



Effect of Chitosan and Rice Starch Coating on the Kraft Paper

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Abstract: The use of chitosan and rice starch as the bio-based coated paper has resulted in a positive effect on physical, mechanical, and optical properties. The research was to show the influence of ultrasonic treatment on the properties of bio-based coated paper. The influence of ultrasonic treatment on the kraft paper with coating solution was determined for the thickness, the tensile strength, and surface morphology analysis. The sample prepared has two types which are uncoated paper coated paper and coated with ultrasonic treatment paper. The coated paper with bio-based coatings has been applied by spray technique. One from both coated samples has been coated with a solution that has been treated. The result shows that the thickness and grammage for both coated papers increased between 0.01 mm to 0.03 mm. Tensile strength has been improved on both coated papers. The higher tensile strength obtained was from the sample in the machine direction, which is 8083.2 N/m. Furthermore, the ultrasonic treatment also gives an improvement in morphology. As expected, the coating gives a surface with fewer and smaller pores. From morphology analysis, the coated paper in which the solution has been treated was smoother, and few pores were detected. From the result, ultrasonic treatment is an environmentally inexpensive process and effective in preparing solutions for bio-based coating. The coatings give better mechanical and morphology properties. Therefore, preparation solution using ultrasonic treatment as pretreatment is an improvement to enhance many properties of bio-based coatings.

Keywords: Coatings, chitosan, rice starch, ultrasonic treatment

1. Introduction

In recent years, the materials that have been utilised in the packaging of products like fruits and vegetables have improved, enabling the development of recyclable packaging from the trash. Consequently, bio-based material makers are motivated to replace oil-based packaging materials with more environmentally friendly alternatives [1, 2].

Kraft paper with high elasticity and resistance to wear [3] is used to manufacture products that require high strength and durability. This sort of paper can be utilised for various purposes, including food packaging, grain bags, and sometimes even cement. Due to the coating application on Kraft paper, such products have added value and improved particular qualities, mainly varying depending on the coating utilised. The coating technique was used to generate the required parameters for the specific packaging while not degrading the qualities that were already present. Polysaccharides are among the natural coating polymers most widely employed in all disciplines of material science and packaging, including food packaging.

Chitosan was shown to be one of the least harmful products generated from the deacetylation of chitin [4]. Chitosan as edible films and coatings have piqued the interest of packaging designers, particularly in the food packaging industry [5, 6]. Because of its excellent barrier properties, chitosan coating can be adopted as a barrier packaging material. Because of its high crystallinity and the presence of a hydrogen link between molecular chains, chitosan exhibits exceptional oxygen characteristics. As a result of the positive charge on the amino group of chitosan, it attracts negatively-charged molecules when exposed to acidic environments. Because of this, it provides a more robust barrier against grease [6].

A coating of chitosan and rice-based biopolymer is applied to Kraft paper to improve the paper's mechanical properties by adding a polymer layer. Previous research has demonstrated that by adding rice starch into chitosan film, Bourtoom and Chinna were able to boost the effect of rice starch considerably. The composite film displayed an increase in strength [7]. This research aimed to determine whether ultrasonic treatment might be used to enhance the mechanical and morphology properties of a bio-based coating on packing paper, and the results were promising.

In recent years, the materials used to package commodities such as fruits and vegetables have improved, allowing the development of waste-free packaging. As a result, manufacturers of bio-based materials are eager to phase out oil-based packaging materials in favour of more sustainable alternatives [1, 2].

Kraft paper is used for products that require a high degree of strength and durability [3]. This paper is suitable for packaging food, grain, and even cement. Coating such items on Kraft paper adds value and improves specific qualities, depending on the coating applied. The coating approach was utilised to produce the conditions necessary for specific packaging without impairing the inherent qualities. Polysaccharides are a class of natural coating polymers frequently employed in material science and packaging.

Chitosan was one of the least hazardous chitin deacetylation products [4]. Chitosan has aroused interest in packaging, particularly food packaging, as an edible film and coating [5, 6]. Chitosan coatings can be utilised as barrier packaging due to their excellent qualities. Chitosan has exceptional oxygen characteristics because of its high crystallinity and the presence of a hydrogen link between the molecular chains. Due to the positive charge on the amino group. As a result, it acts as a more effective grease barrier [6].

To improve the mechanical qualities of Kraft paper, it is coated with a bio-based coating comprised of chitosan and rice. A previous study has established the effect of rice starch, which was integrated into Bourtoom and Chinnan's chitosan film. The composite film's tensile strength rose [7]. The researchers aimed to improve the mechanical and optical qualities of the bio-based coating on packing paper by applying an ultrasonic treatment.

