDHEU ratios, except for the SPI+0.5% DMDHEU and WPI+1.5% DMDHEU coated papers. Notably, the WPI-coated paper with 1.5% DMDHEU addition exhibited a higher burst index value compared to the WPI-coated paper without DMDHEU.

The burst resistance values of papers coated with SPI biopolymer initially increased with the rise in DMDHEU content (0.5% DMDHEU), but then decreased. For papers coated with GG biopolymer, an increase in DMDHEU content (at 0.5% and 1% ratios) led to a decline in burst strength, followed by an increase with 1.5% DMDHEU. All WPI biopolymer-coated papers exhibited lower burst resistance values compared to the control. It was observed that SPI and GG biopolymer-coated papers demonstrated superior burst strength compared to both the control and WPI-coated papers.

Burst resistance, a key property for packaging materials, is defined as the maximum hydrostatic force that the paper can withstand before tearing<sup>6,65,30</sup> and serves as an indicator of the paper's resistance to tearing. The strong bond between fibers plays a crucial role in the tear and burst resistance of the paper. It is believed that the DMDHEU-added biopolymers used in this study enhance the fiber bonds, thereby contributing to an increase in the tear and burst resistance values of the paper.

Figure 3 illustrates the tear resistance values of all test papers. As shown in the figure, the tear resistance values of papers surface-coated with SPI and GG biopolymers (excluding WPI) were higher than those of the control samples across all DMDHEU ratios. Among the DMDHEU-added biopolymers, the highest tear resistance was observed in papers coated with GG+1.0% DMDHEU, while the lowest was recorded for WPI+0.5% DMDHEU-coated papers. It was observed that the comparison of the tear resistance values of the test papers did not reveal a significant difference with the increase in the DMDHEU ratio.

The tear resistance values of papers surface-coated with SPI biopolymer, unlike the others, showed a more pronounced decrease as the DMDHEU ratio increased to 1.5%.

The modification of wood-based products, such as veneer and paper, with DMDHEU results in reduced cell wall flexibility and increased brittleness.<sup>66,61</sup> This explains the moderate variations observed in the mechanical properties, as DMDHEU transforms fibers into a more brittle and rigid structure, despite efforts to enhance flexibility with glycerol. The cross-linking ability of DMDHEU and GG enables the formation of stronger cross-links, which accounts for the higher tear resistance values observed in papers coated with GG+DMDHEU.

## Physical properties

While polysaccharide and protein based biopolymer coatings have high barrier properties against carbon dioxide and oxygen, they have low moisture resistance and vapor barrier properties.<sup>67</sup> Improvements can be achieved by using plasticizers and active compounds to overcome these negative properties.<sup>8</sup> It is well known that due to its hydrophilic nature, paper is not resistant to water and water vapor. To reduce the hydrophilicity of paper packaging materials, some studies have focused on coating the paper surface with biopolymer materials.<sup>68</sup> It has been determined that the dewatering properties of papers produced from cross-linked chemical pulp were improved.<sup>69,70,71</sup> Korpella *et al.*<sup>71</sup> determined that cross-linking with mDMDHEU significantly enhanced the wet strength of the paper sheet, while reducing water absorption. The bonds formed within and between the fibers contribute to increased wet strength and reduced water absorbency of the paper. Therefore, DMDHEU, which has water-repellent properties, was used in this study.

Table 2 presents the water absorption values of papers coated with GG, SPI, and WPI biopolymer solutions containing DMDHEU. It has been determined that the water absorption capacity of the control papers decreases regularly depending on the increase in the DMDHEU ratio. The Cobb values of SPI, GG, and WPI biopolymer-coated papers without DMDHEU addition were found to be lower than those of the control paper. While the Cobb values of biopolymer-coated papers did not exhibit a consistent decrease with increasing DMDHEU ratios, they still showed improvement compared to the control paper. Suikkanen<sup>72</sup> and Korpela *et al.*<sup>73</sup> stated in their studies that cross-linking enhances the wet strength of paper, while reducing its water absorption.

