



Fabrication of flexible chitosan film reinforced with pulping by-product lignosulfonates for cherry-tomato preservation

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ABSTRACT

The massive production of food waste and plastic pollution necessitates innovative solutions. This study reports the first fabrication of a flexible chitosan (CH) film reinforced with lignosulfonate (LS) derived from pulping byproduct as a sustainable alternative to synthetic food packaging. The CH/LS composite film was prepared by a simple casting method with varying LS contents of 1 % and 2 %. Compared to CH film, the addition of 2 % LS increased the tensile strength by over 4 times and decreased water vapor permeability by 11 %. Moreover, the CH/LS film exhibited excellent UV-shielding properties. This novel use of LS to reinforce CH film presents an eco-friendly active packaging material. When used to package cherry tomatoes for 2 weeks, the CH/LS film effectively maintained fruit freshness and hardness while minimizing weight loss. This work provides new scientific evidence on the optimized preparation and application of CH/LS composite films from renewable resources for food preservation.

Introduction

Abundant food loss is a pressing global concern. Among various food categories, the highest proportion of food loss occurs during the post-harvest processing of fruits and vegetables. Cherry tomatoes, known for their nutritional value and significant market segment, are highly susceptible to bacterial invasion due to their high moisture content and nutrition. This can shorten their shelf-life and potentially lead to food-borne illnesses. To extend the shelf life of cherry tomatoes, the food industry has long relied on chemical preservatives such as sulfur dioxide, benzoates, sorbates, isoascorbic acid, sodium erythorbate, thiol-containing amino acids, and 4-hexylresorcinol by inhibiting microbial growth (Oms-Oliu et al., 2010; You et al., 2022). However, many consumers have become increasingly wary of the potential toxicity of these chemical additives. As a result, there is growing demand for more natural ways to preserve fresh cherry tomatoes without compromising their flavor or nutritional value. Food packaging offers a simple and cost-effective method to maintain freshness. However, the use of single-use petroleum-based plastic films for food packaging contributes to the

serious global problem of plastic pollution. Biomass-derived biodegradable films could serve as a viable alternative (Rasheed et al., 2020).

Biomass derived packaging films has been commonly and widely investigated with cellulose, chitosan, and starch, etc. Among the various biopolymer, chitosan (CH) has received particular attention for its potential in food packaging due to its ability to form films and its desirable mechanical, biocompatible, and biodegradable properties. CH is obtained by deacetylation of chitin contained in the shells of crustaceans (López-Carballo et al., 2013; He et al., 2021). It is a natural poly-cation with wide applications in biomedical and food industries. Depending on the intended use, CH can be easily fabricated into various forms such as gels, films, or sponges (Ambaye et al., 2022). Lignosulfonate (LS) is obtained through the sulfonation of lignin from lignocellulosic biomass such as grass or wood (Kumarihami et al., 2022). LS is a natural anionic polymer with numerous anionic polar groups such as phenol, aliphatic hydroxyl, carbonate, and sulfonic acid groups. However, its current applications have primarily been limited to being a binder for concrete and similar purposes (Zhu & Wakisaka, 2021). There have been no reports on the use of LS in food packaging films, likely due to its

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insufficient film-forming ability when used alone (Lora & Glasser, 2002; Marand et al., 2021). A recent proposal suggests the production of a chitosan and lignosulfonate (CH/LS) composite film using the Layer by Layer method, and it was not applied to food preservation (Xu et al., 2021; Ushimaru et al., 2021). The idea of this paper is to produce a CH/LS composite film by mixing both solutions as a polyelectrolyte complex followed by simple casting process for film formation. This CH/LS composite film is expected to offer improved stability, reduced water vapor permeability (WVP), and more effective antimicrobial properties in addition to the benefits of the sole CH film (Zhang et al., 2021).

Herein, this study focused on fabricating bio-composites using CH and LS derived from renewable biomass resources. It should be emphasized that these resources are currently underutilized or wasted. The performance of CH/LS composite films as a potential material for food packaging, specifically for fruits, was evaluated in this research. To assess the suitability of CH/LS films for this purpose, a comprehensive characterization was conducted. This included evaluating mechanical and optical properties, as well as WVP. Moreover, the nutritional changes in cherry tomatoes were monitored over a two-week period to determine the effectiveness of CH/LS film preservation.

Materials and methods

Preparation of CH/LS biocomposite film

Chitosan ($C_6H_{11}NO_4$, $n = 700,000\text{--}800,000$; the deacetylation degree of chitosan $\geq 90\%$) and ascorbic acid (Vc) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD., China. Pulping byproduct sodium lignosulfonate (content $\geq 98\%$, $0.10\text{ USD}\cdot\text{g}^{-1}$) was provided by Guanyun Limin Renewable Resources Technology Development Co., LTD., Jiangsu, China.

The preparation commenced by dissolving 1 g LS powder in 50 mL distilled water. As illustrated in Fig. 1, the resulting solution was then subjected to centrifugation at 6000 rpm for 10 min. Similarly, 1 g CH

powder was dissolved in 50 mL distilled water, along with the addition of Vc (1 g), then centrifuged at 6000 rpm for 10 min. Subsequently, the LS and CH solutions were mixed and stirred continuously for 15 min. To eliminate bubbles in the CH/LS film forming liquid, the mixture underwent degassing (Qin et al., 2021). The plate glass petri dishes (diameter of 15 cm) were utilized to cast 20 mL CH/LS film forming solution. The films were dried at $35\text{ }^\circ\text{C}$ for 24 h until the surface achieved a firm and sticky consistency. Subsequently, they were stored in the dryer (DHG-9000-9005, Heheng Instrument Equipment Co., LTD., Shanghai, China) at 50 % relative humidity at $20\text{ }^\circ\text{C}$ for 30 min. For analysis purposes, the CH/LS films were separated from the glass petri dishes.

Film thickness and mechanical properties

The thickness of the CH/LS biocomposite film was measured at five different points: top, left, right, middle, and bottom using a Digital micrometer (YHT Micrometer, China). The mechanical properties of the film were analyzed using a texture analyzer (TMS-PRO, Food Technology Co., Sterling, USA). The film was cut into a rectangle of $60\text{ mm} \times 10\text{ mm}$ and secured between two metal clips on the texture analyzer. The initial clamping distance was set to 60 mm, and the tensile rate was maintained at 60 mm/min. The tensile strength and elongation at break of the film were calculated as follows (Xiao et al., 2021):

$$\text{Tensile strength : TS(MPa)} = \frac{F}{W \times x} \quad (1)$$

Among them: F represents force (N) to break, W represents width (mm), and x represents thickness (mm) of the film, respectively.

$$\text{Elongation at break : EB(\%)} = \frac{L}{L_0} \times 100 \quad (2)$$

In the formula, L represents the elongation at break of the film (mm), and L_0 represents the original length of the film (mm).

