

Green Coconut (*Cocos nucifera* L.) Husk Extract as Milk Freshness Indicator in Chitosan/ Polyvinyl Alcohol-based Smart Packaging Films

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Abstract

The growing demand for sustainable and eco-friendly food packaging has prompted research into innovative solutions that tackle environmental challenges and consumer health concerns. Food spoilage typically results from microbial activity, which is subsequently influenced by alterations in pH levels within the packaging environment. Plants, such as green coconut husk extract, contain anthocyanin, a water-soluble natural pigment with significant antioxidant and antibacterial properties, whose color changes in response to variations in the surrounding pH. This research focuses on the development of a pH-responsive packaging film utilizing chitosan and polyvinyl alcohol (PVA), integrated with green coconut (*Cocos nucifera* L.) husk extract, through a casting method to monitor milk freshness. An extraction procedure employing a maceration technique was conducted on green coconut husk utilizing methanol solvent with the incorporation of 1 % HCl (v/v). The thickness, mechanical properties, and pH-responsiveness of the resulting films with varying extract to chitosan volume ratios were examined in detail. The films were subsequently employed to monitor real-time applications concerning milk freshness. The results indicated that the addition of green coconut husk extract resulted in significant variations in the thickness, tensile strength, and elongation at the break of the film samples. The films exhibited thicknesses between 0.28 and 0.38 mm, demonstrating optimal mechanical properties at an extract-to-chitosan ratio of 4:1 (v/v), with tensile strength (TS) and elongation at break (EB) recorded at 4.65 MPa and 3.625%, respectively. The films exhibited a pH-sensitive color change from dark red to brown in acidic conditions. The findings indicate that the PVA/chitosan smart film, which contains green coconut husk extract, has the potential to serve as a deterioration indicator in packaged milk products.

Keywords: biopolymer; food packaging; freshness indicator; pH-sensitive; plant extract

Introduction

Food wastage is a significant issue both on a global and national scale, with roughly one-

third of the world's food supply being lost or discarded^[1]. Throughout storage, transportation, and sale, food is susceptible to spoilage from microorganisms, enzymes,

temperature fluctuations, and various other factors, leading to a decline in freshness^[2]. Packaging plays a crucial role in preserving food quality and safety in today's food industry^[3]. In recent years, the growing preference for fresh and safe food consumption has led to heightened consumer demand for effective food packaging, thereby posing new challenges for the advancement of packaging technology^[4]. Conventional food packaging methods are unable to adequately monitor food freshness, leading indirectly to substantial food wastage and the potential emergence of health hazards from foodborne pathogens^[5]. Therefore, easy and real-time methods for monitoring food quality and safety throughout the supply chain are urgently needed to maintain order in the food market and protect the rights and interests of consumers^[2].

Milk, being highly perishable, requires careful storage and temperature control to prevent spoilage. The United States Department of Agriculture (USDA) suggests that milk should be stored at temperatures ranging from 0.0 to 4.4 °C. Nevertheless, milk is frequently exposed to temperature fluctuations due to improper storage practices during distribution, at retail stores, and in home refrigerators^[6]. Fresh milk generally maintains a neutral pH around 6.8–7.2, which declines as microbial activity increases, producing lactic acid and lowering pH levels^[7]. Monitoring these pH fluctuations provides insights into the milk's freshness and microbial quality. Enhancing the contrast of pH-sensitive films to reflect these subtle pH shifts effectively aids in the visual assessment of milk spoilage, reducing waste and ensuring product safety^[8]. For instance, a report illustrated how protein-polysaccharide films containing pH-sensitive pigments could detect spoilage from volatile ammonia and moisture, leveraging anthocyanin's color sensitivity for visible quality control^[9].

Colorimetric indicator films that are sensitive to changes in pH and/or chemical composition are invaluable in creating smart packaging materials for fresh foods^[10]. These substances can detect alterations in the pH of food products or their surroundings, triggering a

color change that visually signals the freshness and quality of the food^[11]. Standard colorimetric indicator films utilize pH-sensitive pigments such as bromophenol blue and chlorophenol red, which were previously regarded as colorants potentially harmful to human health^[12]. Moreover, the extensive use of petroleum-based plastic packaging has become a significant global issue due to the environmental problems associated with their production and disposal. Consequently, smart packaging utilizing natural colorants and biopolymers has emerged as the latest technology in the food packaging sector^[7,13].

Anthocyanins have attracted much attention as pigments commonly used in pH-responsive packaging, and obtain them from various sources such as jambolan (*Syzygium cumini*) fruit^[12], red cabbage^[14], purple sweet potato^[15], red beetroot^[16], black barberry^[17], onion peel^[7], and blueberry^[4,8,18]. The increasing demand for anthocyanins in the food industry underscores the importance of evaluating new potential sources of anthocyanins that could be developed on an industrial scale^[13]. Green coconut (*Cocos nucifera* L.), a readily available agricultural product in Indonesia, possesses a high anthocyanin content in its husk, presenting a valuable opportunity for developing pH-responsive films^[19].

Multiple studies support the effectiveness of anthocyanin-based films for spoilage detection, such as a study which utilized basil seed gum, chitosan, and red cabbage anthocyanin in a film that showed color changes in response to volatile nitrogen compounds from decaying fish, correlating well with microbial counts and pH, thus allowing an estimation of spoilage levels^[20]. Moreover, a previous study demonstrated the use of bilirubin-containing kappa-carrageenan-based films to track pH fluctuations due to microbial or enzymatic activity in food spoilage, underscoring that natural pH-sensitive films can provide clear information on food quality through observable color differences^[21]. Other study noted that films containing Amomum tsao-ko essential oil displayed significant color variation between pH 7 and 8, making them suitable for shrimp

spoilage monitoring, confirming the potential of pH-sensitive natural pigments in smart packaging applications^[22].