It was observed that the water absorption value of papers coated with SPI biopolymer without DMDHEU gave the lowest Cobb value, compared to papers coated with other biopolymers, including the control. By adding 0.5% DMDHEU to the SPI coating, a 43.42% reduction in water absorption was achieved. According to Table 2, papers coated with GG and WPI biopolymers without DMDHEU had lower water absorption values than the control, but higher than those of SPI-coated papers.

The elevated Cobb values observed for GG coated papers can be attributed to the high water absorption capacity of the hydroxyl groups present in GG.<sup>74,63</sup> These groups form strong hydrogen bonds with hydrated molecules, preventing water loss from food products when hydrogel films are used.<sup>75,63</sup> In the Cobb test of GG coated papers, exhibited both absorptive and retentive properties, as water did not pass to the other side of the paper. As a result, GG coating films demonstrated poor barrier properties.<sup>32,76</sup>

In general, the water absorption values obtained for all biopolymers used in the study were lower than those of the control samples. The biopolymers used in the surface coating of kraft papers reduce the water absorption capacity of the paper. Based on the results, DMDHEU is more compatible with SPI biopolymer than with others, and the low water absorption values can be attributed to the effective bond formed between DMDHEU and SPI biopolymer.

Table 2  
Effects of DMDHEU-added SPI, GG, and WPI biopolymers as surface coating on Cobb value of kraft paper

| DMDHEU (%) | Cobb (g/m <sup>2</sup> ) |               |                |               |
|------------|--------------------------|---------------|----------------|---------------|
|            | Control                  | SPI           | GG             | WPI           |
| 0%         | 202.66 (8.38)*           | 81.30 (21.25) | 172.00 (6.93)  | 189.30 (1.9)  |
| 0.5%       | 188.00 (9.21)            | 46.00 (4)     | 200.00 (10.58) | 205.33 (2.30) |
| 1%         | 186.60 (2.38)            | 134.00 (3.83) | 178.60 (4.62)  | 154.00 (5)    |
| 1.5%       | 180.00 (5.65)            | 174.00 (8.33) | 176.00 (4)     | 186.60 (15.4) |

Note: In the preparation of biopolymer solutions, 3% for SPI, 0.5% for GG, and 6% for WPI were used;

\*Numbers in parentheses represent standard deviations

Table 3  
Effects of DMDHEU ratio on air resistance of test papers

| DMDHEU (%) | Air resistance (sn) |             |             |             |
|------------|---------------------|-------------|-------------|-------------|
|            | Control             | SPI         | GG          | WPI         |
| 0%         | 0.43 (0.02)*        | 0.66 (0.05) | 0.80 (0.12) | 0.43 (0.07) |
| 0.5%       | 0.45 (0.11)         | 0.56 (0.04) | 0.63 (0.04) | 0.50 (0.08) |
| 1%         | 0.46 (0.04)         | 0.50 (0.02) | 0.76 (0.06) | 0.53 (0.09) |
| 1.5%       | 0.46 (0.04)         | 0.50 (0.02) | 0.96 (0.12) | 0.50 (0.09) |

Note: In the preparation of biopolymer solutions, 3% for SPI, 0.5% for GG and 6% for WPI were used; \*Numbers in parentheses represent standard deviations

The air permeability values of the test papers are shown in Table 3. A comparison of the control papers with those coated with biopolymers but without DMDHEU additive revealed that papers coated with SPI and GG had higher air resistance values. Air resistance is influenced by the porosity of the paper, including the size, shape, distribution, and number of pores on the surface.<sup>77</sup> A reduction in air permeability indicates the closure or reduction of gaps or pores on the paper surface.<sup>11</sup> In control papers, a slight increase in air resistance was observed with the rising DMDHEU ratio. For biopolymer-coated papers, the increase in DMDHEU ratio led to a moderate decrease in air resistance for SPI-coated papers and an increase for GG-coated papers.