2.0 Experimental

2.1 Preparation of Coating Solution using Ultrasonic Treatment

The rice starch solution was made by dissolving 5 g of rice in 100 mL of distilled water and then filtering the solution. The solution was stirred until it was gelatinised at 90 degrees Celsius for 5 minutes after being cooled to 27 degrees Celsius. The chitosan solution was made by dissolving 3 g of chitosan in 100 mL of malic acid before filtering the solution. Making the rice starch-chitosan solution was as simple as combining one hundred millilitres of three per cent rice starch solution with one hundred millilitres of three per cent chitosan solution. After that, one solution was immersed in an ultrasonic bath for 15 minutes at a continuous 35 kHz frequency for the next 15 minutes. Following the ultrasound treatment, the solutions were allowed into the bath for an additional 15 minutes to cool.

2.2 Coatings on Kraft Paper

After preparing the solutions, the kraft paper was ultrasonically treated. The coating solution was sprayed onto the substrate (kraft paper) with the gun. Ultrasonic treatment was used to treat parts of the kraft paper coated with rice-starch chitosan solution, while others remained untreated. It was then dried for ten minutes at 80 degrees Celsius. Five solutions were put on each paper. This study analysed both uncoated and coated sheets for comparability.

2.3 Characterisation of Kraft Paper

2.3.1 Analysis of Grammage, Thickness, Density, and Specific Surface Volume

Grammage was measured to ensure that each sample had the same quantity of coating. The ASTM D646-96 standard assessed the grammage by weighing five samples of each paper cut to size 10 10 cm. At three random spots on each paper, the thickness of samples was measured using a precision digital micrometre machine. The material's density and specific surface volume were determined using the grammage and thickness.

2.3.2 Mechanical Properties Analysis

A tensile test machine was used to determine the tensile strength of papers. The cross-speed head moved at a rate of 0.15 mm/s. Paper stripes with a length of 18 cm and a width of 1.5 cm were utilised, and a minimum of five specimens in the machine direction (M.D.) and cross-machine direction (CD) were tested for each sample. Following the measurement, the tensile strength was evaluated.

2.3.3 Morphology Properties of Kraft Paper

The micrographs of paper were analysed with advanced optical microscopy. The equipment was set to a magnification of 20.

3.0 Results and Discussions

One of the most significant challenges related to ultrasonic treatment is regulating the interaction between polymers compared to the process without chemical modification [13]. It was discovered in a prior study [17, 18] that ultrasonic treatment of starch solution increases solubility and clarity while decreasing viscosity. There is a relationship between the properties of coated paper and the properties of kraft paper. The perfect forming might result in producing coated paper of high grade. It is also necessary for the paper to have some porosity. The paper utilised in this study was coated for only one layer. The results demonstrate that the changing amount of coating was employed due to a slight error during the coating process, which was discovered throughout the investigation.

3.1 Thickness of Kraft Paper

The grammage had to affect the physical and optical properties the thickness also affects the tensile strength and optical properties. A thickness test was performed to ascertain the thickness and quality of uncoated, coated, and coated with treatment kraft paper.

The thickness of five specimens for each condition is depicted in Fig 1. The value is 0.1715 mm for uncoated paper in the cross-machine direction and 0.1763 mm for uncoated paper in the machine direction. Then, the value is 0.1986 mm for coated paper in the cross-machine direction and 0.2057 mm for coated paper in the machine direction. Finally, the coated with ultrasonic treatment values in cross-machine direction paper are 0.2201 mm, while they are 0.2985 mm for coated with ultrasonic treatment in machine direction paper.

As the paper was covered, its thickness increased. The chitosan molecules overlapped and entwined in a network structure, forming a dense chitosan layer on the paper's surface [19].