Chitosan is a frequently utilized biopolymer for its excellent film-forming, biocompatible, and antimicrobial qualities^[23,24]. In addition, the safety of chitosan for use in commercial food products has been approved by the US Food and Drug Administration (FDA)^[25]. However, its rigidity and limited solubility above pH 6.5 reduce its practical applications without modification^[26]. To enhance its mechanical properties and film stability, chitosan is often combined with Polyvinyl Alcohol (PVA), a polymer with high hydrophilicity, chemical stability, and film-forming capabilities^[13]. PVA possesses a range of beneficial properties that are suitable for food packaging film formulations, including increased hydrophilicity, strong chemical stability, and exceptional film-forming ability^[27]. The use of PVA for food-related purposes has been analyzed by the European Food Safety Authority (EFSA) and has been reported as a coating material for various types of food that does not cause health problems^[28]. Numerous studies have explored chitosan/PVA blends in smart films with natural indicators^[12,13,27], yet none have utilized green coconut husk extract as a color indicator for monitoring food freshness. Therefore, in this research, green coconut husk extract was employed as a natural color indicator within chitosan/PVA-based films to monitor milk freshness.

Given these developments, the use of natural pH-sensitive indicators like anthocyanins in biodegradable film matrices offers a viable approach to enhance food freshness monitoring and tackle sustainability issues. This research focuses on utilizing the anthocyanin content from green coconut husk extract in a chitosan/PVA-based film to develop a colorimetric indicator for assessing milk freshness. This research aims to offer a practical, visually accessible tool for consumers and industry by observing pH-responsive color changes in these films, thereby contributing to food safety and waste reduction in the supply chain.

Experimental

Equipment

Analytical balance (Fisher Scientific), hot plate magnetic stirrer (IKA MAG HS 7), rotary vacuum evaporator (IKA RV 3), Whatman filter paper No. 1, pH meter (Smart Sensor PH818), and aluminium disks for film casting.

Material

Green coconut (*Cocos nucifera* L.) husk was collected from coconut ice sellers in the Cilegon area, Banten, Indonesia. Food-grade chitosan with a deacetylation degree of 87.2 % was produced by PT. Biotech Surindo, Cirebon, Indonesia. The chemicals used in the study comprised polyvinyl alcohol (PVA) fully hydrolyzed, glacial acetic acid (100 %), methanol, hydrochloric acid (HCl) 37 %, and sodium hydroxide (NaOH), all of which were procured from the Merck (Darmstadt, Germany).

Methods

Green Coconut (Cocos nucifera L.) Husk Extractions

Applying a method adapted from the previous publication, an extract was made from green coconut husk waste using the maceration technique^[29]. The current study involved the cleaning of fresh green coconut husks with distilled water to eliminate dirt, followed by the peeling of the husks into small fibers. One hundred grams of fine fiber were extracted using methanol solvent, which was acidified with hydrochloric acid at a concentration of 1 % (v/v). The choice of HCl was informed by prior research demonstrating that extraction solutions with HCl were more effective than those with acetic acid or formic acid in extracting total phenolic compounds, especially anthocyanins^[30]. Maceration was conducted for 24 h at room temperature with a husk sample to solvent weight ratio of 1:10 (w/w), followed by filtration using Whatman No. 1 paper (diameter: 90 mm; CAT No. 1001-090; Whatman International Ltd., Maidstone, UK)^[31]. The supernatant was subjected to a second maceration with methanol solvent containing 1

% HCl (v/v), utilizing a husk-to-solvent weight ratio of 1:10 (w/w) for a duration of 24 h at room temperature. A subsequent filtration step was conducted to collect the supernatant from the second filtration stage. The filtrate from the second filtration was combined with the initial filtrate and concentrated using a rotary evaporator at 50 °C and 80 rpm. The yield of green coconut husk extract was calculated using equation (1).

$$\text{Yield (\%)} = \frac{\text{weight of extract}}{\text{weight of green coconut husk}} \times 100 \quad (1)$$

Sensitivity Test of Green Coconut Husk Extract to pH

The pH sensitivity of green coconut husk extract was investigated using a variety of standard solutions ranging in pH from 5 to 11 produced using H₃PO₄ and NaOH [16], to prove its efficacy as a pH indicator for the manufacturing of food quality film labels. Upon establishing reliable pH sensitivity of the coconut husk extract, it is considered appropriate for the development of smart packaging films.

Smart Films Preparation

The chitosan/PVA based smart films were fabricated followed a sequential procedure reported by previous study^[12] with modifications. Initially, 3.4 g of chitosan was mixed with 80 mL of distilled water containing 10 % (v/v) acetic acid on magnetic stirrer, then left for 24 h at room temperature. 40 mL of distilled water was heated to a temperature of 100 °C, then 1.7 g of PVA was added to it and continued with constant stirring for 2 h until fully dissolved. The PVA solution was cooled to room temperature and then gradually mixed into the chitosan solution, followed by stirring at a constant speed to prevent the formation of lumps.

The incorporation of coconut fiber extract into the PVA and chitosan solution was conducted by adjusting the volume ratio of coconut fiber extract to chitosan at ratios of 1:2, 1:4, 1:6, 2:1, 4:1, and 6:1 (v/v). Subsequently, the film solutions were dispensed using stainless steel

plates with a diameter of 10 cm and left to air-dry for approximately 2 d at room temperature until fully dehydrated. The resulted films were delicately peeled off and stored in sealed containers at room temperature in dark conditions until ready for characterization.

Film Thickness Measurement

The thickness of the films was measured using Mitutoyo No. 293-766 digital micrometer (0.001 mm; Tester Sangyo Co., Ltd., Tokyo, Japan). The average thickness of each film was calculated based on the measurements taken at five different randomly selected positions^[32].