The air resistance values of WPI-coated papers (0.5%, 1%, and 1.5% DMDHEU) were higher than those of the control group with the corresponding DMDHEU ratios. However, this increase did not follow a linear pattern, instead fluctuating without significant differences. The highest air resistance value was recorded for papers coated with GG+1.5% DMDHEU.

Overall, the results indicate that kraft papers coated with SPI, GG, and WPI biopolymers positively impact air permeability, supporting their suitability for applications in the food packaging industry. highlighting SPI+0.5% DMDHEU, GG+1.5% DMDHEU, and WPI+1% DMDHEU as the papers with the most favorable performance.

### Scanning electron microscopy (SEM)

In order to investigate in detail any improvements in the papers coated with biopolymers, SEM images of the samples were examined.

Figure 4 shows the SEM images of control and coated papers with biopolymers at 100X and 250X magnifications. After examining the SEM images, it becomes apparent that, following the application of biopolymers onto the papers characterized by a surface composed of noticeably porous and interlaced cellulose fibers, a reduction in surface voids and an increase in surface density are observed. It can be seen from Figure 4 (c and f) that better results were obtained as a result of surface coating with GG+%0.5 DMDHEU.

In order to further examine the effect of GG surface coating, SEM images were also taken for samples coated without DMDHEU addition and compared with those coated with 0.5% DMDHEU addition (Fig. 5). Although the effect of GG is seen in both SEM images, it can be seen that for the samples with 0.5% DMDHEU addition, the gaps between the fibers are further reduced and the surface is covered densely, without gaps. This is thought to be related to the higher tensile strength of GG-coated papers compared to control papers. The patterns observed with the addition of DMDHEU are also similar.