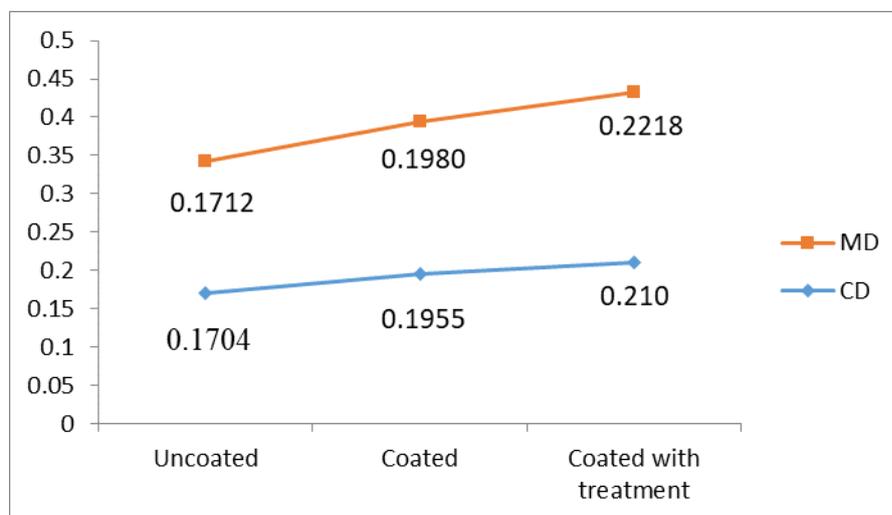


Fig. 1 - Thickness (mm) of uncoated, coated and coated with treated paper

The analysis and attributes of uncoated, coated, and coated with ultrasonic treatment are shown in Table 1. Five bio-based coatings are recommended for coated paper in this table. When handling a spray for coating, an

inaccuracy resulted in a varied value of bio-based coated paper. An error resulted in a discrepancy in the distance between the coating spray gun and the sample's surface. Luangkurlab et al. (2014) researched spray coating material usage and dry film thickness. The spray gun's position must be taken into account, as it significantly affects the coating thickness.

Table 1 - Determination of grammage, density and specific surface volume of uncoated, coated and coated with treatment

Sample	Grammage (gm^{-2})	Density (gm^{-3})	Specific surface volume ($\text{m}^3 \text{g}^{-1}$)
Uncoated (CD)	125	73.43	0.00136
Uncoated (MD)	125	73.09	0.00137
Coated (CD)	129	66.05	0.00152
Coated (MD)	131	66.23	0.00151
Coated with treatment (CD)	130	61.88	0.00162
Coated with treatment (MD)	132	59.57	0.00168

The grammage test was then used to determine the weight of the paper sample per unit area. The mass of a unit area of the paper is determined using a specific test procedure. A grammage is a measurement unit represented in grammes per square metre (gsm). The area of the sample used in this study was 0.01 for five specimens.

The grammage produced for the untreated paper was 125 gsm, as reported in Table 1, which corresponds to the standard for kraft paper used in this investigation. Dependent on fibre-fibre bonding, the strength qualities of dry and free-additive paper are approximately proportional to the material's grammage [20]. The grammage of both coated sheets increases as a result of the coating. The sample with the highest grammage and thickness was coated.

3.2 Paper Weight Measurement

The entire specimen for each sample weight was measured before the entire test on the sample was conducted. The weight of the specimen varies significantly between samples, as shown in Table 2.

The weight obtained for uncoated paper in both directions was 1.25 grammes. As the paper was coated, the weight increased. The weight of coated paper in the machine and cross-machine directions was 1.29 gramme and 1.31 gramme, respectively, while the weight of coated paper with ultrasonic treatment was 1.30 gramme and 1.29 gramme.

It is possible to conclude that the paperweight increased as the paper was coated. The weight of the paper coating increases due to the creation of a large smoothing layer, which results in a small percentage of missing dots. Because of the improved compressibility of the paper, this percentage is decreasing in papers coated with particles with a higher aspect ratio [21].

Table 2 - Weight for each sample (mm)

Sample	CD	MD
Uncoated	1.25	1.25
Coated	1.29	1.31
Coated with treated	1.30	1.29

*CD: Cross machine direction

MD: Machine direction

3.3 Mechanical Properties

The size of the sample, the temperature, and the coatings all affect the test findings. Tensile strength and elongation at break are critical properties for packing materials. The handling and shipping of product specification paper are dependent on the sheet's degree of bonding, with tiny fibre breakage occurring with a higher degree of bonding [22-24]. Tensile characteristics can be enhanced in various ways by the use of a coating. Facilitates the development of fibre linkages in the coating, which can increase the flexibility of the paper.

Tensile strength is shown in Fig 2 for five samples of each condition. The uncoated sample has a maximum strength of 6337.33 N/m in the cross-machine direction and a minimum strength of 6087.33 N/m. Then, in the machine direction, the highest strength for uncoated paper is 7167.33 N/m, while the lowest is 6398.67 N/m.