Mechanical Study

The mechanical characteristics of the film were assessed by gauging its tensile strength (TS) and elongation at break (EB) using an Autograph Universal Testing Machine (Shimadzu Corporation, Kyoto, Japan), following the ASTM standard method D882–02^[33]. The film samples were cut into squares measuring 700 mm × 100 mm, then mounted on two grips and tested with a load speed of 1 mm sec⁻¹. The TS and EB were then determined using equation (2) and equation (3) respectively^[32], as follows:

$$\text{TS (MPa)} = \left(\frac{F_m}{x \times w} \right) \quad (2)$$

$$\text{EB (\%)} = \left(\frac{\Delta L}{L_0} \right) \times 100 \quad (3)$$

where:

F_m : maximum pressure causing film fracture (N)

x : thickness of the film (mm)

w : width of the film (mm)

ΔL : length increase at the film break (mm)

L_0 : initial length of the film (mm)

Application of The Colorimetric Indicator Films for Monitoring Milk Freshness

The pH sensitivity of the resulted film was assessed following the method outlined by previous study^[12], with certain adaptations. 100 mL of milk was placed within a clear glass container and sealed using a transparent plastic cover equipped with a colorimetric indicator

film (2 × 2 cm) attached to the inside wall of the glass. The container was kept at room temperature for 48 h. Film color changes were monitored visually and documented every 8 h, and the corresponding pH value of the milk was also measured with a digital pH meter.

Results and Discussion

Yield of Green Coconut Husk Extract

The green coconut husk was subjected to two 24-h maceration processes with methanol and 1 % HCl respectively. After filtration, the solution was evaporated using a rotary evaporator, and the outcomes are depicted in Figure 1. Concentrated extract from green coconut (*Cocos nucifera* L.) husk displayed a typical dark brown color, similar to the color of coconut (*Cocos nucifera*) husk extract illustrated in a previous report^[34].

This current study achieved a 48 % yield (w/w) of concentrated extract from green coconut husk waste, with approximately 29.83-35.51 mg/g of anthocyanin content, based on previous research^[19]. Earlier research has demonstrated differing extract yields, influenced by the type of coconut and the solvent employed. For instance, some researchers extracted husks from three coconut

varieties which grown in Malaysia utilizing ethanol solvent, resulting in yields ranging from 9.65 % to 16.85 % (w/w)^[35], while other researchers varied the concentration of ethanol solvent from 20 % to 100 % to extract local Thai coconut husk and obtained dry extract yields in the range of 4.2 % to 12.3 % (w/w)^[36].

Color Response to pH Change

Anthocyanins undergo structural alterations depending on pH levels, leading to noticeable changes in color perception. The equilibrium structures include: red flavylium cation (below pH 4), colorless carbinol pseudobase (around pH 4–5), blue/purple quinonoidal anhydrobase (around pH 6–8), and light yellow or colorless chalcone (above pH 8)^[37]. Anthocyanin extract from green coconut husk in this current work was at pH 3 and had a brownish red color. Upon the addition of 2 drops of 0.25 N HCl solution, the extract solution shifted towards increased acidity (pH 0.3), resulting in a change in color to a dark brown hue. This occurs because anthocyanin pigments are mostly flavylium cations which imparting their red color. The formation of the flavylium cation at lower pH level enhances anthocyanin solubility in water and intensifies the red color^[38]. The response of extract color to pH change in acidic condition is shown in Figure 2.

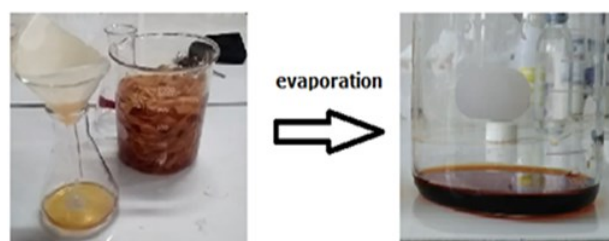


Figure 1. Physical appearance of green coconut husk extract.



Figure 2. The influence of pH on the alteration of color in the extract: (A) Extract color before adding HCl; (B) Extract color after adding HCl

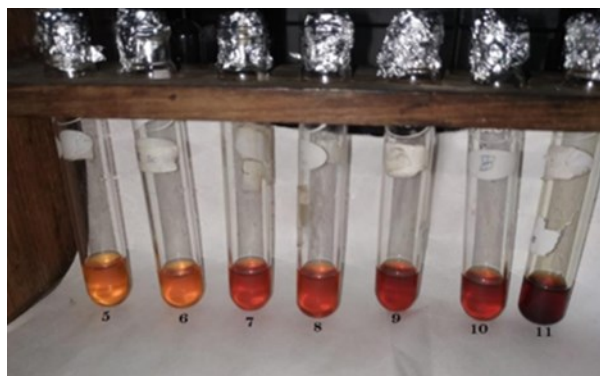


Figure 3. Extract color changes in the pH range from 5 to 11.

The study also conducted pH sensitivity tests of extracts across a range of pH levels, from 5 to 11, utilizing standard solutions of H_3PO_4 and NaOH. The use of H_3PO_4 dan NaOH solutions were performed based on previous literature^[16]. The color differences experienced by green coconut husk extract at various pH values are shown in Figure 3. Figure 3 shows that the color of the extract which was initially brownish red at acidic pH then changed gradually to reddish-purple as the pH value increased to alkaline. The alterations in color indicate that the anthocyanin extract derived from green coconut husk has the potential to serve as an effective indicator of food freshness across a wide pH spectrum. However, the color changes are not very noticeable to the naked eye, which may be due to the low anthocyanin content obtained from the green coconut husk extraction process. In this study, extraction was performed using a methanol solvent with added HCl. The acidic condition of this solvent may be responsible for the degradation of anthocyanins in the green coconut husk extract, as previous research has shown that anthocyanins are unstable in acidic conditions⁽¹⁹⁾.

