AIMS Materials Science, 12(4): 755–774.
DOI: 10.3934/matersci.2025033
Received: 24 May 2025
Revised: 29 July 2025
Accepted: 31 July 2025
Published: 06 August 2025

http://www.aimspress.com/journal/Materials

Research article

Developing eco-friendly coatings from natural materials for water-repellent and antimicrobial kraft paper

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Abstract: Moisture can lead to microbiological growth in paper packaging, which is commonly used in the packaging industry. To enhance its performance, especially in corrugated board for food packaging, microbial growth inhibition is crucial. This research focused on coating kraft paper with three natural components: chitosan (CS)-mixed styrene-acrylate resin, carvacrol (CAR)-mixed styrene-acrylate resin, and CS and CAR-mixed styrene-acrylate resin. The objective was to evaluate the coating's physical and mechanical properties, moisture level, and water resistance, as well as its antimicrobial effectiveness. A central composite design (CCD) with a D-optimal design was employed to determine the optimal coating composition. The results revealed that kraft paper coated with CS demonstrated better water resistance than CAR, while the mixture of CS and CAR showed the lowest water resistance. Microbial analysis demonstrated a reduction in total plate count from 240 CFU/g in uncoated kraft paper to 150 CFU/g with CS coating, further decreasing to 30 CFU/g with CAR coating. Antimicrobial resistance revealed that kraft paper coated with CAR demonstrated the strongest antimicrobial activity, while chitosan provided superior water repellency. The combination of both CS and CAR, mixed with resin, offered a balanced barrier against moisture and microbial contamination.

Keywords: antibacterial properties; carvacrol; chitosan; coating on kraft paper; water-repellent

1. Introduction

Paper is widely used in the packaging industry for various applications. Kraft paper is a type of paper produced through the kraft pulping process, in which wood chips are chemically treated with sodium hydroxide and sodium sulfide to break down lignin and extract long cellulose fibers. This method results in a paper product that is stronger and more durable than paper made using conventional mechanical pulping techniques due to its high tensile strength, tear resistance, and biodegradability. Kraft paper is commonly used in corrugated boxes, wrapping paper, food packaging, envelopes, and industrial liners. Its natural brown appearance, combined with the ability to be recycled and composted, makes it an attractive option in the growing market of sustainable and eco-friendly packaging solutions [1]. However, one of the challenging factors in paper packaging is its performance in humid environments, which directly poses a significant problem and affects its quality.

As a natural material, kraft paper can absorb moisture from the atmosphere. The moisture content increases and the paper becomes more prone to swelling, weakening its mechanical structure and leading to the loss of barrier properties, particularly against water, vapor, grease, and gases [2]. The primary component of paper is cellulose, which is hydrophilic in nature. This increases the limitations against water and moisture. In wet or humid conditions, paper loses its strength and becomes more susceptible to microbial growth [3]. Paper packaging, particularly kraft paper, plays a crucial role in ensuring food safety and preserving product quality. However, bacteria commonly found in kraft paper packaging, especially when in contact with food, can grow under specific conditions of humidity, temperature, and the presence of essential nutrients, leading to food contamination. Studies have identified spore-forming *Bacillus* species, the pathogenic Gram-positive bacterium *Staphylococcus aureus*, and the Gram-negative bacterium *Escherichia coli*, which is known to cause diarrhea, as prominent contaminants in paper-based and corrugated materials [4]. Currently, the issue has been solved by coating paper or corrugated paper with plastic films such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS). Although plastic coatings improve water resistance, they contribute significantly to environmental waste due to their non-biodegradable nature [5]. The increasing demand for sustainable and biodegradable food packaging materials has led researchers to investigate various bio-based polymers and natural additives. Among these, polybutylene adipate-co-terephthalate (PBAT) composites have attracted considerable attention. Recent studies have demonstrated that the incorporation of carbon nanoparticles, lignin–TiO_2 nanoparticles, and bio-based cross-linkers such as gallic acid [6] into PBAT matrices can significantly enhance their mechanical properties, barrier performance, and biological activity. These advancements highlight the potential of functionalized biodegradable polymers for next-generation food packaging applications. Most of these studies focus on fully polymer-based films, which often require industrial processing and are less compatible with paper substrates.

The application of natural materials, particularly biopolymers, as coatings for paper is an effective method to improve barrier properties and functional characteristics [7]. Natural bioactive compounds such as chitosan (CS) and carvacrol (CAR) offer a promising alternative for coating-based functionalization of paper. CS, a deacetylated derivative of chitin, has been widely studied for its excellent film-forming ability, biodegradability, and broad-spectrum antimicrobial activity. It has been successfully applied in food packaging to extend shelf life and inhibit microbial spoilage. These coatings are especially suitable for food packaging. Among the most promising and readily available

natural materials are CS, CAR, and water-based styrene-acrylic resin coatings [8]. Both CS and CAR are natural compounds.

Chitosan, a derivative of chitin found in the shells of aquatic animals such as shrimp and crabs, is the second most abundant biopolymer in nature after cellulose. It is produced through the deacetylation process, which removes acetyl groups from chitin to yield low-acetyl chitosan. These are obtained by immersing the chitin in a strong alkaline solution, chemically known as poly [β-(1→4)-2-amino-2-deoxy-D-glucopyranose]. This is essentially a modified form of chitin, where some of the acetyl groups ($–COCH_3$) on the chitin molecule have been removed, exposing free amino groups ($–NH_2$). It is a polymer that is insoluble in almost all organic solvents and water with neutral pH or alkaline, but is soluble in weak acids. The chemical structure of chitosan as poly-β-(1,4)-2-amino-2-deoxy-D-glucose is shown in Figure 1a. Chitosan exhibits excellent film and fiber-forming properties, low oxygen permeability, and enhanced mechanical strength. It resists tearing, serves as a barrier to gases and fats, and effectively inhibits bacterial growth, thereby extending product shelf life [9]. It has been successfully applied in food packaging to extend shelf life and inhibit microbial spoilage. The developed chitosan-based films blended with tannic acid and *Moringa oleifera* have showed significant efficacy in preserving strawberries, underscoring the effectiveness of natural bioactive agents in prolonging fruit freshness and inhibiting microbial growth [10].

Oregano (*Origanum spp.*) is a medicinal plant that contains a large amount of phenolic compounds from the groups carvacrol and thymol. Oregano essential oils (OEO) have shown the ability to inhibit bacterial growth [11]. The chemical structure of carvacrol [2-methyl-5-(propan-2-yl) phenol or 5-isopropyl-2-methylphenol] is organized as a structural isomer of thymol, which has the same atomic composition but different arrangements of groups on the benzene ring, as shown in Figure 1b. CAR, a phenolic compound found in essential oils such as oregano and thyme, has shown strong antimicrobial and antioxidant properties. Its mechanism of action involves disrupting the integrity of the cell membrane of bacteria and fungi, thereby inhibiting microbial growth [12]. Unlike synthetic preservatives, CAR is naturally derived, being classified as GRAS (generally recognized as safe), and exhibits high efficacy even at low concentrations [13]. However, due to its volatility and hydrophobic nature, its incorporation into polymeric coatings or emulsions is necessary to ensure controlled release and stability. Being a hydrophobic compound, although used in low concentrations, its presence may slightly enhance water repellency by reducing water permeability; at the same time, it has potent antimicrobial activity. It can disrupt bacterial membranes, cause leakage of intracellular components, and interfere with cellular metabolism, being effective against both Gram-positive and Gram-negative bacteria, as well as fungi.