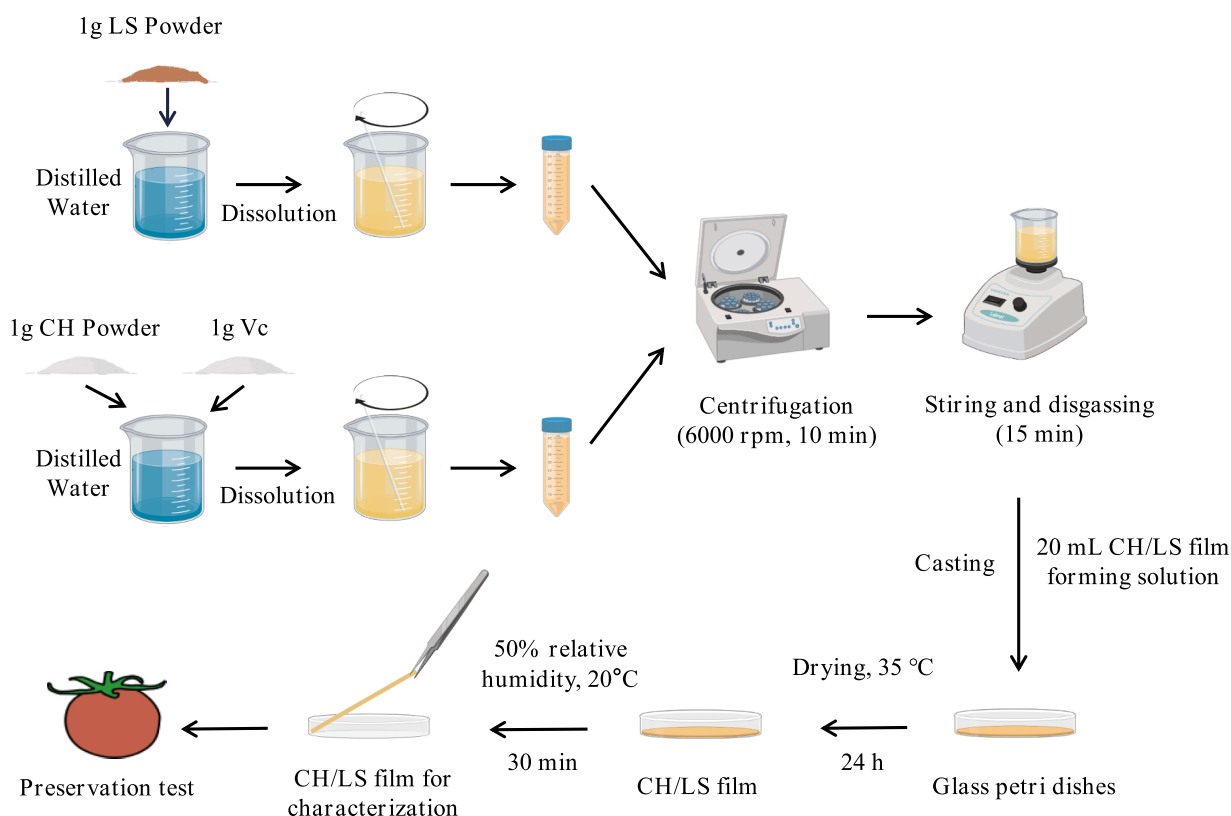


Fig. 1. Preparation of chitosan film reinforced with lignosulfonates for cherry-tomato preservation.

Optical properties

Using the SC-80C colorimeter (Kangguang Instrument Co., LTD., Beijing, China), equipped with a D65 light source and 10° observer, the color of the film was measured. The L*, a*, and b* values were recorded using the CIE-Lab color scale. L* represents lightness, ranging from 0 to 100, indicating the color from dark (black) to light (white); a* represents red-green, with values changing from positive to negative, indicating the color from red (positive) to green (negative); The higher the value of a, the redder the color, and the lower the value of a, the greener the color; b* represents yellow-blue, with values changing from positive to negative, indicating the color from yellow (positive) to blue (negative); The higher the value of b, the more yellow the color, and the lower the value of b, the bluer the color. The instrument was calibrated using a standard white plate (Zhang et al., 2020). L* = 92.94, a* = -0.21, and b* = -0.07 represented color values of standard white plate. Measurements of each film was repeated three times.

FTIR & XRD analysis

The FT-IR spectra of the film were recorded by ATR from 4000 to 400 cm⁻¹ in 32 consecutive scans with a resolution of 0.8 cm⁻¹ using infrared spectrophotometer (Varian 670-IR, Agilent Technologies, Palo Alto, USA) (Cui et al., 2012). XRD patterns of the films from 5° to 75° were measured with an X-ray diffractometer (AXS D8 Advance, Bruker Inc., Karlsruhe, Germany) under 40 kV and 40 mA conditions.

Water vapor permeability (WVP) evaluation

The WVP of the film was determined using a gravimetric method, which involved some modifications to ASTM E96-00 standard. In simpler terms, a film sample measuring 6 cm × 6 cm was sealed on top of a 40 g silicone bottle and placed inside a 20 °C dryer filled with distilled water. The weight gain of the silica gel was measured every 2 h for a total period of 12 h. Each membrane was tested three times. The WVP (kg•s(1-m)) of (kg•s) toxemia (l-m)(toxemia (Pa)) was calculated according to the following formula (Chen et al., 2020):

$$WVP = \frac{W \times X}{S \times P \times T} \quad (3)$$

X is the film thickness, mm; S is the effective area, S = 19.625 × 10⁻⁴ m²; W is the mass of water penetration, g; T is the interval time, h; P is the pressure difference between the two sides of the film (25 °C).

Measurement of light-barrier properties

The light-barrier properties of the film were analyzed by a UV-Vis spectrometer (UKE Instruments Co., LTD., Shanghai) in the wavelength range of 350–1020 nm. A 4 mL quartz cubette was used, and its walls were completely wrapped with the film. Each film measurement was repeated three times.