The color changes of the anthocyanin extract from green coconut husk due to pH differences did not in line with other research observations from different anthocyanin sources. A study observed that anthocyanin extract derived from

jambolan fruit exhibited a characteristic red color at pH levels of 1–2. Within the pH range of 3 to 7, the anthocyanin extract transitioned to a purple shade, while at pH levels above 7, it gradually shifted from purple to blue, and eventually, to green and yellow due to anthocyanin degradation in alkaline conditions^[12]. Substantial alterations in color were likewise noted in bayberry extract abundant in anthocyanins in response to pH variations. Below a pH of 7, the bayberry extract solution exhibited a red/pink hue. Under neutral conditions (pH 7), the solution took on a brown color. Ultimately, at pH levels ranging from 8 to 10, the bayberry solution assumed a purple tint, while at pH 11–12, it transitioned to yellow^[32]. According to a literature, the pH of the solution impacts the color of anthocyanins, attributed to the ionic properties inherent in the molecular structure of anthocyanins^[38].

Color changes at several pH values were also tested on chitosan/PVA films with green coconut husk extract. In this test, indicator films were made with varying volume ratios of coconut husk extract and chitosan, namely 2:1, 4:1, 6:1, 1:2, 1:4, 1:6. The film label was then dripped with a standard solution which has a pH value of 1. Figure 4 shows the color changes that occur during testing the sensitivity of the film to pH.

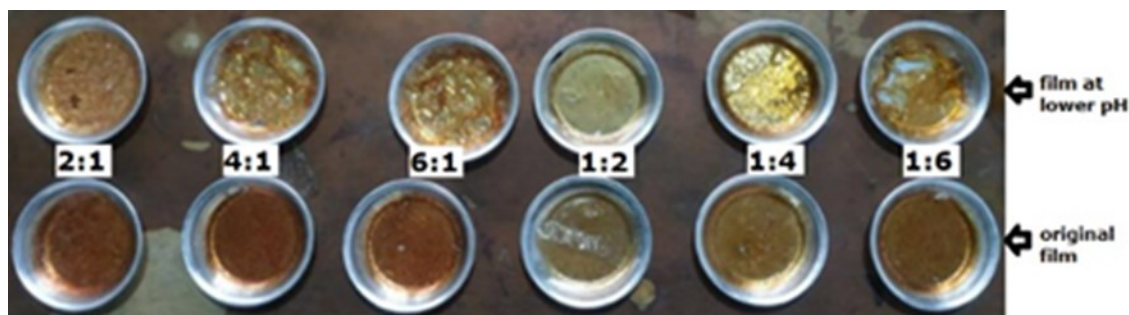


Figure 4. Visual colors of indicator films in a function of extract to chitosan ratio and pH

Figure 4 indicates that the extract content significantly influences the color variation of the indicator film. The introduction of green coconut husk extracts has been shown to darken the color of chitosan films due to the turbidity. This added turbidity affects the optical properties, leading to a more intense yellow appearance^[39]. However, the color of chitosan-based films can be significantly influenced by various factors, such as chitosan concentration, the presence of additives, and the molecular weight of the chitosan itself. Studies indicated that chitosan typically has a yellowish hue due to its chemical structure and chromophores formed during processing. Therefore, with the same extract volume, an increase in chitosan volume will result in a higher color intensity of the film, as observed in the extract-to-chitosan volume ratios of 1:2, 1:4, and 1:6 (v/v).

The color reaction to pH variation in the indicator films was in contrast with the color alteration observed in the green coconut husk extract. All film samples showed a paler color after being treated using HCl solution (pH 1). The results obtained in this study are consistent with previous research^[12], where the film containing anthocyanins from jambolan fruit extract initially exhibited a red color, which then slightly faded when immersed in a lower pH medium (acidic conditions) and shifted to a bluish-purple hue at higher pH levels (alkaline conditions). Moreover, the color change of films based on chitosan, PVA, and jambolan fruit extract became more apparent with rising anthocyanin concentration. The results of this research show that chitosan/PVA films added with extracts from green coconut husk are

sensitive to pH and have great potential for application in smart food packaging.

Thicknesses of Indicator Films

The thickness of the film is essential in influencing its mechanical strength, water vapor permeability, and light transmission characteristics^[40]. Figure 5 illustrates that the thickness of chitosan/PVA-based smart films ranged from 0.28 to 0.38 mm. The incorporation of anthocyanin extract from green coconut husk into chitosan produces thinner films, unlike films derived from chitosan/PVA that utilize anthocyanin from jambolan fruit extract^[12]. Following the previous research, elevated extract levels can yield a more intricate matrix and lead to augmented film thickness^[41]. Nonetheless, the results of this investigation reveal an opposing outcome. The diminished anthocyanin concentration in coconut husk extract may account for the reduction in film thickness as the volume ratio of extract to chitosan increases, as indicated by literature suggesting that variations in composition and anthocyanin levels in the extract can lead to differences in the thickness of the resultant films^[42]. A separate investigation indicated that a high concentration of Chinese bayberry extract integrated into intelligent films derived from cassava starch did not significantly alter the film's thickness^[32]. A separate investigation indicated that a high concentration of Chinese bayberry extract integrated into intelligent films derived from cassava starch did not significantly alter the film's thickness. It is essential to assess the film's thickness with other properties for a thorough evaluation^[43].