These compounds exhibit antibacterial properties and strong antioxidant effects. Styrene-acrylic resin was selected as a binder matrix for its ability to enhance the adhesion, flexibility, and mechanical strength of the coating layer on kraft paper. As a water-based emulsion polymer, it provides good film-forming properties while maintaining compatibility with both hydrophilic and hydrophobic additives [14]. In contrast to petroleum-based wax or polyethylene coatings, which hinder recyclability and biodegradability, styrene-acrylic emulsions enable the formulation of environmentally friendly coating systems when used in conjunction with natural additives. Styrene-acrylic resins, on the other hand, are synthetic polymers or copolymers derived from acrylic acid, such as methacrylic acid, and esters in Figure 1c. They are widely used in surface coating industries and can be manufactured in various physical forms, including solids, solutions, and emulsions. Solid thermoplastic resins are typically methacrylate-based beads, while styrene-acrylic resins are prepared as aqueous emulsions.

The type of surfactant used in emulsion polymerization affects the water resistance of the dried film. These resins, primarily composed of methacrylate ester homopolymers or copolymers, are highly resistant to ultraviolet (UV) radiation, hydrolysis, corrosive chemicals, and mechanical impacts. Acrylic resin films exhibit high gloss, strong pigment adhesion, excellent surface bonding capabilities, outstanding durability, and superior mechanical strength, making them suitable for a wide range of industrial coating applications [15]. The chemical structures of chitosan, carvacrol, and styrene-acrylic resin are shown in Figure 1.

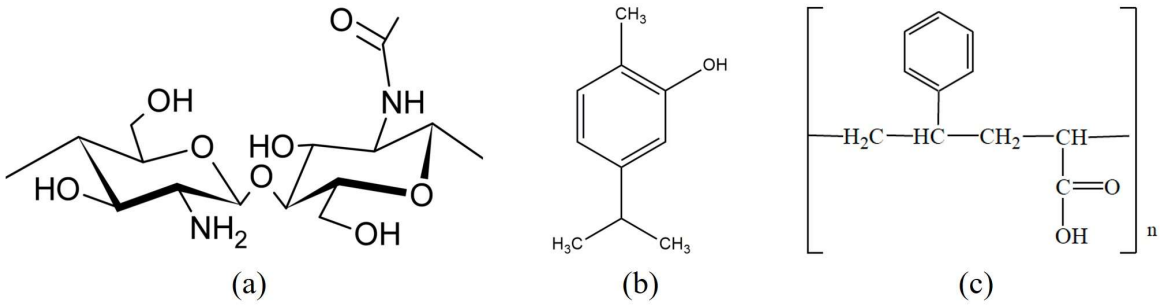

Figure 1. Chemical structure of (a) chitosan, (b) carvacrol, and (c) styrene-acrylic resin.

The increasing demand for environmentally friendly and biodegradable packaging materials has driven significant interest in enhancing paper-based substrates with natural coatings. This study focuses on developing eco-friendly coatings from natural materials for water-repellent and antimicrobial kraft paper. Three formulations were evaluated: chitosan, carvacrol, and a chitosan–carvacrol composite, each blended with a water-based styrene-acrylic resin. These natural agents are recognized for their intrinsic water resistance and antimicrobial activities, making them promising candidates for sustainable and food-safe packaging applications. The research further aims to identify the optimal formulation ratio to achieve maximum protection against moisture and microbial contamination. A comprehensive evaluation of coating performance is conducted through multi-faceted analyses, including surface morphology, physical and mechanical properties, and chemical characterization.

2. Materials and methods

2.1. Materials

The materials used in this research included brown kraft paper, KS 230 g, from S. VIWATPAPER (1994) Co., Ltd. The antimicrobial agents used in the coating formulations were chitosan and carvacrol, which were extracted from oregano oil, both sourced from Xi'an Henrikang Biotech Co., Ltd. These antimicrobial agents were tested at concentrations ranging from 0% to 50% by weight. Additionally, a water-based styrene-acrylic resin additive from Anwill (Thai) Co., Ltd. was incorporated into the coatings at concentrations ranging from 50% to 90% by weight to enhance performance and adhesion properties.

2.2. Design of the experiment using a mixture design

To determine the optimal coating ratio for kraft paper, a mixture design approach was employed using three key components: CS, CAR, and styrene-acrylic resin (used as an additive). The proportions of these components were expressed in weight percentages. A central composite design (CCD), integrated with a D-optimal design strategy, was implemented using Design Expert software (Stat-Ease® software). This experimental design enabled efficient statistical modeling and prediction of optimal coating compositions by evaluating interactions between variables across a constrained mixture space. The detailed formulation matrix used for the experiment is presented in Table 1 [16].

Table 1. The three-variable mixture design, as composed by Design Expert software.

Standard order	A: CS% (w/w)	B: CAR% (w/w)	C: Styrene% (w/w)
0	0	0	0
1	15	15	70
2	0	30	70
3	10	0	90
4	25	25	50
5	12.5	7.5	80
6	50	0	50
7	30	0	70
8	0	50	50
9	7.5	32.5	60
10	25	25	50
11	50	0	50
12	0	10	90
13	3	20	77
14	32.5	7.5	60
15	0	30	70
16	30	0	70
17	0	50	50

2.3. Solution preparation

The coating formulations were developed based on the composition listed in Table 1, focusing on the novel integration of natural bioactive agents (chitosan and carvacrol) with a synthetic styrene-acrylic resin binder. This hybrid approach combined natural and synthetic components to create water-based emulsions suitable for kraft paper coating. The coating formulations were prepared based on Table 1 to determine the optimal mixture ratios. The components were mixed using a homogenizer at 625 rpm for 1 h. The prepared coatings were then applied as thin films on KS 230 g kraft paper using a bar coater no. 25 or thickness 25 μm [17]. The coated paper was then dried in a hot-air oven at 50 °C for 10 h. After drying, the coated paper was stored at 25 °C under 65% relative humidity for at least 24 h to

stabilize the coating. Once stabilized, the samples were cut into sizes of 10 × 10 cm and 12.5 × 12.5 cm and used for testing in subsequent steps.

2.4. Testing the performance of coated kraft paper

2.4.1. Thickness test

The thickness was measured using a digital micrometer with a precision of 0.001 mm (Mitutoyo, Japan), following the standard method TAPPI T411 (ASTM-D-645 and D-646). Paper samples of 10 × 10 cm were used for the test. For each kraft paper–coated sample, five measurements were collected at different points, and the average thickness was determined.