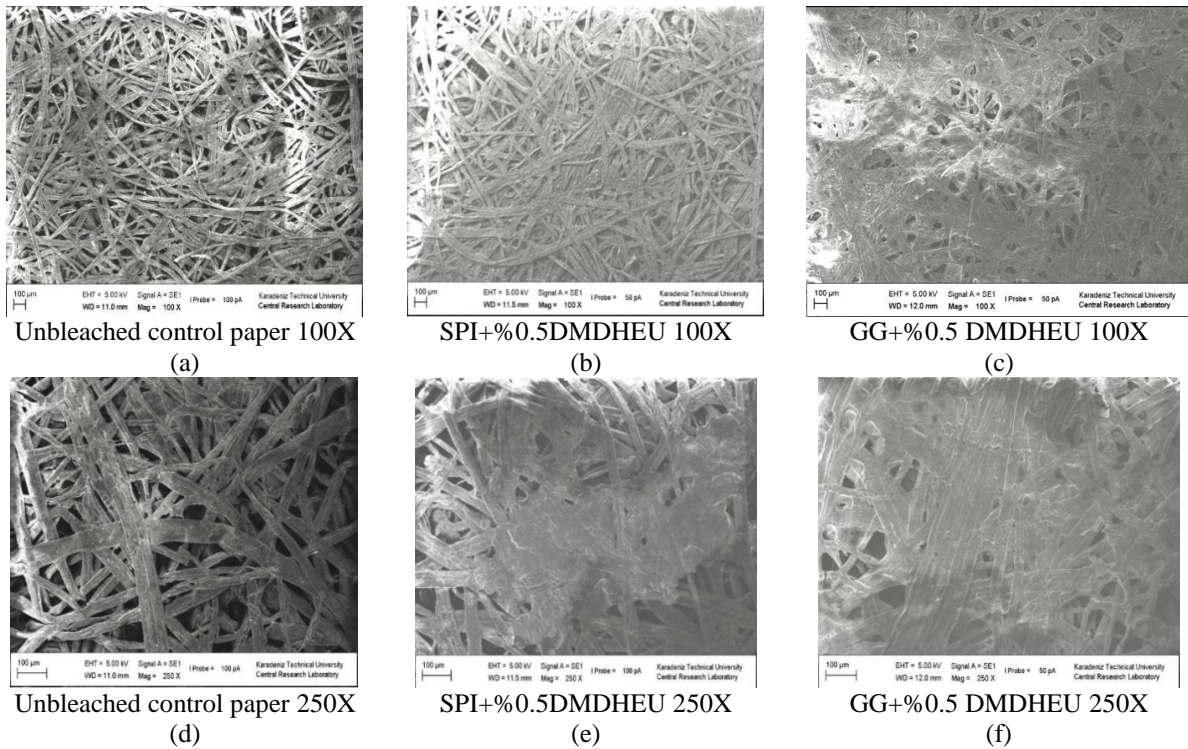


Figure 4: Scanning electron microscopy (SEM) images of unbleached kraft control papers at 100X (a) and 250X magnification (d); and those of papers coated with SPI+%0.5DMDHEU at 100X (b) and at 250X (e), with GG+%0.5 DMDHEU at 100X (c) and 250X (f)

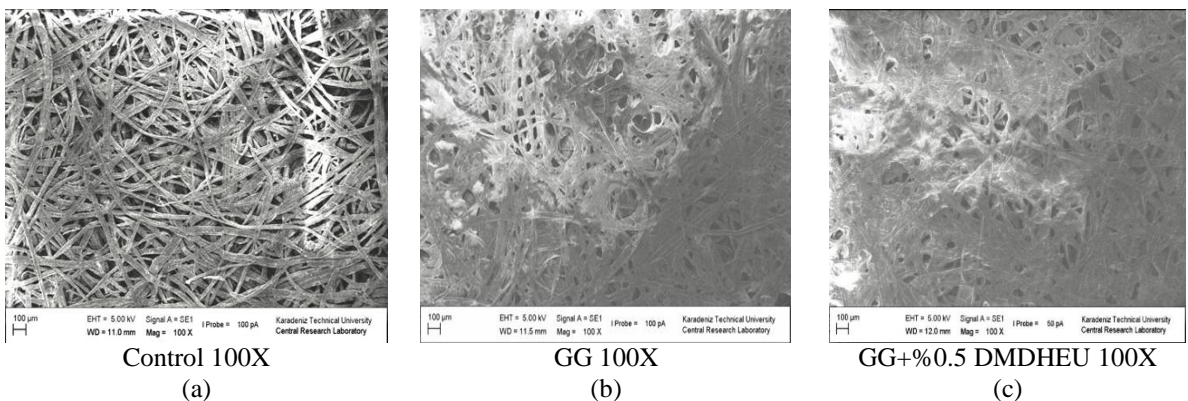


Figure 5: Scanning electron microscopy images (100X) of unbleached kraft control papers (a), GG coated papers (c) and GG+%0.5 DMDHEU coated papers

## CONCLUSION

The mechanical properties, water absorption, and air permeability resistance of papers coated with GG, SPI, and WPI biopolymers suggest their potential suitability for use in the packaging industry, depending on the specific application. Papers coated with GG and SPI biopolymers demonstrated improved tear resistance, while SPI-coated papers showed the lowest water absorption capacity. Additionally, GG-coated papers exhibited superior air resistance compared to other biopolymer-coated papers, with all biopolymer-coated papers surpassing the air resistance of the control sample. These findings represent a promising step toward advancing sustainability goals in the packaging industry.