The coated sample has a maximum strength of 8378.0 N/m and a minimum strength of 7106.0 N/m in the cross-machine direction. Then, in the machine direction, the highest strength is 8736.67 N/m, and the lowest is 6950.0 N/m for coated paper. It can be concluded that after coating, the tensile strength increases.

Bourtoom & Chinnan investigated the effects of chitosan on a biodegradable coating solution derived from rice starch (2008). After integrating chitosan, biodegradable rice starch coatings solution demonstrated increased tensile strength. Although the addition of chitosan improves the crystalline peak of the structure coatings solution, phase separation between the starch and chitosan might occur at excessive chitosan concentrations.

Finally, the highest strength value for coated with treatment samples in the cross-machine direction is 7614.67 N/m, while the lowest is 6829.33 N/m. The highest strength is 7920.0 N/m when coated with the treated sample in the machine direction, while the lowest is 6578.67 N/m.

As a consequence of the results, it can be concluded that the coated sample's tensile strength is greater than the coated sample's tensile strength after ultrasonic treatment. These occur during the coating process, when solvent penetration and coating material are absorbed into the cellulose structure of the paper, interfering with fibre-to-fibre interaction [25].

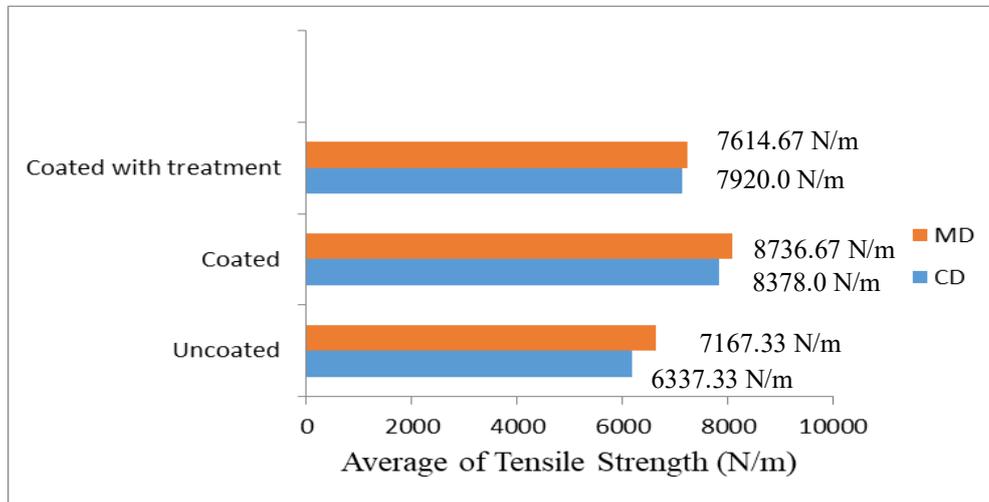


Fig. 2 - Tensile strength for uncoated, coated, and coated with treated paper

Due to the difference in the coating, there is a difference in the tensile strength of different sheets. Kraft paper is manufactured using the sulphate method, primarily utilised in the packaging industry [26]. As expected, the tensile strength dropped slightly in the machine direction for both coated sheets. Coatings have been shown to reduce tensile strength and enhance elasticity [26, 27]. This is due to the coating material's interface with the fibres' molecular interactions [28].

In contrast to the obtained result, the tensile strength in the M.D. direction was higher, 8083.2 N/m, than in the CD direction, 7224.80 N/m. According to Petri Penttinen (2012), the tensile strength of paper is direction-dependent. The tensile strength of paper is more significant in the machine direction due to fibre production, and the fibre bonding is more robust than in the cross-machine direction.

In general, coated or uncoated papers are less flexible in the M.D. direction when subjected to a particular load. Nonetheless, papers are more extensible and less rigid in the CD direction, with a more excellent elongation at the break. However, it has been demonstrated that the coating weight, base structure, additional plasticiser, and coating polymers are mainly reliant on the tensile properties of bio-based coated sheets [29-32].