Preservation test

Fresh cherry tomatoes (Pearl red variety, sourced from Guangdong, China) of the current season were selected for this study. Cherry tomatoes of comparable size and quality were packaged using CH and CH/LS (2 %) films, and their performance was compared to that of polyethylene films (20 cm × 20 cm, purchased from RT-Mart, Yangzhou). Each package contained two cherry tomatoes. The packaged tomatoes were stored in an incubator at 17 °C and a relative humidity (RH) of 68 % for two weeks. The degree of rot was determined by visual observation of the tomatoes' appearance on a daily basis. Signs of deterioration such as wrinkling, mold growth, and leakage were checked, and all other parameters of two cherry tomatoes in each package were measured three times. Weight changes were measured by weighing packaged

cherry tomatoes on an analytical balance (AL204, METTLER TOLEDO, Shanghai) for two weeks. Weight loss rate (%) was calculated by the following formula:

$$\text{Weight loss rate (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (4)$$

W_i is the initial weight; W_f is the final weight.

The hardness was measured using a fruit hardness tester (FR-5105, Felles Photonic Instruments Co., Ltd., HK), which is typically expressed in units of pressure that the testing machine can withstand (N). Total soluble solids (TSS) content was measured using a digital refractometer (WZ-103, Topyun, Hangzhou). Cherry tomato juice was extracted by squeezing and a drop was placed on the refractometer prism. TSS was measured in °Brix units at room temperature. The titratable acid (TA) content was determined by titrating cherry tomato juice with 0.1 N NaOH solution using phenolphthalein as indicator.

Statistical analysis

The data were processed using SPSS 23.0 software and statistical difference was determined by Duncan test and ANOVA in a 95 % confidence interval.

Results

Characterization of CH/LS composite film (FTIR & XRD)

The absorption peaks of CH/LS film matrix as characterized by FTIR spectroscopy were shown in Fig. 2a, including stretching peaks of O—H (3308 cm⁻¹), single bond C—H stretching (2942 cm⁻¹), C—O single bond (1038 cm⁻¹), and C=O stretching on the benzene ring/ketone group (1378 cm⁻¹). There was no significant difference in the absorption patterns between the CH/LS composite film and CH film, indicating that the original functional groups were preserved during the binding process (Cui et al., 2011). However, after adding LS, the absorbance of each functional group increased. This could be attributed to the formation of a more ordered and dense structure in the CH/LS film. The characteristic bands of CH/LS conjugate at 1714 cm⁻¹ and 1142 cm⁻¹ were not found in the CH film, corresponding to the special C=O stretching on the benzene ring of sodium lignosulfonate and O-R stretch. It is worth noting that the O—H stretching band of CH/LS films also underwent a slight shift from 3308 cm⁻¹ to 3313 and 3320 cm⁻¹ after adding LS to the films (Han et al., 2018). This shift is caused by hydrogen bonding between the CH and LS. In the spectrum below 800 cm⁻¹, variations in the aromatic C—H peak were observed due to the single-bond stretching vibration. This could explain the distinct odor brought by the addition of LS to the film (Moradi et al., 2019). Furthermore, the peak areas around 3320 cm⁻¹ and 2942 cm⁻¹ are much higher compared to those of single CH or LS, providing evidence of covalent linkage between CH and LS via imine and ester bonds, forming a poly-electrolyte complex.

XRD analysis revealed the crystallinity of CH and CH/LS composite films (Fig. 2b). The CH film exhibited five peaks at 9.2°, 11.8°, 16.9°, 18.4°, and 21.6°, in line with the ordered semi-crystallinity of CH (Mahmood et al., 2012). The CH/LS film showed diffraction planes at approximately 2θ = 10.2° and 20.2°, respectively. The peak intensity of the CH/LS film vanished at 2θ = 10.2° and 20.2°, while a distinctive steamed peak emerged at 2θ = 20.8°. The incorporation of LS influenced the film's crystallization properties through hydrogen bonding and electrostatic interaction (Liu et al., 2020). In the case of the CH film, a broader peak was observed instead of a single peak. The broadening of peaks indicates the amorphous properties of the composite films (Shahbazi et al., 2016). The presence of multiple peaks with varying heights and widths at 2θ = 20.8° in the CH/LS hybrid film suggests that the initially apparent amorphous structure of the composite film transformed into a more crystalline form after drying at 35 °C for 24 h. The

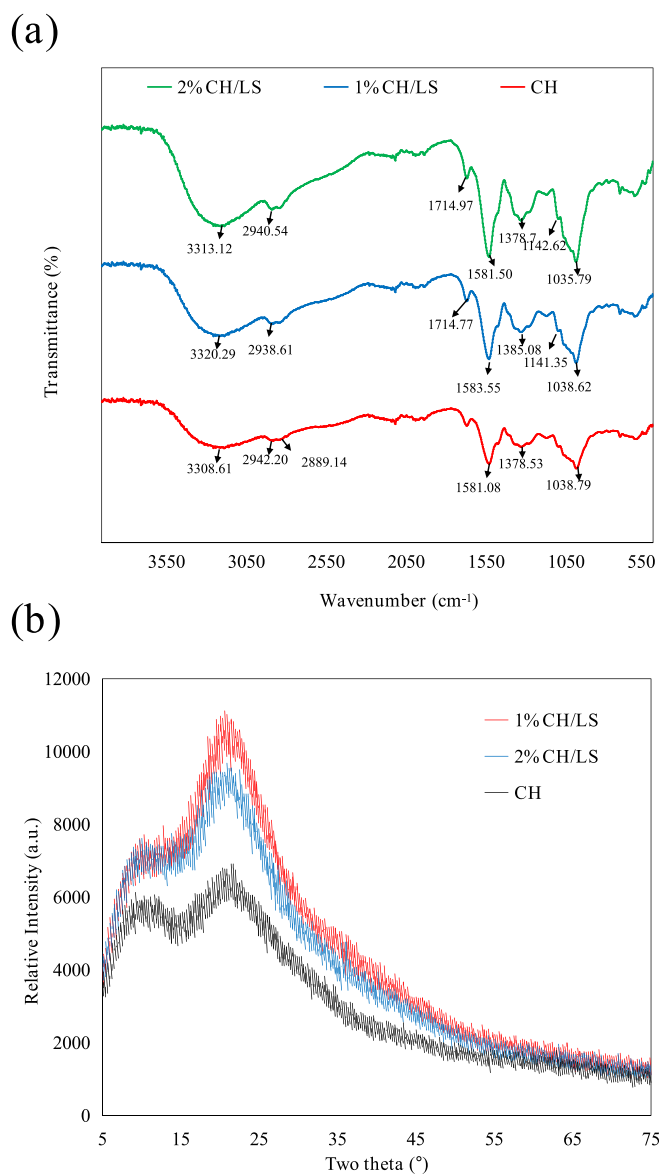


Fig. 2. Profile of FTIR (a) and XRD analysis (b) of CH/LS composite films.

increased crystallinity and interfacial interactions contributed to a denser structure, resulting in enhanced compatibility of the LS.