## REFERENCES

- <sup>1</sup> S. Z. Popović, V. L. Lazić, N. M. Hromiš, D. Z. Šuput and S. N. Bulut, in “Biopolymers for Food Design”, edited by A. M. Grumezescu and A. M. Holban, Academic Press, 2018, pp. 223–277, <https://doi.org/10.1016/B978-0-12-811449-0.00008-6>
- <sup>2</sup> O. I. Şahin and A. A. Bayazit, *Türkiye 10. Gıda Kongresi*, Erzurum, Türkiye, 21-23 May, 2008
- <sup>3</sup> G. Davis and J. H. Song, *Ind. Crop. Prod.*, **23**, 147 (2006), <https://doi.org/10.1016/j.indcrop.2005.05.004>

- <sup>4</sup> İ. Çelik and G. Tümer, *Akademik Gıda*, **14**, 180 (2016)
- <sup>5</sup> M. G. Kontominas, *Foods*, **9**, 1440 (2020), <https://doi.org/10.3390/foods9101440>
- <sup>6</sup> P. K. Kunam, D. Ramakanth, K. Akhila and K. K. Gaikwad, *Biomass Convers. Biorefin.*, **14**, 1 (2022), <https://doi.org/10.1007/s13399-022-03241-2>
- <sup>7</sup> A. Kumar, R. K. Deshmukh and K. K. Gaikwad, *Biomass Convers. Biorefin.*, **14**, 6311 (2024), <https://doi.org/10.1007/s13399-022-02708-6>
- <sup>8</sup> V. K. Rastogi and P. Samyn, *Coatings*, **5**, 887 (2015), <https://doi.org/10.3390/coatings5040887>
- <sup>9</sup> P. Nechita and M. Roman, *Coatings*, **10**, 566 (2020), <https://doi.org/10.3390/coatings10060566>
- <sup>10</sup> B. Keskin, *PhD Thesis*, Gazi Üniversitesi, Fen Bilimleri Enstitüsü, Ankara, Kasım, 2020
- <sup>11</sup> S. Kopacic, A. Walzl, A. Zankel, E. Leitner and W. Bauer, *Coatings*, **8**, 235 (2018), <https://doi.org/10.3390/coatings8070235>
- <sup>12</sup> R. Battisti, N. Fronza, Á. V. Júnior, S. M. da Silveira, M. S. P. Damas *et al.*, *Food Packag. Shelf Life*, **11**, 115 (2017), <https://doi.org/10.1016/j.fpsl.2017.01.009>
- <sup>13</sup> H. T. Ong, H. Samsudin and H. Soto-Valdez, *Crit. Rev. Food Sci. Nutr.*, **62**, 957 (2022), <https://doi.org/10.1080/10408398.2020.1830747>
- <sup>14</sup> G. De Feo, C. Ferrara and F. Minichini, *J. Clean. Prod.*, **333**, 130158 (2022), <https://doi.org/10.1016/j.jclepro.2021.130158>
- <sup>15</sup> M. Mujtaba, J. Lipponen, M. Ojanen, S. Puttonen and H. Vaitinen, *Sci. Total Environ.*, **851**, 158328 (2022), <https://doi.org/10.1016/j.scitotenv.2022.158328>
- <sup>16</sup> N. Chausali, J. Saxena and R. Prasad, *J. Agric. Food Res.*, **7**, 100257 (2022), <https://doi.org/10.1016/j.jafr.2021.100257>
- <sup>17</sup> J. Nilsen-Nygaard, E. N. Fernández, T. Radusin, B. T. Rotabakk, J. Sarfraz *et al.*, *Compreh. Rev. Food Sci. Food Saf.*, **20**, 1333 (2021)
- <sup>18</sup> Y. Peng, J. Guo, Y. Gao, X. Li, M. Ni *et al.*, *Food Hydrocoll.*, **149**, 109624 (2024), <https://doi.org/10.1016/j.foodhyd.2023.109624>
- <sup>19</sup> M. R. N. Fazita, K. Jayaraman, D. Bhattacharyya, M. K. Mohamad Haafiz, C. K. Saurabh *et al.*, *Materials*, **9**, 435 (2016), <https://doi.org/10.3390/ma9060435>