2.4.2. Water absorption

To evaluate water absorption, the TAPPI T441 (Cobb Test) was applied on five samples for each composition. Kraft paper samples, both coated and uncoated, were cut into 12.5 × 12.5 cm pieces. The testing procedure was as follows: the paper was weighed before testing and then placed on a rubber mat mounted on the metal base of the testing device. A metal ring was positioned over the sample and secured by tightening it with a metal clamp. 100 mL of water was poured into the metal ring covering the sample, and the setup was left undisturbed for 2 min. Afterward, the sample was removed and placed on absorbent paper to blot away any excess water until no visible moisture remained on the surface. Finally, the sample was weighed again to determine water absorption. Water absorption was calculated using Eq 1.

$$\text{Water absorption (\%)} = \left(\frac{W_2 - W_1}{A}\right) \times 100\% \quad (1)$$

Where: W_1 is the weight of the paper sample before water absorption (g); W_2 is the weight of the paper sample after water absorption (g); and A is the surface area of the paper sample (m^2).

2.4.3. Moisture content

Moisture content was tested according to ASTM D 2216-10 and ISO 18134-1:2017. Kraft paper samples were cut into 10 × 10 cm, with three samples for each batch. The initial weight of each sample was measured before (W_w) and after drying (W_d). The samples were then subjected to the oven-drying method. Drying was carried out at a temperature of 105 °C until the mass of the samples remained constant. After drying, the final weight of each sample was recorded to determine the moisture content. The result is expressed as moisture content (%) as calculated using Eq 2.

$$\text{Moisture content (\%)} = \left(\frac{W_w - W_d}{W_d}\right) \times 100\% \quad (2)$$

2.4.4. Water resistance

The water resistance of coated kraft paper was evaluated through static water contact angle measurement, a sensitive technique widely used to quantify surface wettability. This method provides

insight into how effectively the coating repels water by observing the shape of a water droplet placed on the surface. The contact angle (θ) is defined as the angle between the tangent at the droplet's edge and the solid surface, reflecting the balance between adhesive forces (interaction between the liquid and solid) and cohesive forces (interaction within the liquid molecules). A higher contact angle ($\theta > 90°$) indicates stronger water repellency and reduced surface wettability, while a lower angle suggests increased absorption or spreading. In this study, measurements were conducted using a contact angle goniometer (KINO, SL150E) with a measurement range of $0° < \theta < 180°$. The method allows for comparative analysis of surface hydrophobicity resulting from different coating compositions, offering an understanding of how bioactive agents and binders influence water resistance.

2.4.5. Tensile test and elongation

The tensile test was performed according to ASTM D882 and ISO 527. Samples were cut into 1.5 × 21 cm, with five samples for each batch to ensure accuracy and reliability of the results [18]. The Universal Testing Machine (UTM; HT-2402, HUNGTA INSTRUMENT, China) at a tensile speed of 210 mm/min was used. Prior to testing, samples were conditioned for 24 h at a temperature of 25 °C and a relative humidity of 65%. Percentage of elongation is the percentage increase in a material's length before breaking, representing its ability to stretch under tensile stress. It is calculated by comparing the sample's length during testing to its original length. It was calculated using Eq 3.

$$\text{Elongation (\%)} = \left(\frac{\text{Length after break} - \text{Origin Length}}{\text{Original Length}}\right) \times 100\% \quad (3)$$

2.4.6. Bursting test

The bursting test was conducted in accordance with TAPPI T403 standards. The testing procedure involved preparing test specimens from paper samples that were free from wrinkles and watermarks and had been conditioned under test conditions for 24 h. Each specimen was placed between the upper and lower rings, ensuring that its edges extended at least 2.5 cm beyond the rings. The specimen was then securely clamped with a pressure of not less than 200 psi to prevent slippage during testing. Pressure was applied at a uniform rate until the specimen ruptured or burst. The maximum pressure at the breaking point was displayed on the gauge and recorded. For each sample, a minimum of five specimens per sample were required for testing.

2.4.7. Fourier Transform infrared spectroscopy (FTIR) analysis

The chemical composition of the samples was analyzed using an FTIR spectrometer (Spectrum 65 FTIR; Perkin Elmer, USA). Functional groups in the organic compound molecules were identified by scanning with infrared radiation in the electromagnetic spectrum range of 4000–500 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}. The analysis was conducted using attenuated total reflectance–Fourier Transform infrared spectroscopy (ATR-FTIR) to evaluate interactions between the kraft paper and the coating layer. Kraft paper samples were cut into 10 × 10 cm for testing. Finally, ATR-FTIR was employed to analyze the coated samples, detecting residual chitosan and carvacrol on the paper surface.

2.4.8. Scanning electron microscope (SEM)

The surface morphology and characteristics of uncoated and coated kraft paper were analyzed using a SEM (Thermo Fisher Scientific, Phenom ProX, Ireland). SEM images of both uncoated and coated paper were captured at magnifications of 500× and 1000× to observe changes in surface morphology. Paper samples were cut into 1 × 1 cm for analysis. Prior to scanning, the samples were coated with a 5 nm thick gold film to enhance conductivity and imaging quality.

2.4.9. Antibacterial analysis barrier properties (total plate count)

Antimicrobial activity analysis of kraft paper coated with styrene-acrylic combined with CS, CAR, or a mixture of both was conducted by evaluating the total plate count (TPC), which measures the total number of viable microorganisms, including yeast and bacteria [3]. The result was expressed in CFU/g (colony-forming units per gram). Paper samples coated with CS, CAR, and a CS–CAR mixture in the specified ratio were compared to uncoated kraft paper in order to evaluate their antimicrobial effectiveness. The comparison aimed to assess the reduction in microbial growth due to the applied coatings.

2.4.10. Statistical analysis

One-way analysis of variance (ANOVA) was used to evaluate the statistical significance of differences among coating formulations, with the analysis conducted using Microsoft Excel® software. For antimicrobial activity, regression analysis based on a mixture design was implemented using Design Expert (Stat-Ease®) software; the special cubic model represented the relationship between component ratios and antibacterial performance. A significance level of $p < 0.05$ was used throughout to ensure statistical reliability and confidence in the observed differences [8].

3. Results and discussion

3.1. Characterization of coated kraft paper

The results of coating formulations on coated kraft paper are summarized in Table 2.

Table 2. Characterization of different coated kraft paper samples.

Run	CS% (w/w)	CAR% (w/w)	Styrene% (w/w)	Thickness (mm)	Cobb test (g/m^2)	Moisture content (%)	Tensile strength (Nf/mm^2)	Yield strength (Nf/mm^2)	Elongation (%)	Burst testing (kgf/cm^2)	Total plate count (CFU/g)
0	0	0	0	0.29	60	5.14	4.5	4	17.12	1	240
1	15	15	70	0.34	54	5.71	4.5	4	20.9	1.2	210
2	0	30	70	0.32	41	6.25	4.5	3	21.39	1.2	50
3	10	0	90	0.33	-1	6.38	4.5	4	20.58	1.4	150
4	25	25	50	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
5	12.5	7.5	80	0.35	37	6.84	4.5	5	21.1	1	40
6	50	0	50	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7	30	0	70	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
8	0	50	50	0.33	28	4.40	4.5	3	17.53	1.4	30
9	7.5	32.5	60	0.32	46	5.18	4.5	5	21.96	1	120
10	25	25	50	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	50	0	50	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
12	0	10	90	0.31	4	6.06	4.5	4	16.87	1	170
13	3	20	77	0.33	41	5.70	4.5	5	22.28	1.2	120
14	32.5	7.5	60	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
15	0	30	70	0.31	49	6.33	4.5	4	18.15	1.6	70
16	30	0	70	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
17	0	50	50	0.32	28	4.98	4.5	4	18.9	1.6	60