Optical properties of CH/LS film

The optical properties of CH/LS film including the L value (lightness), b value (yellowness) and a value (redness), were analyzed and the results were summarized in Table S1. The yellowness and redness increased as the LS content increased, while the lightness decreased (Nada et al., 1989). These findings are consistent with the macroscopic observation of the films shown in Fig. S1. Compared to pure CH, CH/LS films containing 1 %-2% LS showed an increase in redness due to the presence of sulfonated lignin (Sarathy & Mohseni, 2007). This is because lignin contains a significant number of auxiliary pigment groups and chromophores such as quinone groups, conjugated double bonds, carbonyl groups, and free radicals, as well as auxiliary pigments like phenolic hydroxyl, hydroxyl, and carboxyl groups (Qian et al., 2014; Qian et al., 2017). However, the increased redness of the film is considered a desirable characteristic for food packaging as it provides protection against light (He et al., 2022).

The compatibility of the CH/LS composite was evaluated by

macroscopic observation of the films (Shariat et al., 2013). The resulting CH/LS films were semi-translucent, as depicted in Fig. S1. The words covered by the film remained clearly visible, indicating good transparency. Homogeneous films were obtained by uniformly mixing the CH and LS solutions before casting. While the CH film exhibited slight yellowing, the addition of LS caused the film to become brownish and darker. The surface of the CH/LS film was smooth, and no agglomeration was observed.

Mechanical properties of CH/LS film

Mechanical properties of CH/LS films were summarized in Table 1. The prepared films, with a thickness of approximately 0.05 mm, had a water content ranging from 37.55 % to 44.87 %, respectively. As LS was added, the CH/LS film exhibited better compactness compared to the CH film due to increased density of the composite film. The appropriate amount of water content in the film provided flexibility suitable for food packaging. Increasing the LS content could help reduce the moisture content of the CH/LS film (Qin et al., 2020). Lower water content in the films could effectively inhibit microbial activity (Rubilar et al., 2013).

The tensile strength of the CH/LS composite film was four times higher than that of the CH film. This increase in tensile strength was attributed to the intermolecular hydrogen bonding of CH/LS complexes, which contributed to the toughness of the film (Zamudio-Flores et al., 2015). Additionally, the tensile strength of the CH/LS films might also be enhanced by the internal network formed by LS and CH through covalent crosslinking. On the other hand, LS significantly improved the elongation at break of the CH film, allowing for larger deformation of the CH/LS film, which was desirable for food packaging (Kanatt, 2020).

WVP and UV-shielding properties of CH/LS films

The water vapor barrier property of the films is reflected by the WVP. Packaging applications require a low WVP value to restrict the transfer of water vapor between the food and the external atmosphere. As shown in Fig. 3a, CH film exhibited a high WVP value ($\sim 17.11 \times 10^{-8} \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$), which could be attributed to its abundant hydrophilic groups. However, the addition of LS led to a decrease in the WVP of CH films ($\sim 15.19 \times 10^{-8} \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$). This was due to the dense polymeric network formed by CH and LS polyelectrolyte complexes, which narrowed the path for water vapor (Oymaci & Altinkaya, 2016). Similar findings were previously reported for antimicrobial films containing CH and modified starch (CH-MS) (Zamudio-Flores et al., 2010).

The transmittance of food packaging film is critically important. Nutrient loss, discoloration, and odor can easily occur due to the oxidation of food exposed to UV and visible light (Liu et al., 2017). The transmittance of the films was different from the LS content, as shown in Fig. 3b. The optical properties of the CH and CH/LS films were determined. All films exhibited an increase in light transmittance and remained unchanged after 800 nm of wavelength. Higher clarity of CH film showed slightly higher transmittance for a wide range from UV to visible wavelengths. When LS content increased to 2 %, CH/LS film showed the lowest transmittance. LS contains abundant unsaturated bonding, such as π -bonded C=C, benzene rings, and C=O unsaturated groups, which contribute to the UV-shielding effect in the UV range

Table 1
Mechanical properties of the CH/LS films.

Films	T (mm)	TS (MPa)	EB (%)
CH-films	0.056 ± 0.002^a	4.73 ± 1.72^b	9.18 ± 2.11^b
CH/LS (1 %)-films	0.056 ± 0.001^a	20.90 ± 3.73^a	21.47 ± 8.83^a
CH/LS (2 %)-films	0.051 ± 0.001^b	21.75 ± 2.18^a	26.52 ± 2.18^a

Note: Values are mean \pm SD (n = 5). Different letters in the same column represent significant difference in the analysis (P < 0.05). T: Thickness; TS: tensile strength; EB: elongation at break.

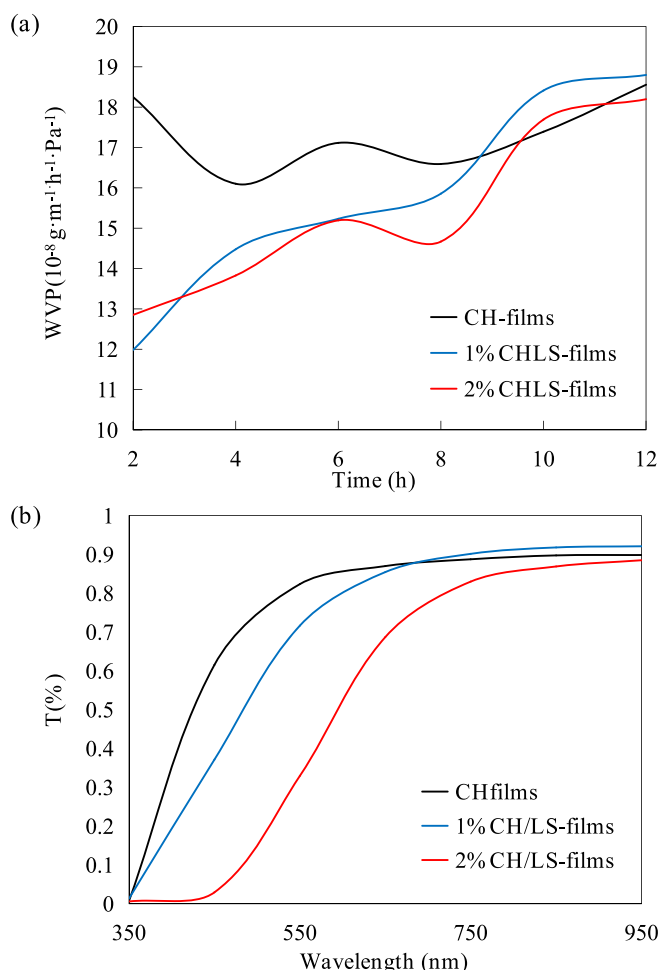


Fig. 3. The water vapor permeability (a) and transmittance (b) of the CH film and CH/LS composite films.