- <sup>20</sup> L. Sun, J. Sun, L. Chen, P. Niu, X. Yang *et al.*, *Carbohydr. Polym.*, **163**, 81 (2017), <https://doi.org/10.1016/j.carbpol.2017.01.016>
- <sup>21</sup> S. Shankar and J. W. Rhim, in “Reference Module in Food Science”, Elsevier, 2018, vol. 1, pp. 1-10, <https://doi.org/10.1016/B978-0-08-100596-5.21875-1>
- <sup>22</sup> P. Marimuthu, *Quart. J. Indian Pulp Pap. Techn. Assoc.*, **35**, 119 (2023)
- <sup>23</sup> C. Ge, H. N. Cheng, N. Ribalko, C. A. Joshi and N. Strong, *Food Packag. Shelf Life*, **40**, 101222 (2023)
- <sup>24</sup> R. Chandra and R. Rustgi, *Progress Polym. Sci.*, **23**, 1273 (1998), [https://doi.org/10.1016/S0079-6700\(97\)00039-7](https://doi.org/10.1016/S0079-6700(97)00039-7)
- <sup>25</sup> H. Çelebi and S. Dehmen, *Sigma Mühendislik ve Fen Bilimleri Dergisi*, **31**, 53 (2013)
- <sup>26</sup> M. Çabuk, M. Yavuz and J. Hlaváč, *Erciyes Üniversitesi Fen Bilimleri Enstitüsü Fen Bilimleri Dergisi*, **27**, 247 (2011)
- <sup>27</sup> S. N. Syahida, M. R. Ismail-Fitry, Z. M. A. Ainun and Z. N. Hanani, *Food Packag. Shelf Life*, **28**, 100640 (2021)
- <sup>28</sup> L. Averous, in “Monomers, Polymers and Composites from Renewable Resources”, edited M. N. Belgacem and A. Gandini, Elsevier Ltd., 2008, pp. 433–450, <https://doi.org/10.1016/B978-0-08-045316-3.00021-1>
- <sup>29</sup> I. S. Tawakkal, M. J. Cran, J. Miltz and S. W. Bigger, *J. Food Sci.*, **79**, R1477 (2014), <https://doi.org/10.1111/1750-3841.12534>
- <sup>30</sup> M. OndaraL and E. E. Kalyoncu, *Bartın Orman Fakültesi Dergisi*, **26**, 46 (2024), <https://doi.org/10.24011/barofd.1381005>
- <sup>31</sup> J. Gómez-Estaca, R. Gavara, R. Catala and P. Hernández-Muñoz, *Packag. Technol. Sci.*, **29**, 203 (2016)
- <sup>32</sup> E. Tavassoli-Kafrani, M. V. Gamage, L. F. Dumée, L. Kong and S. Zhao, *Crit. Rev. Food Sci. Nutr.*, **62**, 2432 (2022), <https://doi.org/10.1080/10408398.2020.1853038>
- <sup>33</sup> H. Yadav, A. K. Prasad, P. Goswami, S. Pednekar, E. Haque *et al.*, Guar Industry Outlook 2015. Report made for National Commodity & Derivatives Exchange Limited, India, 2013
- <sup>34</sup> B. Sharma, A. Sandilya, U. Patel, A. Shukla and S. D. Sadhu, *Int. J. Adhes. Adhes.*, **110**, 102946 (2021), <https://doi.org/10.1016/j.ijadhadh.2021.102946>
- <sup>35</sup> H. Jooyandeh, *Pakistan J. Nutr.*, **10**, 296 (2011)
- <sup>36</sup> M. Schmid, S. Sänglerlaub, L. Wege and A. Stäbler, *Packag. Technol. Sci.*, **27**, 799 (2014), <https://doi.org/10.1002/pts.2071>
- <sup>37</sup> M. Walait, H. R. Mir and A. Anees, Natural Resources for Human Health, 2022, <https://doi.org/10.53365/nrfhh/149622>
- <sup>38</sup> K. Liu, “Soybean as Functional Foods and Ingredients”, AOCS Press, Champaign, Illinois, 2004, pp. 51-72