3.1.1. Thickness

The average thickness of kraft paper increased by approximately 0.04 mm when coated with the three natural substance mixtures (chitosan-based coating, carvacrol-based coating, with carvacrol extracted from oregano oil, and chitosan–carvacrol composite coating) combined with a water-based styrene-acrylic resin as an additive, compared to uncoated kraft paper (Table 2). The slight increase in thickness may be attributed to the penetration of chitosan and carvacrol solutions into the cellulose network [19] and the application of both coatings. The average thickness was 0.33 mm, with the coating concentration ranging from 0% $_{(w/w)}$ to 50% $_{(w/w)}$, while the styrene-acrylate resin additive concentration ranged from 50% $_{(w/w)}$ to 90% $_{(w/w)}$. Thickness is a critical factor as it directly influences the physical and optical properties of kraft paper.

3.1.2. Water absorption

The Cobb test was used to evaluate the changes in water absorption capabilities of kraft paper coated with chitosan and carvacrol under various coating mixture conditions [17]. According to Table 2, the uncoated kraft paper presented a water absorption rate of 60 g/m^2, indicating its high water-absorption capacity. However, these characteristic limits its application in water and moisture-resistant packaging [20]. By comparing the water absorption of chitosan-coated kraft paper, carvacrol-coated kraft paper, and a chitosan–carvacrol mixture, the results showed that kraft paper coated with a mixture of 12.5% chitosan and 7.5% carvacrol with styrene-acrylic resin at 80% (run 5 in Table 2) had a water absorption rate of 37 g/m^2. This was higher than the carvacrol-coated kraft paper 50% (run 8 in Table 2), with a water absorption rate of 28 g/m^2. The carvacrol-coated paper exhibited lower water absorption than the chitosan–carvacrol mixture, suggesting that carvacrol coating helps reduce water absorption to some extent. However, the kraft paper coated with 10% chitosan alone demonstrated the lowest water absorption, with a water absorption rate of −1.00 g/m^2. This remarkable reduction is due to chitosan's deacetylation reaction, which enhances its film-forming and fiber-forming properties and contributes to low oxygen permeability, significantly improving water resistance [21]. In contrast, carvacrol, which exhibits antibacterial growth inhibition and antioxidant properties, helps reduce paper degradation but has higher water absorption compared to chitosan. Nevertheless, kraft paper coated with these substances exhibited significantly lower water absorption than uncoated kraft paper, highlighting their potential for moisture-resistant packaging applications [22].

3.1.3. Moisture content

The moisture content of kraft paper coated with a chitosan and carvacrol mixture ranged from 4.40% to 6.84%, with an average moisture content of 5.69% (Table 2). Most values were between 5% and 6%. The kraft paper coated with chitosan and carvacrol, with styrene-acrylic resin as an additive, exhibited a higher moisture content compared to the kraft paper coated with only chitosan. In contrast, the lowest moisture content was observed in kraft paper coated with carvacrol alone. The presence of the coating influences key material properties, including strength, water resistance, and durability [23]. Overall, the moisture content values obtained are considered appropriate and do not negatively impact the mechanical properties or storage of the coated kraft paper.

3.1.4. Water resistance

The contact angle test was conducted to evaluate the wetting behavior of kraft paper, both uncoated and coated with chitosan, carvacrol, and a chitosan–carvacrol mixture, using styrene-acrylic resin as an additive. The contact angle was measured before and after coating to assess changes in surface properties. The results, as seen in Figure 2 showed that uncoated kraft paper had a contact angle of 97.874° (Figure 2a), indicating a relatively hydrophilic surface, as water spread easily across it [24]. A contact angle above 90° suggests high water absorption capacity. After coating with chitosan, the contact angle increased to 102.031° (Figure 2b), demonstrating a shift from hydrophilic to hydrophobic characteristics [25]. This increase can be attributed to chitosan's ability to form a water-resistant coating layer, making the surface more water-repellent. Statistical analysis confirmed that this change was statistically significant (p-value < 0.05). Kraft paper coated with carvacrol (Figure 2c) had a contact angle of 98.055°, showing only a slight increase from the uncoated paper [26]. This minor change suggests that while carvacrol influences surface wetting behavior, the surface remains more hydrophilic compared to chitosan-coated paper. When coated with a mixture of chitosan and carvacrol, the contact angle increased to 99.610° (Figure 2d), indicating a slight improvement in hydrophobicity compared to carvacrol alone, though still lower than chitosan-only coatings. Overall, chitosan-coated kraft paper exhibited the most hydrophobic surface properties [27], likely due to chitosan's strong film-forming and water-resistant characteristics. While coatings with carvacrol and the chitosan–carvacrol mixture also increased the contact angle compared to uncoated kraft paper, they did not achieve the same level of hydrophobicity as chitosan alone. These findings highlight the importance of selecting appropriate coating materials to improve the surface properties of kraft paper, particularly for applications requiring water resistance or moisture protection.

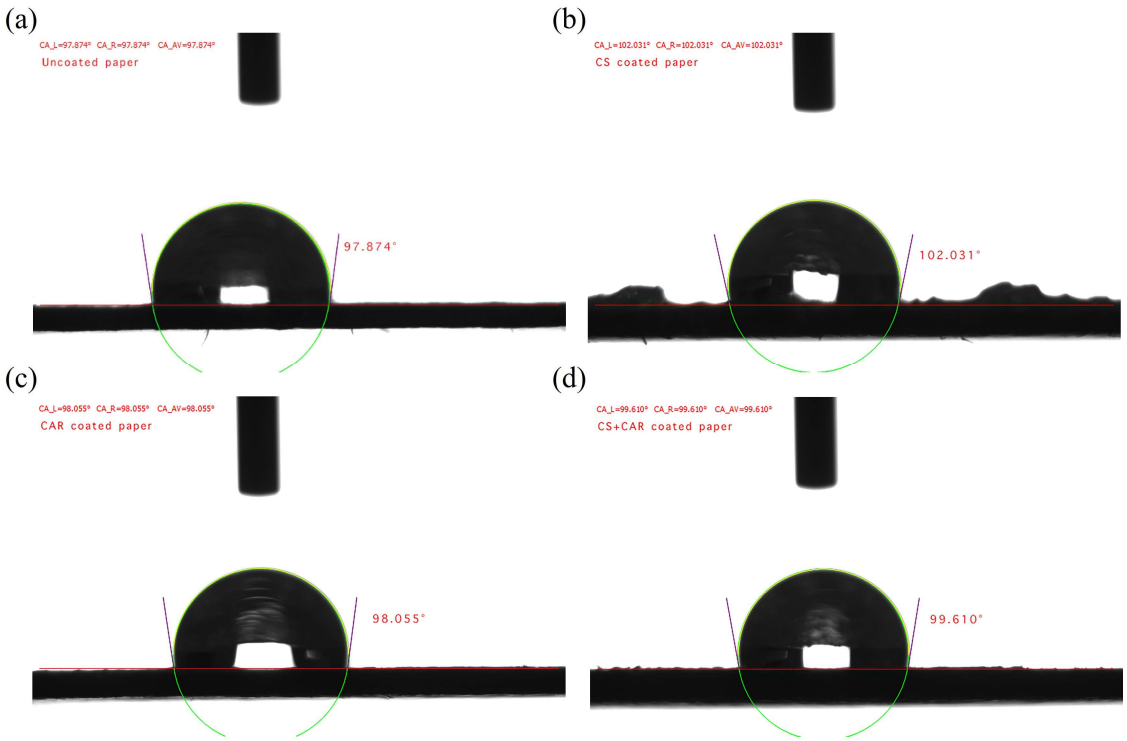

Figure 2. The contact angle test on coated paper: (a) uncoated paper; (b) chitosan-coated paper; (c) carvacrol-coated paper; (d) mix of chitosan and carvacrol coated paper.