between 350 and 600 nm (Sivarooaban et al., 2008). The film containing LS could effectively prevent UV-induced oxidation and deterioration of food, especially protein- or vitamin-rich foods (Bitencourt et al., 2014).

Preservation of cherry tomatoes with CH/LS film

Based on the characterization results in Sections “Optical properties of CH/LS film” and “WVP and UV-shielding properties of CH/LS films”, the 2 % CH/LS film exhibited optimal improvements in mechanical properties and moisture barrier compared to the 1 % CH/LS film. Specifically, the 2 % CH/LS film showed higher tensile strength and lower water vapor permeability than 1 % CH/LS film. Therefore, only the 2 % CH/LS film formulation was selected for testing the preservation of cherry tomatoes. The effectiveness of this optimized 2 % CH/LS nano-composite film to maintain cherry tomato quality attributes during storage was evaluated over a two week period. As shown in Fig. S2, internal decay and surface wrinkles were observed in control groups wrapped with polyethylene films. The formation of calyx folds on cherry tomatoes surfaces was faster than that of CH/LS film because of the high WVP of CH film. Cherry tomatoes wrapped with CH/LS films were plump and maintained good appearances with fewer wrinkles on their surfaces.

The biggest changes in color values (ΔE) during preservation of cherry tomatoes were observed in control groups wrapped with polyethylene films compared to cherry tomatoes wrapped with CH or CH/LS film (Fig. 4). ΔE is defined as the total color difference of the sample, but it cannot indicate the deviation direction of the color difference of the sample. It is calculated by the following formula: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ (Yao et al., 2021). The subtle changes of darkening and increase of redness were observed using the CIE lab color scale, and this difference was usually more obvious under strong light illumination. As the CH/LS films with UV-shielding effects protected the cherry tomatoes from light damage, no significant color difference was observed. Thus, CH/LS film is considered to be effective for keeping the fruits appearances good during long-term storage.

CH/LS (2 %) films were most effective in avoiding physiological changes in cherry tomatoes such as firmness, weight loss, TSS, and titratable acid content (Fig. 5). The firmness of cherry tomatoes gradually decreased with time from an initial value of 19.4 N (Fig. 5a). As the degree of wrinkle formation is closely related to firmness, the CH/LS

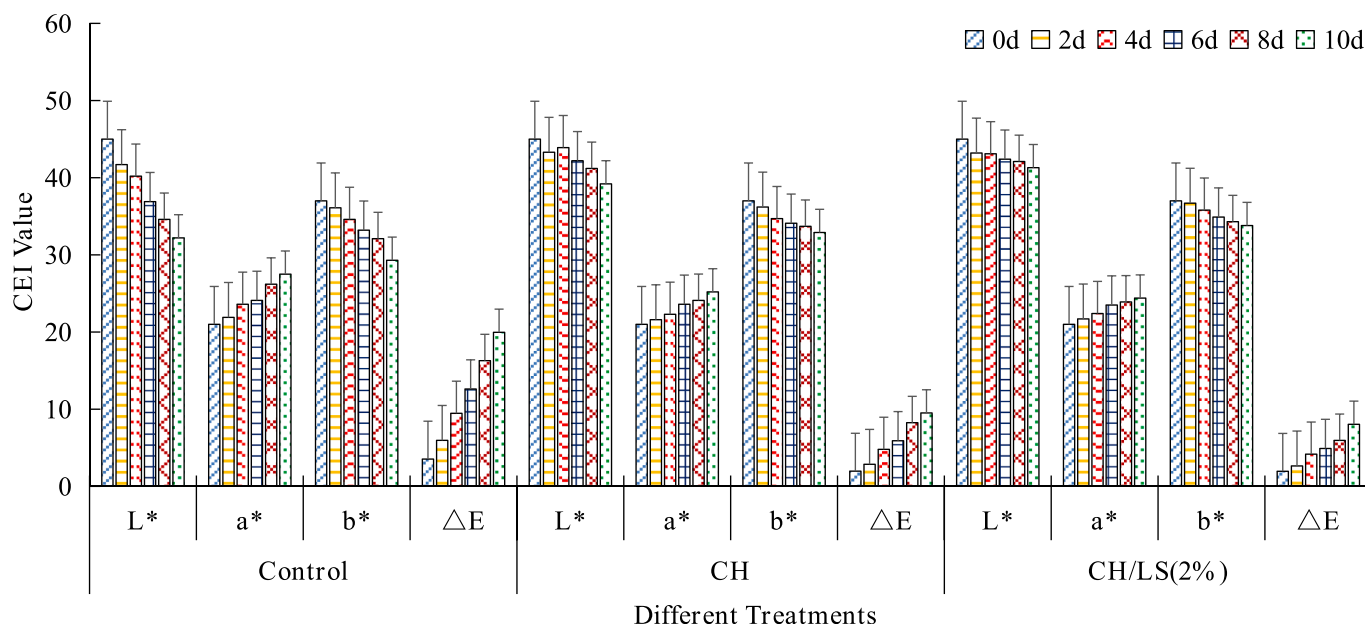


Fig. 4. Changes in the color values of the cherry tomatoes during preservation (n = 3).