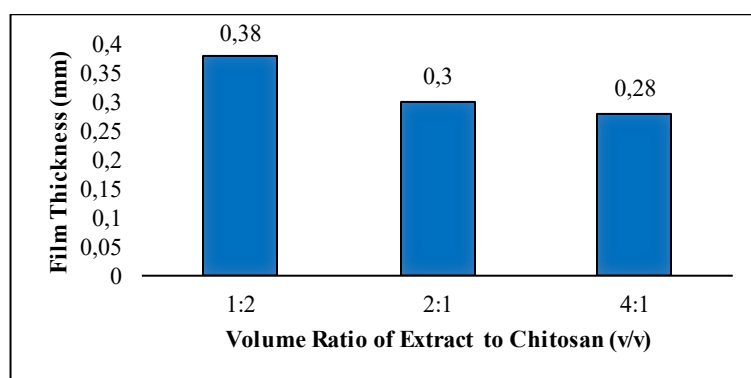


Figure 5. Thicknesses of films

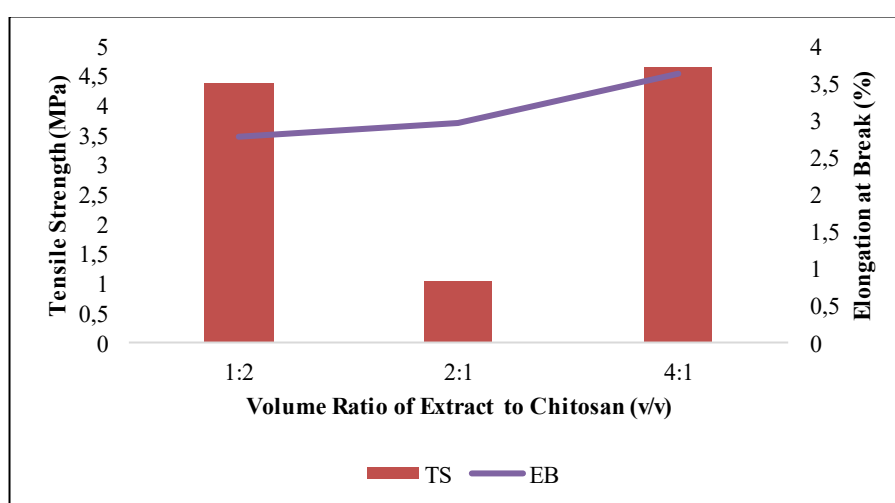


Figure 6. Tensile strength (TS) and Elongation at Break (EB) of films

Mechanical Properties

The mechanical properties of films utilized in food packaging are essential during handling and must withstand external pressures^[44]. The mechanical properties of colorimetric films composed of chitosan/PVA and green coconut husk extract were evaluated using tensile strength (TS) and elongation at break (EB), with the results presented in Figure 6.

TS and EB are the two primary mechanical characteristics that indicate the resistance and stretchability of the films, respectively^[45]. As shown in Figure 6, the TS value of the film exhibited a notable decrease from 4.39 MPa to 1.03 MPa as the extract to chitosan ratio was increased from 1:2 to 2:1. Similar phenomenon was reported^[46]. It was found that the TS of cassava starch/k-carrageenan film was

decreased with the increase of the addition amount of black nightshade (*Solanum nigrum* L.) fruit extract. The decrease in TS of anthocyanin-rich films might be due to the formation of a less dense and fragmented microstructure^[41]. Also, this could be linked to the development of particular interactions between the extract and the composites, as well as the plasticizing effects of green coconut husk extract. These factors influence the positioning of hydrogen bonds within polymer chains, enhancing molecular mobility. As a result, this disrupts the structural integrity network, thereby reducing the tensile strength of the anthocyanin-incorporated film^[45]. Surprisingly, there was a remarkable rise in TS from 1.03 to 4.65 MPa, as the ratio of extract to chitosan was raised from 2:1 to 4:1. Films containing greater amounts of extract exhibited higher TS than

those with lower amounts, suggesting that incorporating green coconut husk extract can enhance the TS of chitosan/PVA films. This could be attributed to the hydrogen bonds that form between the hydroxyl groups of anthocyanin and the polymers (chitosan and PVA), thereby enhancing their adhesion at the interface^[47].

Figure 6 indicates that the addition of green coconut husk extract elevated the EB value from 2.775% to 3.625%. The film enriched with green coconut husk extract exhibited a flexible structure, suggesting its viability for freshness indications. A comparable tendency was noted in chitosan/gelatin films infused with anthocyanin from *Zingiber striolatum* Diels for assessing fish freshness^[48]. The anthocyanin molecule diminished the interactions among adjacent macromolecules and augmented the accessible area for molecular chains to move freely, hence enhancing the film's flexibility^[43].

Application of The Colorimetric Film in Monitoring Milk Freshness

Figure 7 illustrates the variation in milk pH across various storage durations, accompanied by the particular film color reactions. The chitosan/PVA film containing green coconut husk extract exhibits a progressive color change when retained at room temperature for prolonged durations. After 16 h, the pH of the milk declined from 6.91 to 6.82, resulting in a color change of the film to pale brown. Upon reaching a storage duration of 48 h, the pH fell to 5.49, and the film displayed a deeper hue. This decrease in pH resulted in a reduction in the brightness of the film, as the anthocyanins from the coconut husk extract are more stable and intense in higher pH conditions, but lose their vibrancy in more acidic environments. In these conditions, the milk emits a distinct rancid odor, signifying spoiling. The literature attributes these findings to microbial multiplication and lactic acid buildup in milk, leading to substantial CO₂ generation^[49]. In high-humidity situations, acidic gasses increase the acidity of milk, resulting in a fall in pH. The pH alteration subsequently causes a discernible color change in the film containing anthocyanin derived from green coconut husk extract.

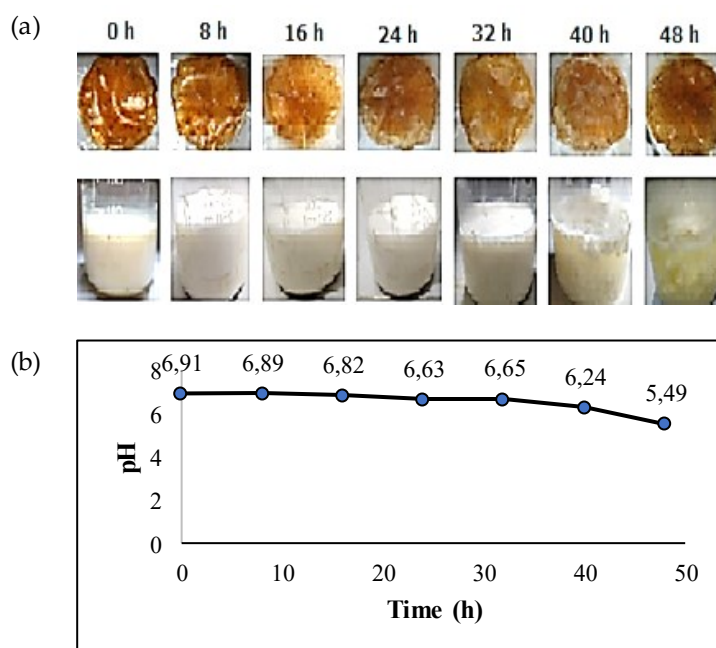


Figure 7. Color response of the film for milk freshness monitoring within 48 h at room temperature, (a) film color difference and milk appearance, (b) the change of pH level of stored milk