3.1.5. Tensile strength and elongation

The tensile strength of kraft paper coated with chitosan, carvacrol, and chitosan–carvacrol composite coatings showed an average value of 4.5 Nf/mm^2. This result indicates that the coating materials slightly enhanced the mechanical properties of the kraft paper, providing moderate tensile strength suitable for packaging applications that require flexibility combined with basic strength performance.

The tensile testing results, as presented in Table 2, showed that the average percentage elongation was approximately 19.7% (Figure 3). The stress–strain patterns of both coated and uncoated kraft paper appeared similar, which can be attributed to the inherently brittle nature of paper. The low elongation observed is characteristic of paper materials and is consistent with findings from previous studies, which indicate that paper possesses limited elongation capacity [28].

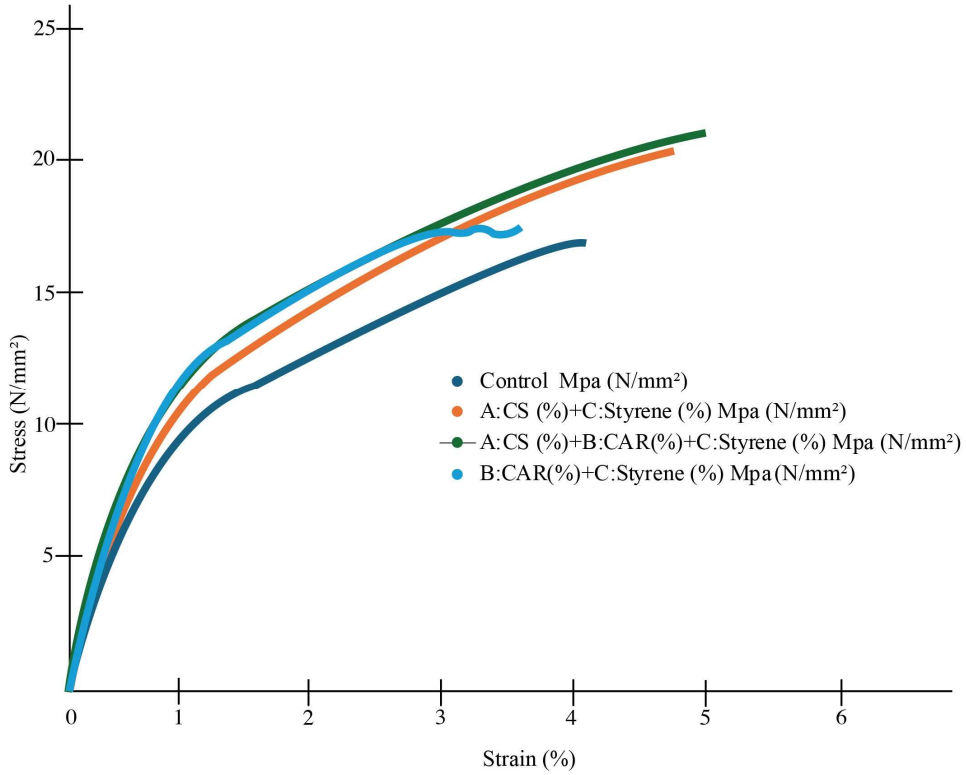

Figure 3. Run stress report.

3.1.6. Bursting strength

Kraft paper coated with chitosan, carvacrol, and a composite coating of chitosan and carvacrol exhibited a maximum bursting strength of 200 psi or 1.2–1.6 kgf/cm^2. This indicates that materials coated with these substances possess excellent pressure resistance. There was no statistically significant difference observed in the tests at a 95% confidence level. Therefore, both chitosan and carvacrol are suitable for applications requiring high pressure resistance, such as the production of corrugated packaging boxes designed to withstand compression and crushing forces.

3.1.7. FTIR of uncoated and coated paper

FTIR analysis was conducted to identify molecular interactions between the functional groups of chitosan and carvacrol blended with a water-based styrene-acrylic coating. Figure 4 shows the FTIR spectra of kraft paper coated with chitosan blended with the water-based styrene-acrylic coating in the range of 4000–500 cm^{-1}. The FTIR spectra of kraft paper samples coated with chitosan and carvacrol at varying concentrations displayed distinct characteristic bands [29]. The bands observed between 4000 and 500 cm^{-1} correspond to the stretching vibrations of the $–NH_2$ and –OH groups of chitosan, with an absorption peak at approximately 3,478.68 cm^{-1}, indicating hydrogen bonding between chitosan and carvacrol or between chitosan and the styrene-acrylic matrix [30]. Hydrogen bonding often leads to broadening or shifting of these peaks to lower wavenumbers, suggesting interaction rather than simple mixing. The appearance or intensification of the C=O stretching band of 2000–1000 cm^{-1} suggests that the carboxylic or ester groups from the acrylic resin are engaging in dipole–dipole interactions or hydrogen bonding with chitosan's amino groups [31]. The presence of a vinyl group (CH_2=CH–) peak at 1600 cm^{-1} confirms the contribution of styrene units [32]. If this peak changes in intensity upon the addition of chitosan or carvacrol, it may imply interactions that disrupt the conjugation or alignment of vinyl groups, further supporting the presence of molecular-level interactions. Changes in the peak at 1,116 cm^{-1}, associated with the styrene-acrylic component and –OH groups, may also reflect a rearrangement or partial interaction within the polymer matrix upon blending with chitosan and carvacrol. Thus, by comparing peak positions, intensities, and profiles across different formulations, the FTIR analysis enables the identification of chemical interactions (e.g., hydrogen bonding) rather than just physical mixing, confirming that the materials are interacting at a molecular level within the coating matrix. Figure 4 shows that the coated kraft paper samples contained the tested substances, allowing differentiation in the arrangement of the coating and interactions among its components [33]. The presence of styrene-acrylic promoted changes and increased light absorption at specific peaks.