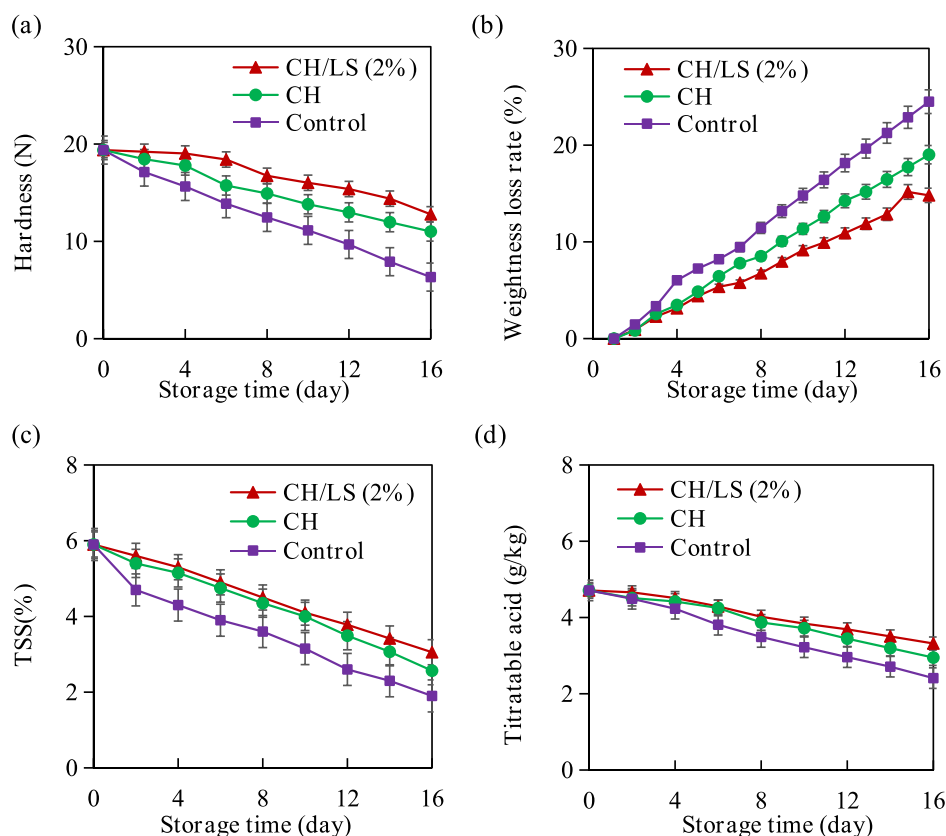


Fig. 5. Profiles of hardness (a), weight loss rate (b), total suspended solid (c), and titratable acid (d) of cherry tomatoes during preservation with different composite films ($n = 6$).

group showed the best protective effect on cherry tomatoes, which had a smooth and plump texture on their surface. Weight loss is mainly due to the loss of water that occurs during the transpiration process. Water is very important for respiration, which continues even after picking fruits and vegetables. CH/LS films form a barrier that hinders the water volatilization from the cherry tomatoes, thus reducing the weight losses. As shown in Fig. 5b, the control film exhibited higher weight loss of cherry tomatoes compared to the CH/LS film, which was surprising since polyethylene films typically provide good moisture barrier properties. The specific polyethylene film used in this study was a 20 μm thick commercial food packaging film (purchased from RT-Mart, Yangzhou). The higher moisture permeability of this polyethylene film was likely due to its relatively low thickness and density compared to high barrier polyethylene films used in other produce packaging studies. The improved moisture barrier provided by the crosslinked CH/LS film nanostructure resulted in reduced weight loss compared to the control. While further testing with high barrier commercial polyethylene films would be useful, these results still demonstrated the potential of the CH/LS composite film to minimize weight loss and extend the shelf life of cherry tomatoes. TSS content is related to the maturity and senescence of fruits, and the least loss of TSS content indicates a good preservation quality of the fruits (Xiang et al., 2021). The TSS of cherry tomatoes gradually decreased with time from an initial value of 6% (Fig. 5c). TSS content of more than 3% was obtained with CH/LS films, while the lowest was 1.9% (control). Meanwhile, the titratable acid (TA) value reflects the nutritional and physiological status of fruits and vegetables. TA decreased with time due to microbial respiration or consumption (Yong & Liu, 2021). Both CH and CH/LS films with antimicrobial activities were effective in minimizing the reduction of TA. CH/LS film successfully kept the freshness of cherry tomatoes for 14 days. Optimal atmosphere and storage temperature inside the CH/LS film packaging might result in lowering the respiration rate and deterioration of the

product.

Conclusions

Flexible and self-standing CH/LS composite film were successfully fabricated by simple casting method at moderate conditions. Our finding reveals that the addition of 2% LS in the CH matrix enhanced the UV-shielding effect and mechanical properties, which are excellent properties of food packaging film. The reason for this best fresh-keeping effect of the CH/LS composite film is considered to be the synergistic effect of reduced water vapor permeability due to the composite in addition to the antibacterial and UV shielding effects derived from CH and LS, respectively. CH/LS films derived from renewable biomass resources with unique functions such as UV-shielding could be a good alternative for petroleum-based single-use plastic packaging. Further research is needed to optimize the composite formula for different food types, analyze food-packaging interactions, scale up production, evaluate costs, analyze environmental impacts, assess end-of-life management options, and evaluate commercial potential to determine the overall feasibility and real-world viability of implementing CH/LS-based biopolymer films as sustainable and active food packaging on an industrial level.

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CRediT authorship contribution statement

Jiangyu Zhu: Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **Yujie Fang:** Writing – original draft, Software, Resources, Methodology, Formal analysis, Data curation, Conceptualization. **Minato Wakisaka:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Halimatun Saadiyah Hafid:** . **Zhengfei Yang:** Supervision, Project administration, Formal analysis. **Yongqi Yin:** Supervision, Resources, Project administration. **Taku Omura:** Visualization, Methodology, Formal analysis. **Weiming Fang:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fochx.2024.101181>.