This observation is consistent with previous findings^[50], which reported significant color transformations of films prepared from *Aronia melanocarpa* anthocyanins, cassava starch, and PVA to a pink hue after 12 h of milk storage, with further darkening observed after 36 h at 40 °C. Moreover, an investigation about the possible use of black carrot anthocyanins to create pH-responsive indicator films in a cellulose/chitosan matrix had been conducted and noted color variations of these films when exposed to fresh pasteurized milk and spoiled milk stored at 20 °C^[51]. The findings highlight the capability of green coconut husk anthocyanins to change color, serving as an effective indicator for assessing milk quality under different pH conditions.

Conclusions

Colorimetric films responsive to pH were effectively synthesized utilizing chitosan, PVA, and extract from green coconut husk. The extract-to-chitosan volume ratio of 4:1 is the most preferred among the various films with differing extract and chitosan compositions. The material exhibited superior mechanical properties, attaining a maximum tensile strength (TS) of 4.65 MPa and an elongation at break (EB) of 3.625%. The addition of green coconut husk extract resulted in a chitosan/PVA film exhibiting satisfactory pH sensitivity. The film exhibited significant color changes that correlated with pH variations in milk samples, indicating its effectiveness for monitoring milk freshness. This sets forth its potential as an advanced smart packaging material, allowing consumers to visually evaluate milk freshness.

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Declaration of Generative AI and AI-Assisted Technologies

The authors declare that no generative AI or AI-assisted technologies were used in the preparation of this manuscript.

Author Contributions

M.Y.: Methodology, investigation, data collection, and formal analysis. J.: Data curation, visualization, and writing —original draft preparation. H.R.S.: Methodology, validation, and writing —review and editing. R.M.P: Methodology, data curation, and visualization D.R.B.: Conceptualization, corresponding author responsibilities and, and supervision. Both authors have read and approved the final version of the manuscript.

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Declaration of Conflicting Interests

The authors declare no conflict of interest.

References

1. Blakeney M. Chapter 1-Food loss and waste and food security. *Food Loss and Food Waste: Causes and Solutions*, Edward Elgar Publishing, 1–26 (2019).
2. Shao P, Liu L, Yu J, Lin Y, Gao H, Chen H, & Sun P., An overview of intelligent freshness indicator packaging for food quality and safety monitoring. *Trends Food Sci Technol.* 118: 285–96 (2021).
3. Karimi Sani I, Masoudpour-Behabadi M, Alizadeh Sani M, Motalebinejad H, Juma ASM, Asdagh A, Eghbaljoo H, Khodaei S, Rhim J, & Mohammadi F., Value-added utilization of fruit and vegetable processing by-products for the manufacture of biodegradable food packaging films. *Food Chem.*, 405: 134964 (2023).
4. Zhang Q, Lin G, Wang H, Jin MC, Dang H, Zhang J, Guo R, Yan H, Niu B, & Wang H., Development of smart packaging film incorporated with sodium alginate-chitosan quaternary ammonium salt nanocomplexes encapsulating anthocyanins for monitoring