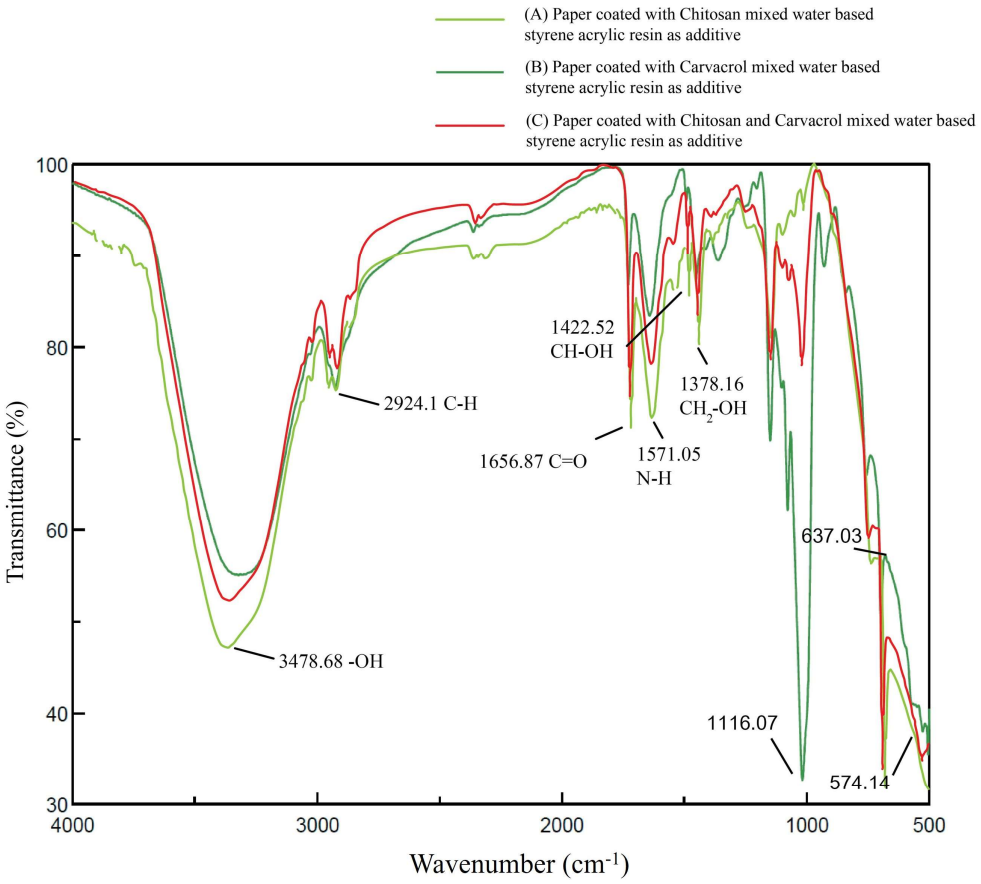

Figure 4. FTIR spectra of three types of coated paper: (A) paper coated with chitosan mixed with water-based styrene-acrylic resin as an additive; (B) paper coated with carvacrol mixed with water-based styrene-acrylic resin as an additive; (C) paper coated with chitosan and carvacrol mixed with water-based styrene-acrylic resin as an additive.

3.1.8. Scanning electron microscopy (SEM)

SEM images (300 μm, 10 kV) of uncoated kraft paper and kraft paper coated with chitosan, carvacrol, and their combination using a water-based styrene-acrylic resin as an additive clearly revealed changes in surface morphology across the different samples. The uncoated kraft paper (Figure 5a) showed irregular fiber aggregation with clearly visible voids between fibers. Numerous fine particles were scattered on and between the fibers, suggesting incomplete fiber distribution and poor surface uniformity. Upon coating with chitosan (Figure 5b), the surface appeared more homogeneous, and the voids between fibers were reduced compared to the uncoated paper. However, the coating layer exhibited larger chitosan particles, which partially filled the voids. The relatively large particle size contributed to a less refined coating structure, leading to some surface irregularities. In contrast, the carvacrol-coated paper (Figure 5c) showed a more refined and uniform surface morphology. No visible voids remained between fibers, and the particles formed by carvacrol were significantly smaller than those of chitosan, allowing for better penetration into fiber gaps. This resulted in a more continuous and compact coating layer, indicating improved coating efficiency. The paper coated with a chitosan–carvacrol mixture (Figure 5d) demonstrated the most favorable morphological characteristics

among all samples. The surface was highly uniform, with no observable fiber voids and fewer fine particles. The combination of both agents enhanced the coating refinement beyond that achieved by chitosan alone, producing a more consistent, compact, and high-quality coating layer. These morphological changes reflect the impact of each coating formulation on the structural integrity and surface quality of the paper, suggesting potential improvements in barrier or antimicrobial performance for samples with finer and more complete coatings.

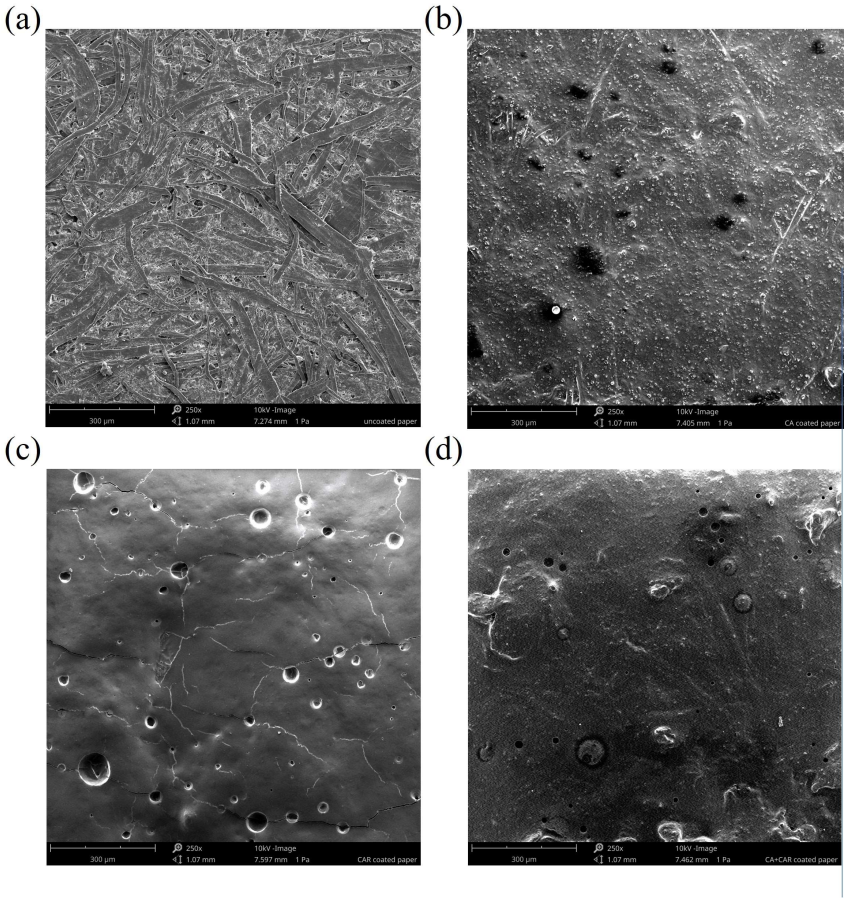

Figure 5. SEM of (a) uncoated paper; (b) chitosan-coated paper; (c) carvacrol-coated paper; (d) mix of chitosan and carvacrol coated paper.