- <sup>39</sup> J. G. Endres, "Soy Protein Products: Characteristics, Nutritional Aspects, and Utilization", The American Oil Chemists Society, AOCS Press, Indiana, 2001
- <sup>40</sup> J. Duan, Q. Zhou, M. Fu, M. Cao, M. Jiang *et al.*, *Food Bioprocess Technol.*, **16**, 2443 (2023)
- <sup>41</sup> Z. Y. Karagöz, PhD Thesis, Ankara Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı, 2007
- <sup>42</sup> H. J. Park, S. H. Kim, S. T. Lim, D. H. Shin, S. Y. Choi *et al.*, *J. Am. Oil Chem. Soc.*, **77**, 269 (2000), <https://doi.org/10.1007/s11746-000-0044-2>
- <sup>43</sup> A. H. Brandenburg, C. L. Weller and R. F. Testin, *J. Food Sci.*, **58**, 1086 (1993), <https://doi.org/10.1111/j.1365-2621.1993.tb06120.x>
- <sup>44</sup> P. Navi and D. Sandberg, "Thermo-Hydro-Mechanical Processing of Wood", CRC Press, Taylor and Francis Group, LLC, USA, 2012
- <sup>45</sup> W. J. Homan and A. J. Jorissen, *Heron*, **49**, 361 (2004)
- <sup>46</sup> J. Wang, K. Fang, X. Liu, S. Zhang, X. Qiao *et al.*, *Ind. Crop. Prod.*, **200**, 116831 (2023), <https://doi.org/10.1016/j.indcrop.2013.116831>
- <sup>47</sup> H. Militz, *Wood Sci. Technol.*, **27**, 347 (1993)
- <sup>48</sup> Y. Xie, A. Krause, H. Militz and C. Mai, *Progress Org. Coat.*, **57**, 291 (2006), <https://doi.org/10.1016/j.porgcoat.2006.06.010>
- <sup>49</sup> A. Pfeffer, C. Mai and H. Militz, *Eur. J. Wood Wood Prod.*, **70**, 165 (2012), <https://doi.org/10.1007/s00107-011-0520-8>
- <sup>50</sup> M. Çiçekler, A. Tutuş and N. Kızılbağlı, in *Procs. 1<sup>st</sup> International Mediterranean Science and Engineering Congress (IMSEC 2016)*, Adana/Turkey, October 26-28, 2016, pp. 586-590
- <sup>51</sup> Tappi T 205 sp-12, Forming Handsheets for Physical Tests of Pulp, 2018
- <sup>52</sup> Tappi T 402 om-93, Standard Conditioning and Testing Atmospheres For Paper, Board, Pulp Handsheets, and Related Products, Tappi Press, Atlanta, 1993
- <sup>53</sup> S. Li, E. Donner, H. Xiao, M. Thompson, Y. Zhang *et al.*, *Mater. Sci. Eng. C*, **69**, 947 (2016), <https://doi.org/10.1016/j.msec.2016.07.079>
- <sup>54</sup> H. Jiang, W. Zhang, L. Chen, J. Liu, J. Cao *et al.*, *Food Hydrocoll.*, **136**, 108278 (2023), <https://doi.org/10.1016/j.foodhyd.2022.108278>
- <sup>55</sup> S. G. Zavareh, M. J. Dakheli and B. Tajeddin, *Food Sci. Nutr.*, **9**, 6762 (2021)
- <sup>56</sup> Tappi 494 om-13, Tensile Breaking Strength and Elongation of Paper and Paperboard (using pendulum-type tester) Tappi Test Methods, Tappi Press, Atlanta, 2013
- <sup>57</sup> Tappi 403 om-15, Bursting Strength of Paper, Tappi Test Methods, Tappi Press, Atlanta, 2015