- milk freshness. *Int J Biol Macromol.*, 263: 130336 (2024).
5. Lin WF, Guo HQ, Zhu LJ, Yang K, Li HZ, & Cui L., Temporal variation of antibiotic resistome and pathogens in food waste during short-term storage. *J Hazard Mater.*, 436: 129261 (2022).
 6. Hwang JH, Jung AH, Yu SS, Park SH., Rapid freshness evaluation of cow milk at different storage temperatures using in situ electrical conductivity measurement. *Innovative Food Science & Emerging Technologies*, 81: 103113 (2022).
 7. Devi D, Kumar S, & Mukherjee A., Onion peel extract as milk freshness indicator in biopolymer-based intelligent packaging films. *Food and Humanity*, 2: 100223 (2024).
 8. Gao R, Hu H, Shi T, Bao Y, Sun Q, Wang L, Ren Y, Jin W, & Yuan L., Incorporation of gelatin and Fe²⁺ increases the pH-sensitivity of zein-anthocyanin complex films used for milk spoilage detection. *Curr Res Food Sci.*, 5: 677–86 (2022).
 9. Yun Y, Xu J, Chi W, Liu R, Liu W, Li J, Wang L, & Zhan X., Green Production of Anthocyanin-Fixed Poplar Veneers toward a Smart Label with Higher and Long-Term Accuracy for Supervising the Freshness of Pork. *ACS Sustain Chem Eng.*, 11(5) (2023).
 10. Alizadeh-Sani M, Mohammadian E, & McClements DJ., Eco-friendly active packaging consisting of nanostructured biopolymer matrix reinforced with TiO₂ and essential oil: Application for preservation of refrigerated meat. *Food Chem.*, 322: 126782 (2020).
 11. Bao Y, Cui H, Tian J, Ding Y, Tian Q, Zhang W, Wang M, Zang Z, Sun X, Li D, Si X, & Li B., Novel pH sensitivity and colorimetry-enhanced anthocyanin indicator films by chondroitin sulfate co-pigmentation for shrimp freshness monitoring. *Food Control*, 131: 108441 (2022).
 12. Merz B, Capello C, Leandro GC, Moritz DE, Monteiro AR, & Valencia GA., A novel colorimetric indicator film based on chitosan, polyvinyl alcohol and anthocyanins from jambolan (*Syzygium cumini*) fruit for monitoring shrimp freshness. *Int J Biol Macromol.* 153: 625–32 (2020).
 13. Khan J, An H, Alam S, Kalsoom S, Huan Chen S, Ayano Begeno T, & Du Z., Smart colorimetric indicator films prepared from chitosan and polyvinyl alcohol with high mechanical strength and hydrophobic properties for monitoring shrimp freshness. *Food Chem.*, 445: 138784 (2024).
 14. Chen M, Yan T, Huang J, Zhou Y, & Hu Y., Fabrication of halochromic smart films by immobilizing red cabbage anthocyanins into chitosan/oxidized-chitin nanocrystals composites for real-time hairtail and shrimp freshness monitoring. *Int J Biol Macromol.* 179: 90–100 (2021).
 15. Zong Z, Liu M, Chen H, Farag MA, Wu W, Fang X, Niu B, & Gao H., Preparation and characterization of a novel intelligent starch/gelatin binary film containing purple sweet potato anthocyanins for *Flammulina velutipes* mushroom freshness monitoring. *Food Chem.* 405: 134839 (2023).
 16. Ranjbar M, Azizi Tabrizzad MH, Asadi G, & Ahari H., Investigating the microbial properties of sodium alginate/chitosan edible film containing red beetroot anthocyanin extract for smart packaging in chicken fillet as a pH indicator. *Heliyon*, 9: e18879 (2023).
 17. Heydarian A & Shavisi N., Multifunctional food packaging materials: Electrospun mats based on gelatin-xanthan gum containing chitin nanofibers and black barberry anthocyanins for freshness monitoring and enhancing the shelf-life quality of Pacific white shrimps. *Food Packag Shelf Life.* 40: 101219 (2023).
 18. Ma Y, Li S, Ji T, Wu W, Sameen DE, Ahmed S, Qin W, Dai J, & Liu Y., Development and optimization of dynamic gelatin/chitosan nanoparticles incorporated with blueberry anthocyanins for milk freshness monitoring. *Carbohydr Polym.*, 247: 116738 (2020).
 19. Rodiah MH & Ariyani R., Effects of different physical parameters on the stability of anthocyanin from coconut (*Cocos nucifera*) husk. *Journal of Tropical Resources and Sustainable Science (JTRSS)*, 11(2): 11–6 (2023).
 20. Nadi M, Razavi SMA, Shahrampour D. Fabrication of green colorimetric smart packaging based on basil seed gum/chitosan/red cabbage anthocyanin for real-time monitoring of fish freshness. *Food Sci Nutr.* 2023 Oct 1;11(10):6360–75.
 21. Liu Y, Tong F, Xu Y, Hu Y, Liu W, Yang Z, Liao L, Li X, Wang Z, Li J, & Zhou W., Development of antioxidant and smart NH₃-sensing packaging film by incorporating bilirubin into κ-carrageenan matrix. *J Sci Food Agric.* 103(14): 7030–9 (2023).
 22. He Y, Yuan Y, Gao Y, Chen M, Li Y, Zou Y, et al. Enhancement of Colorimetric pH-Sensitive Film Incorporating *Amomum tsaoko*