3.1.9. Antibacterial analysis barrier properties

According to the results of the antimicrobial activity shown in Table 2, the uncoated kraft paper exhibited the highest total plate count of 240 CFU/g, indicating its inability to inhibit microbial growth. In comparison, the kraft paper coated with chitosan and styrene-acrylic resin at a ratio of 10:90 showed a reduced microbial count of 150 CFU/g, demonstrating the antimicrobial potential of chitosan. This property is attributed to amino groups ($–NH_2$) in chitosan, which can interact with microbial cell walls, disrupt cell membrane integrity, and ultimately inhibit microbial growth [34].

Moreover, kraft paper coated with a chitosan–carvacrol composite coating, containing 12.5% chitosan, 7.5% carvacrol, and 80% styrene-acrylic resin, exhibited a significantly lower microbial count of 40 CFU/g. This result confirms the synergistic antimicrobial effect between chitosan and carvacrol. Carvacrol, a natural phenolic compound, exhibits potent antimicrobial activity through a

mechanism involving disruption of the cell membrane, leakage of intracellular components, and interference with essential cell functions, leading to cell death [35].

Notably, the kraft paper coated with 50% carvacrol exhibited the most effective antimicrobial activity, with the lowest total plate count of only 30 CFU/g. This finding highlights the high potential of carvacrol as a natural antimicrobial agent, especially when applied in an appropriate concentration. Furthermore, the incorporation of carvacrol in the coating formulation provided superior antimicrobial properties compared to chitosan alone. These results suggest that natural-based coatings, particularly those incorporating carvacrol, can be effectively developed for active packaging applications to extend the shelf life and enhance the safety of food products [31].

3.1.10. Regression analysis of the mixture design

The summary of the statistics for the antimicrobial effect model shows that the special cubic model is better than the other models (Table 3). The special cubic model has a higher adjusted R^2 value and predicted R^2, which means that the model can describe the response variations for all design points better than the quadratic model. After the backward elimination was applied to the special cubic model, the fittest model, transforming the formula into the actual components, is obtained as follows (Eq 4):

$$TPC = 355.8187\, x'_A + 2.0437\, x'_B + 1.6687\, x'_C + 4.65\, x'_A x'_B - 3.9537\, x'_A x'_C - 0.0562\, x'_B x'_C - 0.134\, x'_A x'_B x'_C \quad (4)$$

where x'_A, x'_B, and x'_C represent the proportions of chitosan (A), carvacrol (B), and additive (C), respectively. The numbers in the parentheses indicate the standard error for the parameter coefficients.

The estimated equation reveals that chitosan significantly increases the TPC, with the highest positive coefficient of 355.8187, indicating lower antimicrobial effectiveness. In contrast, carvacrol shows a much lower TPC contribution of 2.0437, suggesting better antimicrobial properties. Notably, the interaction between chitosan and the styrene-acrylic resin additive results in a strong negative effect on TPC (–3.9537), highlighting their synergistic antimicrobial activity. Among all tested combinations, the carvacrol coating with styrene-acrylic resin demonstrated the greatest antimicrobial effect, exhibiting the most negative coefficient (–0.0562). These findings suggest that while chitosan increases microbial presence, the combination of carvacrol and the additive is most effective in microbial inhibition.

Table 3. Regression analysis of the mixture design for antibacterial effects.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	58.15	0.3741	0.1952	–0.4771	55850.38	
Quadratic	45.73	0.7788	0.5022		+	
Special cubic	14.72	0.9828	0.9484		+	Suggested
Cubic					+	Aliased

4. Conclusions

This study investigated the performance of kraft paper coatings formulated with natural compounds and a water-based styrene-acrylic resin (SAR) additive. Kraft paper coated with 10% chitosan and 90% SAR exhibited the lowest water absorption value of –1.00 g/m^2 and a contact angle

of 102.031°, indicating a significant shift from hydrophilic to hydrophobic behavior. However, this formulation showed the least antimicrobial activity.

In contrast, the kraft paper coated with 50% carvacrol and 50% SAR demonstrated higher water absorption but achieved superior antimicrobial effectiveness. This is attributed to the presence of phenolic compounds in carvacrol, which are known for their potent antimicrobial properties. Additionally, composite coating comprised of 12.5% chitosan, 7.5% carvacrol, and 80% SAR achieved improved antimicrobial performance compared to the chitosan-only formulation, although with a modest compromise in water resistance.

Overall, the findings suggest that a chitosan–carvacrol composite coating offers a promising balance between moisture resistance and microbial protection. This makes it a strong candidate for sustainable, active packaging applications, particularly in transportation contexts where durability and hygiene are critical.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

Acknowledgments

This work was financially supported by the Petchra Pra Jom Klao Master's Degree Research Scholarship from King Mongkut's University of Technology Thonburi. The authors would like to express their sincere gratitude to Dr. Tanatorn Tongsumrith and Asst. Prof. Dr. Nitus Tipsotraiyana from the Department of Printing and Packaging Technology, Faculty of Industrial Education and Technology, for their valuable guidance and support throughout this research.

Author contributions

Nichapat Nonthaphathorn: conceptualized and designed the study, performed the experiments, analyzed the data, and drafted the manuscript; Tanatorn Tongsumrith& Nitus Tipsotnaiyana: provided supervision, methodological guidance, and critical revision of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

References

1. Siracusa V, Rocculi P, Romani S, et al. (2008) Biodegradable polymers for food packaging: A review. *Trends Food Sci Tech* 19: 634–643. https://doi.org/10.1016/j.tifs.2008.07.003
2. Reis AB, Yoshida CM, Reis APC, et al. (2011) Application of chitosan emulsion as a coating on Kraft paper. *Polym Int* 60: 963–969. https://doi.org/10.1002/pi.3023
3. Shankar S, Rhim JW (2018) Antimicrobial wrapping paper coated with a ternary blend of carbohydrates (alginate, carboxymethyl cellulose, carrageenan) and grapefruit seed extract. *Carbohyd Polym* 196: 92–101. https://doi.org/10.1016/j.carbpol.2018.04.128