- <sup>58</sup> Tappi 414 om-21, Internal Tearing Resistance of Paper (Elmendorf-type method), Tappi Test Methods, Tappi Press, Atlanta, 2021
- <sup>59</sup> Tappi T 441 om-20, Water Absorptiveness of Sized (Non-Bibulous) Paper, Paperboard, and Corrugated Fiberboard (Cobb Test), Tappi Press, Atlanta, 2020
- <sup>60</sup> Tappi T 460 om-21, Air Resistance of Paper (Gurley Method), Tappi Press, Atlanta, 2021
- <sup>61</sup> R. Hosseinpourpia, S. Adamopoulos and C. Mai, *J. Appl. Polym. Sci.*, **132**, (2015), <https://doi.org/10.1002/app.41290>
- <sup>62</sup> N. Suderman, M. I. N. Isa and N. M. Sarbon, *Food Biosci.*, **24**, 111 (2018), <https://doi.org/10.1016/j.fbio.2018.06.006>
- <sup>63</sup> S. Sudheer, S. Bandyopadhyaya and R. Bhat, *Int. J. Biol. Macromol.*, **248**, 125845 (2023), <https://doi.org/10.1016/j.ijbiomac.2023.125845>
- <sup>64</sup> A. Khoddami, O. Avinc and F. Ghahremanzadeh, *Progress Org. Coat.*, **72**, 299 (2011), <https://doi.org/10.1016/j.porgcoat.2011.04.020>
- <sup>65</sup> A. Bayatkashkoli, *J. Indian Acad. Wood Sci.*, **10**, 55 (2013)
- <sup>66</sup> Y. Xie, A. Krause, H. Militz, H. Turkulin, K. Richter *et al.*, *Holzforschung*, **59**, 484 (2007), <https://doi.org/10.1515/HF.2007.008>
- <sup>67</sup> A. Adibi, B. M. Trinh and T. H. Mekonnen, *Progress Org. Coat.*, **181**, 107566 (2023), <https://doi.org/10.1016/j.porgcoat.2023.107566>
- <sup>68</sup> Q. Li, S. Wang, X. Jin, C. Huang and Z. Xiang, *Polymers*, **12**, 1837 (2020), <https://doi.org/10.3390/polym12081837>
- <sup>69</sup> P. H. Westervelt and C. Elston, *Nonwovens Conference, TAPPI Proceeding*, Atlanta, GA, USA, 1995, pp. 69-72
- <sup>70</sup> A. Korpela and A. Tanaka, *Japan TAPPI J.*, **69**, 747 (2015), <https://doi.org/10.2524/jtappij.1505>
- <sup>71</sup> A. Korpela, A. Tanaka and A. W. King, *BioResources*, **18**, 937 (2023), <https://doi.org/10.15376/biores.18.1.937-948>
- <sup>72</sup> T. Suikkanen, Master's Thesis, Lappeenranta University of Technology, Finland, 2015

- <sup>73</sup> A. Korpela, A. Tanaka and J. Asikainen, *BioResources*, **18**, 6336 (2023), <https://doi.org/10.15376/biores.18.3.6336-6347>
- <sup>74</sup> S. Oprea, *Compos. Part B*, **44** (1) 76–83, (2013), <https://doi.org/10.1016/j.compositesb.2012.07.018>.
- <sup>75</sup> S. Thakur, B. Sharma, A. Verma, J. Chaudhary, S. Tamulevicius, *et al.*, *Int. J. Polym. Anal. Charact.*, **23**, 621 (2018), <https://doi.org/10.1080/1023666X.2018.1488661>
- <sup>76</sup> H. Jiang, W. Zhang, L. Chen, J. Liu, J. Cao *et al.*, *Food Hydrocoll.*, **136**, 108278 (2023), <https://doi.org/10.1016/j.foodhyd.2022.108278>
- <sup>77</sup> L. Pal, M. K. Joyce and P. D. Fleming, *TAPPI J.*, **5**, 10 (2006)