References

- Ambye, T. G., Vaccari, M., Prasad, S., van Hullebusch, E. D., & Rtimi, S. (2022). Preparation and applications of chitosan and cellulose composite materials. *Journal of Environmental Management*, 301, Article 113850. <https://doi.org/10.1016/j.jenvman.2021.113850>
- Bitencourt, C. M., Fávoro-Trindade, C. S., Sobral, P. J. D. A., & Carvalho, R. A. D. (2014). Gelatin-based films additivated with curcuma ethanol extract: Antioxidant activity and physical properties of films. *Food Hydrocolloids*, 40, 145–152. <https://doi.org/10.1016/j.foodhyd.2014.02.014>
- Chen, H. Z., Zhang, M., Bhandari, B., & Yang, C. H. (2020). Novel pH-sensitive films containing curcumin and anthocyanins to monitor fish freshness. *Food Hydrocolloid*, 100, Article 105438. <https://doi.org/10.1016/j.foodhyd.2019.105438>
- Cui, H. L., Wang, Z. H., Jiao, H. W., Lu, S. X., & Xu, W. G. (2011). Preparation of EVOH Film and Infrared Spectroscopic Study of Its Heat Preservation Property. *Spectroscopy and Spectral Analysis*, 31(6), 1518–1520. [https://doi.org/10.3964/j.issn.1000-0593\(2011\)06-1518-03](https://doi.org/10.3964/j.issn.1000-0593(2011)06-1518-03)
- Cui, H. L., Xu, W. G., He, F. Q., Wang, Z. H., Jiao, H. W., & Lu, S. X. (2012). The Relationship between FTIR Spectra of PVA Film and Its Heat Preservation Capability. *Spectroscopy and Spectral Analysis*, 32(1), 96–98. [https://doi.org/10.3964/j.issn.1000-0593\(2012\)01-0096-03](https://doi.org/10.3964/j.issn.1000-0593(2012)01-0096-03)
- Han, Y., Yu, M., & Wang, L. (2018). Physical and antimicrobial properties of sodium alginate/carboxymethyl cellulose films incorporated with cinnamon essential oil. *Food Packaging and Shelf Life*, 15, 35–42. <https://doi.org/10.1016/j.foodpack.2017.11.001>
- He, X., Li, M., Gong, X. C., Niu, B. L., & Li, W. F. (2021). Biodegradable and antimicrobial CSC films containing cinnamon essential oil for preservation applications. *Food Packaging and Shelf Life*, 29, Article 100697. <https://doi.org/10.1016/j.foodpack.2021.100697>
- He, Y., Lu, L., Lin, Y., Li, R., Yuan, Y., Lu, X., & Li, J. (2022). Intelligent pH-sensing film based on polyvinyl alcohol/cellulose nanocrystal with purple cabbage anthocyanins for visually monitoring shrimp freshness. *International Journal of Biological Macromolecules*, 218, 900–908. <https://doi.org/10.1016/j.ijbiomac.2022.07.194>
- Kanatt, S. R. (2020). Development of active/intelligent food packaging film containing Amaranthus leaf extract for shelf life extension of chicken/fish during chilled storage. *Food Packaging and Shelf Life*, 24, Article 100506. <https://doi.org/10.1016/j.foodpack.2020.100506>
- Kumarihami, H. M. P. C., Kim, Y. H., Kwack, Y. B., Kim, J., & Kim, J. G. (2022). Application of chitosan as edible coating to enhance storability and fruit quality of Kiwifruit: A Review. *Scientia Horticulturae*, 292, Article 110647. <https://doi.org/10.1016/j.scienta.2021.110647>
- Liu, J., Liu, S., Wu, Q., Gu, Y., Kan, J., & Jin, C. (2017). Effect of protocatechuic acid incorporation on the physical, mechanical, structural and antioxidant properties of chitosan. *Food Hydrocolloids*, 73, 90–100. <https://doi.org/10.1016/j.foodhyd.2017.06.035>
- Liu, F., Chang, W., Chen, M., Xu, F., Ma, J., & Zhong, F. (2020). Film-forming properties of guar gum, tara gum and locust bean gum. *Food Hydrocolloids*, 98, Article 105007. <https://doi.org/10.1016/j.foodhyd.2019.03.028>
- López-Carballo, G., Higuera, L., Gavara, R., & Hernández-Muñoz, P. (2013). Silver ions release from antibacterial chitosan films containing in situ generated silver nanoparticles. *Journal of Agricultural and Food Chemistry*, 61(1), 260–267. <https://doi.org/10.3390/ma13112484>
- Lora, J. H., & Glasser, W. G. (2002). Recent industrial applications of lignin: A sustainable alternative to nonrenewable materials. *Journal of Polymers and the Environment*, 10(1), 39–48. <https://doi.org/10.1364/OL.27.001914>
- Mahmood, A., Bano, S., Sang-Gyun, K., & Kew-Ho, L. (2012). Water-methanol separation characteristics of annealed SA/PVA complex membrane. *Journal of Membrane Science*, 415–416, 360–367. <https://doi.org/10.1016/j.memsci.2012.05.020>
- Marand, S. A., Almasi, H., & Marand, N. A. (2021). Chitosan-based nanocomposite films incorporated with NiO nanoparticles: Physicochemical, photocatalytic and antimicrobial properties. *International Journal of Biological Macromolecules*, 190, 667–678. <https://doi.org/10.1016/j.ijbiomac.2021.09.024>
- Moradi, S., Hamed, H., Tonelli, A. E., & Hudson, S. M. (2019). Preparation and characterization of chitosan–alginate polyelectrolyte complexes loaded with antibacterial thyme oil nanoemulsions. *Applied Sciences*, 9, 3933. <https://doi.org/10.3390/app9183933>
- Nada, A. M. A., El-Diwany, A. I., & Elshafei, A. M. (1989). Infrared and antimicrobial studies on different lignins. *Acta Biotechnologica*, 9(3), 295–298. <https://doi.org/10.1002/abio.370090322>
- Oms-Oliu, G., Rojas-Graü, M. A., González, L. A., Varela, P., Soliva-Fortuny, R., Hernando, M. I. H., & Martín-Belloso, O. (2010). Recent approaches using chemical treatments to preserve quality of fresh-cut fruit: A review. *Postharvest biology and technology*, 57(3), 139–148. <https://doi.org/10.1016/j.postharvbio.2010.04.001>
- Oymaci, P., Altinkaya, S. A. (2016). Improvement of barrier and mechanical properties of whey protein isolate based food packaging films by incorporation of zein nanoparticles as a novel bionanocomposite. *Food Hydrocolloids*, 54, 1–9. <https://doi.org/10.1016/j.foodhyd.2015.08.030>
- Qian, Y., Deng, Y. H., Li, H., & Qiu, X. Q. (2014). Reaction-Free Lignin Whitening via a Self-Assembly of Acetylated Lignin. *Industrial & Engineering Chemistry Research*, 53(24), 10024–10028. <https://doi.org/10.1021/ie5010338>
- Qian, Y., Zhong, X. W., Li, Y., & Qiu, X. Q. (2017). Fabrication of uniform lignin colloidal spheres for developing natural broad-spectrum sunscreens with high sun protection factor. *Industrial Crops And Products*, 101, 54–60. <https://doi.org/10.1016/j.indcrop.2017.03.001>
- Qin, Y., Xu, F. F., Yuan, L. M., Hu, H. X., Yao, X. Y., & Liu, J. (2020). Comparison of the physical and functional properties of starch/polyvinyl alcohol films containing anthocyanins and/or betacyanins. *International Journal of Biological Macromolecules*, 163, 898–909. <https://doi.org/10.1016/j.ijbiomac.2020.07.065>
- Qin, Y., Yun, D., Xu, F., Chen, D., Kan, J., & Liu, J. (2021). Smart packaging films based on starch/polyvinyl alcohol and Lycium ruthenicum anthocyanins-loaded nanocomplexes: Functionality, stability and application. *Food Hydrocolloids*, 119, Article 106850. <https://doi.org/10.1016/j.foodhyd.2021.106850>
- Rasheed, P. A., Pandey, R. P., Jabbar, K. A., Samara, A., Abdullah, A. M., & Mahmoud, K. A. (2020). Chitosan/Lignosulfonate Nanospheres as “Green” Biocide for Controlling the Microbiologically Influenced Corrosion of Carbon Steel. *Materials*, 13(11), 2484. <https://doi.org/10.3390/ma13112484>
- Rubilar, J. F., Cruz, R. M. S., Silva, H. D., Vicente, A. A., Khmelinskii, I., & Vieira, M. C. (2013). Physico-mechanical properties of chitosan films with carvacrol and grape seed extract. *Journal of Food Engineering*, 115, 466–474. <https://doi.org/10.1016/j.jfoodeng.2012.07.009>
- Sarathy, S. R., & Mohseni, M. (2007). The impact of UV/H2O2 advanced oxidation on molecular size distribution of chromophoric natural organic matter. *Environmental Science & Technology*, 41(24), 8315–8320. <https://doi.org/10.1021/es071602m>
- Shahbazi M., Rajabzadeh G., Ettelaie R., Rafe A. (2016). Kinetic study of κ-carrageenan degradation and its impact on mechanical and structural properties of chitosan/κ-carrageenan film. *Carbohydrate Polymers*, 142, 167–176. <https://doi.org/10.1016/j.carbpol.2016.01.037>
- Shariat, S. Z. A. S., Mostafavi, S. A., & Khakpour, F. (2013). Antioxidant Effects of Vitamins C and E on the Low-Density Lipoprotein Oxidation Mediated by Myeloperoxidase. *Iranian Biomedical Journal*, 17(1), 22–28. <https://doi.org/10.6091/ibj.1092.2012>
- Sivarooan, T., Hettiarachchy, N. S., & Johnson, M. G. (2008). Physical and antimicrobial properties of grape seed extract, nisin, and EDTA incorporated soy protein edible films. *Food Research International*, 41, 781–785. <https://doi.org/10.1016/j.foodres.2008.04.007>
- Ushimaru, K., Morita, T., Watanabe, R., & Fukuoka, T. (2021). Biobased and mechanically stiff lignosulfonate/cationic-polyelectrolyte/sugar complexes with coexisting ionic and covalent crosslinks. *Polymer Journal*, 53(9), 1037–1045. <https://doi.org/10.1038/s41428-021-00501-2>
- Xiao, J., Ma, Y., Wang, W., Zhang, K., Tian, X., Zhao, K., & Guo, Y. (2021). Incorporation of gelatin improves toughness of collagen films with a homo-hierarchical structure. *Food Chemistry*, 345, Article 128802. <https://doi.org/10.1016/j.foodchem.2020.128802>
- Xiang, F., Xia, Y. T., Wang, Y., Wang, Y. X., Wu, K., & Ni, X. W. (2021). Preparation of konjac glucomannan based films reinforced with nanoparticles and its effect on