4. Ramos M, Jiménez A, Peltzer M, et al. (2013) Characterization and antimicrobial activity studies of polypropylene films with carvacrol and thymol for active packaging. *J Food Eng* 109: 513–519. https://doi.org/10.1016/j.jfoodeng.2011.10.031
5. Siracusa V (2012) Food packaging permeability behaviour: A report. *Int J Polym Sci* 2012: 302029. https://doi.org/10.1155/2012/302029
6. Venkatesan R, Dhilipkumar T, Shankar KV, et al. (2024) Eco-friendly food packaging: gallic acid as a cross-linking agent in PBAT/cellulose composite films. *Cellulose* 31: 8105–8125. https://doi.org/10.1007/s10570-024-06046-w
7. Rastogi V, Samyn P (2015) Bio-based coatings for paper applications. *Coatings* 5: 887–930. https://doi.org/10.3390/coatings5040887
8. Aider M (2010) Chitosan application for active bio-based films production and potential in the food industry: Review. *Lwt-Food Sci Technol* 43: 837–842. https://doi.org/10.1016/j.lwt.2010.01.021
9. Shahidi F, Arachchi JKV, Jeon YJ (1999) Food applications of chitin and chitosans. *Trends Food Sci Tech* 10: 37–51. https://doi.org/10.1016/S0924-2244(99)00017-5
10. Venkatesan R, Vetcher AA, Al-Asbahi BA, et al. (2024) Chitosan-based films blended with tannic acid and Moringa oleifera for application in food packaging: The preservation of strawberries (Fragaria ananassa). *Polymers* 16: 937. https://doi.org/10.3390/polym16070937
11. Zheng ZL, Justin YW Tan, Liu HY, et al. (2009) Evaluation of oregano essential oil (Origanum heracleoticum L.) on growth, antioxidant effect and resistance against Aeromonas hydrophila in channel catfish (Ictalurus punctatus*). Aquaculture* 292: 214–218. https://doi.org/10.1016/j.aquaculture.2009.04.025
12. Burt S (2004) Essential oils: Their antibacterial properties and potential applications in foods—A review. *Int J Food Microbiol* 94: 223–253. https://doi.org/10.1016/j.ijfoodmicro.2004.03.022
13. Rout S, Tambe S, Deshmukh RK, et al. (2022) Recent trends in the application of essential oils: The next generation of food preservation and food packaging. *Trends Food Sci Tech* 129: 421–439. https://doi.org/10.1016/j.tifs.2022.10.012
14. Eckersley ST, Rudin A (1994) Drying behavior of acrylic latexes. *Prog Org Coat* 23: 387–402. https://doi.org/10.1016/0033-0655(94)87007-1
15. Bechi DM, de Luca MA, Martinelli M, et al. (2013) Organic–inorganic coatings based on epoxidized castor oil with APTES/TIP and TEOS/TIP. *Prog Org Coat* 76: 736–742. https://doi.org/10.1016/S0141-8130(02)00039-9
16. Pelissari FM, Yamashita F, Garcia MA, et al. (2012) Constrained mixture design applied to the development of cassava starch–chitosan blown films. *J Food Eng* 108: 262–267. https://doi.org/10.1016/j.jfoodeng.2011.09.004
17. Gatto M, Ochi D, Yoshida CMP, et al. (2019) Study of chitosan with different degrees of acetylation as cardboard paper coating. *Carbohydr Polym* 210: 56–63. https://doi.org/10.1016/j.carbpol.2019.01.053
18. Wang F, Wang L, Zhang X, et al. (2022) Enhancement of oil resistance of cellulose packaging paper for food. *J Food Eng* 332: 111039. https://doi.org/10.1016/j.jfoodeng.2022.111039
19. Khwaldia K, Basta AH, Aloui H, et al. (2014) Chitosan-caseinate bilayer coatings for paper packaging materials. *Carbohydr Polym* 99: 508–516. https://doi.org/10.1016/j.carbpol.2013.08.086

20. Bordenave N, Grelier S, Pichavant F, et al. (2007) Water and moisture susceptibility of chitosan and paper-based materials: Structure-property relationships. *J Agric Food Chem* 55: 9479–9488. https://doi.org/10.1021/jf070595i
21. Kittur FS, Prashanth HKV, Sankar KU, et al. (2002) Characterization of chitin, chitosan and their carboxymethyl derivatives by differential scanning calorimetry. *Carbohydr Polym* 49: 185–193. https://doi.org/10.1016/S0144-8617(01)00320-4
22. Habibie S, Hamzah M, Anggaravidya M, et al. (2016) The effect of chitosan on physical and mechanical properties of paper. *J Chem Eng Mater Sci* 7: 1–10. https://doi.org/10.5897/JCEMS2015.0235
23. Aloui H, Khwaldia K, Slama MB, et al. (2011) Effect of glycerol and coating weight on functional properties of biopolymer-coated paper. *Carbohydr Polym* 86: 1063–1072. https://doi.org/10.1016/j.carbpol.2011.06.026
24. Farris S, Introzzi L, Biagioni P, et al. (2011) Wetting of biopolymer coatings: Contact angle kinetics and image analysis investigation. *Langmuir* 27: 7563–7574. https://pubs.acs.org/doi/abs/10.1021/la2017006
25. McHugh TH, Avena-Bustillos, RJ, Krochta JM (1993) Hydrophilic edible film: Modified procedure for water vapor permeability and explanation of thickness effects. *J Food Sci* 58: 899–903. https://doi.org/10.1111/j.1365-2621.1993.tb09387.x
26. Rulon J, Robert H (1966) *Wetting of Low-Energy Surfaces*, JC Berg Ed., New York: Marcel Dekker, 4–73.
27. Zhang Y, Bi J, Wang S, et al. (2019) Functional food packaging for reducing residual liquid food: Thermo-resistant edible superhydrophobic coating from coffee and beeswax. *J Colloid Interface Sci* 533: 742–749. https://doi.org/10.1016/j.jcis.2018.09.011
28. Seth RS, Page DH (1981) The stress-strain curve of paper. The role of fundamental research in paper-making, Trans. of the VIIth Fund. Res. Symp. Cambridge, 1981, (Fundamental Research Committee, ed.), Manchester, 421–452. https://doi.org/10.15376/frc.1981.1.421
29. Bobu E, Nicu R, Obrocea P, et al. (2016) Antimicrobial properties of coatings based on chitosan derivatives for applications in sustainable paper conservation. *Cellul Chem Technol* 50: 689–699. Available from: https://cellulosechemtechnol.ro/pdf/CCT5-6(2016)/p.689-699.pdf.
30. Focher B, Naggi A, Torri G (1992) Chitosans from *Euphausia superba.* 2: Characterization of solid-state structure. *Carbohydr Polym* 18: 43–49. https://doi.org/10.1016/0144-8617(92)90186-T
31. Gupta S, Ivvala J, Grewal HS (2021) Development of natural wax based durablesuperhydrophobic coatings. *Ind Crops Prod* 171: 113871. https://doi.org/10.1016/j.indcrop.2021.113871
32. Duarte ML, Ferreira MC, Marvão MR, et al. (2002) An optimized method to determine the degree of acetylation of chitin and chitosan by FTIR spectroscopy. *Int J Biol Macromol* 31: 1–8. https://doi.org/10.1016/S0141-8130(02)00039-9
33. Ferreira PJ, Gamelas JA, Moutinho IM, et al. (2009) Application of FT-IR-ATR spectroscopy to evaluate the penetration of surface sizing agents into the paper structure. *Ind Eng Chem Res* 48: 3867–3872. https://doi.org/10.1021/ie801765c
34. Zakaria S, Chia CH, Ahmad W, et al. (2015) Mechanical and antibacterial properties of paper coated with chitosan. *Sains Malaysiana* 44: 905–911. https://doi.org/10.17576/jsm-2015-4406-18

35. Souza A, Santos N, Torin R, et al. (2020) Synergic antimicrobial properties of Carvacrol essential oil and montmorillonite in biodegradable starch films. *Int J Biol Macromol* 164: 1737–1747. https://doi.org/10.1016/j.ijbiomac.2020.07.226