3.4 Surface Morphology Analysis

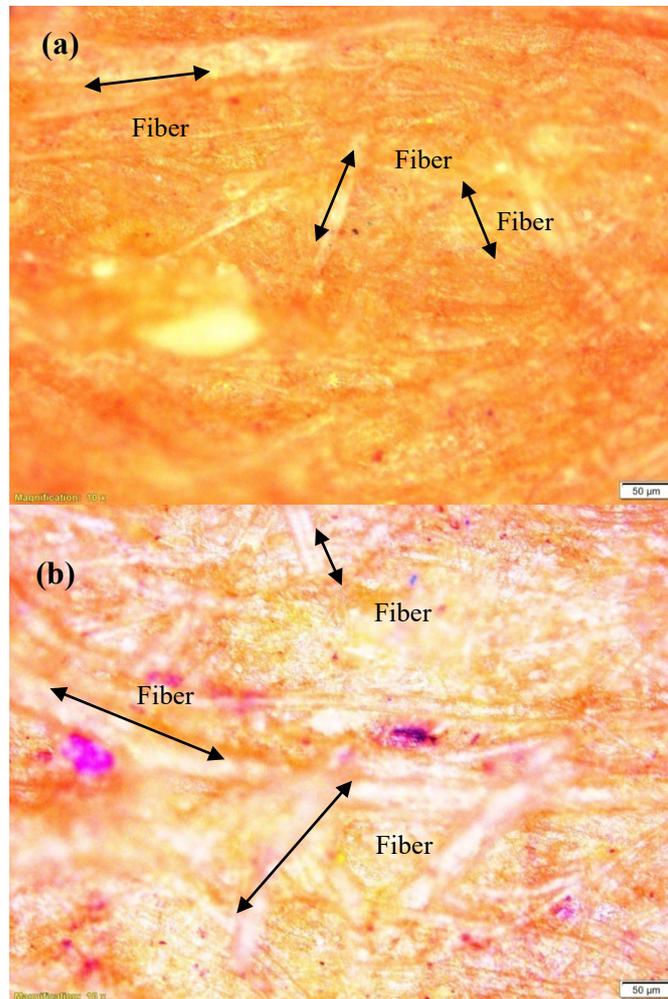
An optical microscope was used to determine the surface morphology of three samples: untreated paper, coated paper, and ultrasonic treatment paper. Using an optical microscope, it is possible to detect that the surface of the uncoated paper is less smooth than that of both coated samples. The microstructure images in Fig-3 and Fig-4 below show the sample untreated, coated, and coated with ultrasonic treatment in both cross-machine directions (CD) and machine direction (M.D.).

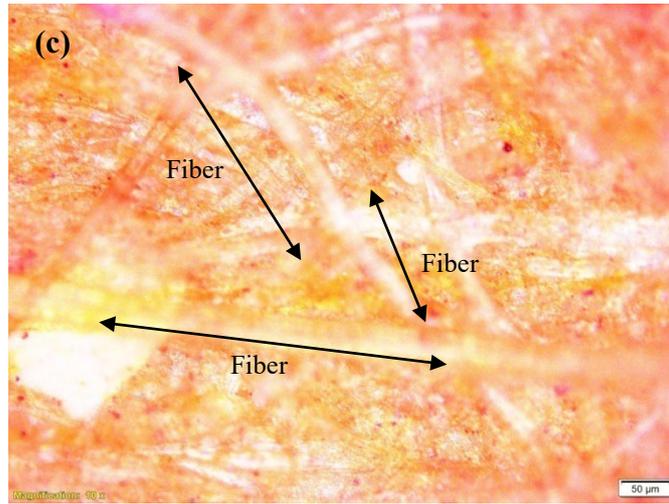
Each micrograph depicts the paper surface at a magnification of 20. The micrograph reveals a rougher and less smooth surface for the uncoated surface (Fig.3a, Fig.4a). Then, a smoother and more equal surface was revealed for coated paper surfaces (Fig. 3b, 4b). This is more noticeable on the surface of coated paper treated with ultrasound (Fig.3c, Fig.4c). It is well established that ultrasonic treatment increased dispersion capacity, defined as the amount of free mobile macromolecules in rice starch, promoting chain-to-chain interaction [33].

Dai & Long (2011) conducted a previous study investigating water-soluble chitosan derivatives utilised to enhance the performance of coated paper. Kraft paper has a rough surface where fibres cross and generate numerous pores. During the coating process, microporous pores were filled with rice-starch chitosan, and a layer of rice-starch chitosan film was created on the uncoated paper.