- cherry tomatoes preservation. *Food Packaging and Shelf Life*, 29, Article 100701. <https://doi.org/10.1016/j.fpsl.2021.100701>
- Xu, Y. S., Adekunle, K., Ramamoorthy, S. K., Skrifvars, M., & Hakkarainen, M. (2021). Methacrylated lignosulfonate as compatibilizer for flax fiber reinforced biocomposites with soybean-derived polyester matrix. *Composites Communications*, 22, Article 100536. <https://doi.org/10.1016/j.coco.2020.100536>
- Yao, X. Y., Qin, Y., Zhang, M., Zhang, J. X., Qian, C. L., & Liu, J. (2021). Development of active and smart packaging films based on starch, polyvinyl alcohol and betacyanins from different plant sources. *International Journal of Biological Macromolecules*, 183, 358–368. <https://doi.org/10.1016/j.fpsl.2020.100520>
- Yong, H., & Liu, J. (2021). Active packaging films and edible coatings based on polyphenol-rich propolis extract: A review. *Comprehensive Reviews in Food Science and Food Safety*, 20, 2106–2145. <https://doi.org/10.1111/1541-4337.12697>
- You, Y., Zhou, Y., Duan, X., Mao, X., & Li, Y. (2022). Research progress on the application of different preservation methods for controlling fungi and toxins in fruit and vegetable. *Critical Reviews in Food Science and Nutrition*, 1–12. <https://doi.org/10.1080/10408398.2022.2101982>
- Zamudio-Flores, P. B., Torres, A. V., Salgado-Delgado, R., & Bello-Perez, L. A. (2010). Influence of the Oxidation and Acetylation of Banana Starch on the Mechanical and Water Barrier Properties of Modified Starch and Modified Starch/Chitosan Blend Films. *Journal of Applied Polymer Science*, 115(2), 991–998. <https://doi.org/10.1002/app.31047>
- Zamudio-Flores, P. B., Ochoa-Reyes, E., Ornelas-Paz, J. D. J., Tirado-Gallegos, J. M., Bello-Pérez, L. A., Rubio-Ríos, A., & Cárdenas-Felix, R. G. (2015). Physicochemical, mechanical, and structural features of oxidized oat and banana starch films enriched with betalains. *Agrociencia*, 483–498.
- Zhang, X. H., Ismail, B. B., Cheng, H., Jin, T. Z., Qian, M. Y., Arabi, S. A., Liu, D. H., & Guo, M. M. (2021). Emerging chitosan-essential oil films and coatings for food preservation-A review of advances and applications. *Carbohydrate Polymers*, 273, Article 118616. <https://doi.org/10.1016/j.carbpol.2021.118616>
- Zhu, J., & Wakisaka, M. (2021). Application of lignosulfonate as the growth promoter for freshwater microalga *Euglena gracilis* to increase productivity of biomass and lipids. *Fuel*, 283, Article 118920. <https://doi.org/10.1016/j.fuel.2020.118920>