- Essential Oil as Antibacterial for Mantis Shrimp Spoilage Tracking and Fresh-Keeping. *Foods*, 13(11) (2024).
23. Păușescu I, Dreavă DM, Bîtcă I, Argetoianu R, Dăescu D, & Medeleanu M., Bio-Based pH Indicator Films for Intelligent Food Packaging Applications. *Polymers (Basel)*, 14(17): 3622 (2022).
 24. Ezati P & Rhim JW., pH-responsive chitosan-based film incorporated with alizarin for intelligent packaging applications. *Food Hydrocoll.*, 102: 105629 (2020).
 25. Kadam S, Patil-Sankpal P, Hajare A, Jangade N, Patil S, Patil P, Mohite K, Suryawanshi S, & Patil P., Chapter 18 - Safety, regulations, and economic impact of chitosan nanostructures. *Chitosan-Based Hybrid Nanomaterials*, (Ed: Ali N, Bilal M, Khan A, & Nguyen TA.), Elsevier, 333–8 (2024).
 26. LogithKumar R, KeshavNarayan A, Dhivya S, Chawla A, Saravanan S, & Selvamurugan N., A review of chitosan and its derivatives in bone tissue engineering. *Carbohydr Polym.*, 151: 172–88 (2016).
 27. Yu Z, Li B, Chu J, & Zhang P., Silica in situ enhanced PVA/chitosan biodegradable films for food packages. *Carbohydr Polym.*, 184: 214–20 (2018).
 28. Youssef AM, Assem FM, Abdel-Aziz ME, Elaaser M, Ibrahim OA, Mahmoud M, & Abd El-Salam M., Development of bionanocomposite materials and its use in coating of Ras cheese. *Food Chem.*, 270: 467–75 (2019).
 29. Sik B, Hanczné EL, Kapcsándi V, & Ajtony Z., Conventional and nonconventional extraction techniques for optimal extraction processes of rosmarinic acid from six Lamiaceae plants as determined by HPLC-DAD measurement. *J Pharm Biomed Anal.*, 184: 113173 (2020).
 30. Stanoeva JP, Stefova M, Balshikevska E, Tusevski O, & Simic SG., Comparison of the Effect of Acids in Solvent Mixtures for Extraction of Phenolic Compounds From *Aronia melanocarpa*. *Natural Product Communications*, 15(7): 1-10 (2020).
 31. Buamard N & Benjakul S., Improvement of gel properties of sardine (*Sardinella albella*) surimi using coconut husk extracts. *Food Hydrocoll.*, 51: 146–55 (2015).
 32. Yun D, Cai H, Liu Y, Xiao L, Song J, & Liu J., Development of active and intelligent films based on cassava starch and Chinese bayberry (*Myrica rubra* Sieb. et Zucc.) anthocyanins. *RSC Adv.*, 9(53):30905–16 (2019).
 33. Helmiyati H, Hidayat ZSZ, Sitanggang IFR, & Liftyawati D., Antimicrobial packaging of ZnO–Nps infused into CMC–PVA nanocomposite films effectively enhances the physicochemical properties. *Polym Test.*, 104:107412 (2021).
 34. Akinpelu DA, Alayande KA, Aiyegoro OA, Akinpelu OF, & Okoh AI., Probable mechanisms of biocidal action of *Cocos nucifera* Husk extract and fractions on bacteria isolates. *BMC Complement Altern Med.*, 15(1): 116 (2015).
 35. Wahab M, Rushdan Zaim IN, Ismail HF, Othman N, Hara H, & Md Akhir FN., Evaluation of flavonoid compound in coconut waste and its antioxidant activity. In: *IOP Conf. Ser.: Earth Environ. Sci.*, 1144: 012006 (2023).
 36. Olatunde OO, Benjakul S, & Vongkamjan K., Coconut husk extract: antibacterial properties and its application for shelf-life extension of Asian sea bass slices. *Int J Food Sci Technol.*, 54(3): 810–22 (2019).
 37. Halász K & Csóka L., Black chokeberry (*Aronia melanocarpa*) pomace extract immobilized in chitosan for colorimetric pH indicator film application. *Food Packag Shelf Life.*, 16: 185–93 (2018).
 38. Turturica M, Oancea AM, Rapeanu G, & Bahrim G., Anthocyanins: Naturally occurring fruit pigments with functional properties. *Annals of the University Dunarea de Jos of Galati*, 39: 9–24 (2015).
 39. Shiekh KA, Liangpanth M, Luesuwan S, Kraisthisirintr R, Ngwangam K, Rawdkuen S, Rachtanapun P, Karbowiak T, & Tongdeesontorn W., Preparation and Characterization of Bioactive Chitosan Film Loaded with Cashew (*Anacardium occidentale*) Leaf Extract. *Polymers (Basel)*, 14(3): 540 (2022).
 40. Toro-Márquez LA, Merino D, Gutiérrez TJ., Bionanocomposite Films Prepared from Corn Starch With and Without Nanopackaged Jamaica (*Hibiscus sabdariffa*) Flower Extract. *Food Bioproc Tech.*, 11(11): 1955–73 (2018).
 41. Yong H & Liu J., Recent advances in the preparation, physical and functional properties, and applications of anthocyanins-based active and intelligent packaging films. *Food Packag Shelf Life.*, 26: 100550 (2020).
 42. Lozano-Navarro JI, Díaz-Zavała NP, Velasco-Santos C, Martínez-Hernández AL, Tijerina-Ramos BI, García-Hernández M, Rivera-Armenta JL, Páramo-García U, & Reyes-de la Torre A., Antimicrobial, optical and

- mechanical properties of Chitosan–Starch films with natural extracts. *Int J Mol Sci.*, 18(5): 997 (2017).
43. Xu H, Shi Y, Gao L, Shi N, Yang J, & Hao R., Preparation and characterization of PH-responsive polyvinyl alcohol/chitosan/anthocyanin films. *Food Science and Technology (Brazil)*, 43: e98022 (2023).
 44. Mirzaei A, Bina Jorshari Y, Jananshir S, Noori M, & Mahdavi M., Colorimetric pH-sensitive hydrogel film based on kappa-carrageenan containing quercetin or eucalyptus leaf extract for freshness monitoring of chicken meat. *Food Chem X.*, 22: 101307 (2024).
 45. Narayanan GP, Radhakrishnan P, Baiju P, & S AM., Fabrication of Butterfly Pea Flower Anthocyanin-Incorporated Colorimetric Indicator Film Based on Gelatin/Pectin for Monitoring Fish Freshness. *Food Hydrocolloids for Health*, 4: 100159 (2023).
 46. Cao J, Wang C, Zou Y, Xu Y, Wang S, Jiang C, Liu T, Zhou X, Zhang Q, & Li S., Colorimetric and antioxidant films based on biodegradable polymers and black nightshade (*Solanum nigrum* L.) extract for visually monitoring *Cyclina sinensis* freshness. *Food Chem X.*, 18: 100661 (2023).
 47. Koosha M & Hamedi S., Intelligent Chitosan/PVA nanocomposite films containing black carrot anthocyanin and bentonite nanoclays with improved mechanical, thermal and antibacterial properties. *Prog Org Coat.*, 127: 338–47 (2019).
 48. Qin Y, Wang Y, Tang Z, Chen K, Wang Z, Cheng G, Chi H, & Soteyome T., A pH-sensitive film based on chitosan/gelatin and anthocyanin from *Zingiber striolatum* Diels for monitoring fish freshness. *Food Chem X.*, 23: 101639 (2024).
 49. Moazami Goodarzi M, Moradi M, Tajik H, Forough M, Ezati P, & Kuswandi B., Development of an easy-to-use colorimetric pH label with starch and carrot anthocyanins for milk shelf life assessment. *Int J Biol Macromol.*, 153: 240–7 (2020).
 50. Wu X, Yan X, Zhang J, Wu X, Luan M, & Zhang Q., Preparation and characterization of pH-sensitive intelligent packaging films based on cassava starch/polyvinyl alcohol matrices containing *Aronia melanocarpa* anthocyanins. *LWT.*, 194: 115818 (2024).
 51. Ebrahimi Tirtashi F, Moradi M, Tajik H, Forough M, Ezati P, & Kuswandi B., Cellulose/chitosan pH-responsive indicator incorporated with carrot anthocyanins for intelligent food packaging. *Int J Biol Macromol.*, 136: 920-6 (2019).