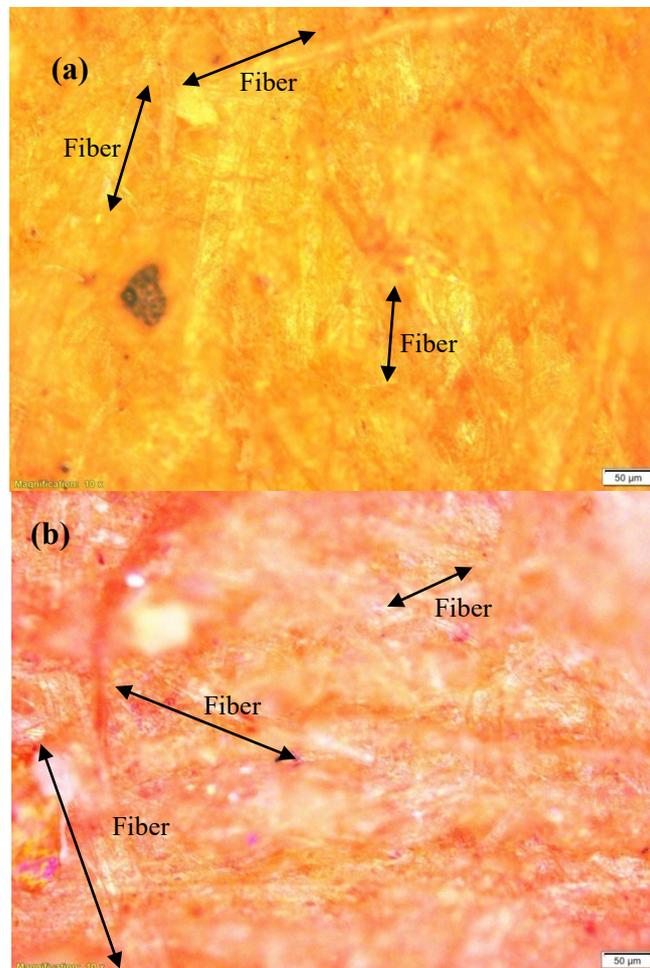
The improved surface distribution caused by the reduction of pores on the surface affects the ultrasonic treatment in the coating solution. A bio-based coating creates a denser structure on the surface, increasing the barrier to water vapour molecules flowing through.

The increased mechanical properties of coated paper were demonstrated by comparing both coated micrographs in both orientations. The thickness, moisture content, and roughness of the uncoated paper all significantly affect the coatings' qualities.





**Fig. 3 - Surface Morphology of uncoated and coated Kraft paper for cross-machine direction:
a) uncoated; b) coated; c) coated with treated**



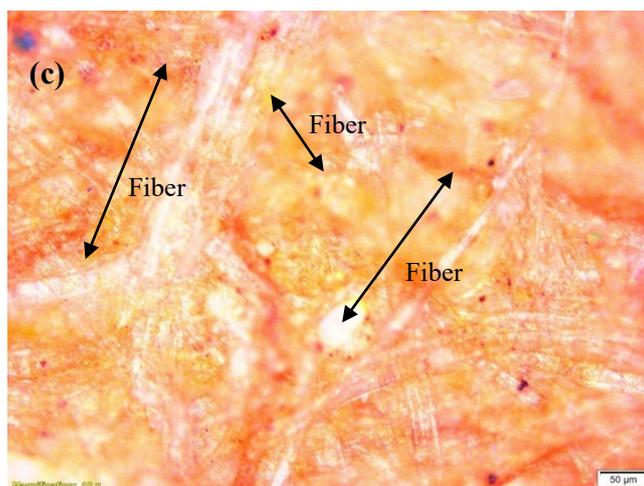


Fig. 4 - Surface Morphology of uncoated and coated kraft paper for machine direction: (a) uncoated; (b) coated; (c) coated with treated

4. Conclusions

In conclusion, a bio-based coating of chitosan and rice starch was coated on Kraft paper to improve its mechanical qualities. Additionally, because chitosan coating has excellent barrier features such as grease, mechanical resistance, and antibacterial properties, it is well suited for usage as a barrier in packing. When exposed to acid, the positive charge between amino groups causes chitosan to bind negatively-charged molecules, resulting in good barrier characteristics. The optical microscope revealed the coating that altered the surface, resulting in smaller and fewer holes and increased surface smoothness. It has been demonstrated that ultrasonic therapy has a more significant influence on the coating than physical, mechanical, or visible surface treatment. According to the tests conducted, the grammage achieved is relatively similar, approximately 125 for untreated paper and around 129 to 132 for coated paper with a coating of 5. The paper's thickness also increases because of the coating. According to the results of the tensile tests, the coating and ultrasonic treatment influenced the average tensile strength of the paper. The treated coated paper has a lower tensile strength than coated paper. The coated paper in M.D. has a greater tensile strength of 8083.2 N/m.

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