

Thymol Encapsulated Pickering Emulsion Coated Paper for Enhancing Cherry Tomato Preservation Performance

Lei Zhu, Chunxia Pang,* Yiwei Xiao, Yuanjia Zhang, Jiahui Wang, Li Hu, Yang Fu, Ting Li, and Wenjun Li *

Thymol, a natural phenolic compound with broad-spectrum antimicrobial activity and high antioxidant capacity, faces limitations in food preservation due to its volatility. This study developed a thymol-loaded Pickering emulsion stabilized by zein/pectin (ZP) composite colloidal particles. The effects of thymol concentration (0.5 to 2.5 wt%) on encapsulation efficiency, colloidal stability, and functional properties were investigated. The resultant functionalized paper was evaluated for cherry tomato preservation. Optimal performance was achieved at 2 wt% thymol, yielding a high encapsulation efficiency of 91.4% and superior stability. The paper demonstrated robust antimicrobial efficacy, sustained release, and a 98.2% DPPH radical scavenging efficacy. In storage trials, it significantly outperformed controls by better maintaining firmness, mitigating weight loss, and reducing the spoilage rate to 7.3% after 15 days, while most effectively preserving soluble solids content. This work demonstrates the ZP particle-stabilized, thymol-loaded Pickering emulsion-based paper as a highly effective strategy for postharvest preservation.

DOI: 10.15376/biores.21.1.1669-1689

Keywords: Thymol; Pickering emulsion; Coated paper; Fruit preservation

Contact information: Key Laboratory of Bamboo Fiber Materials Engineering of China Light Industry, School of Food and Liquid Engineering, Sichuan University of Science and Engineering, Yibin, Sichuan, PRC; *Corresponding authors: Pcxia@suse.edu.cn; 564081057@qq.com

INTRODUCTION

Cherry tomatoes have gained global popularity and have become an indispensable healthy fruit in modern diets due to their small size, vibrant color, and sweet-tart flavor. However, due to their thin skin and high water content, they are extremely susceptible to dehydration and wilting post-harvest. Additionally, the abundant nutrients in the fruit provide an ideal environment for microbial growth, leading to rapid deterioration processes such as rotting, browning, and softening. During peak market periods, they usually lose their commercial value within 3 to 7 days of storage (Zhu *et al.* 2018; Sakthiselvi *et al.* 2020; Hu *et al.* 2026). This not only results in significant economic losses but also exacerbates resource waste and environmental pollution. Therefore, the development of efficient, safe, and environmentally friendly post-harvest preservation technologies for cherry tomatoes has considerable practical significance and economic value, as it plays a crucial role in reducing food waste, ensuring food safety, and promoting sustainable agricultural development (Teng *et al.* 2021).

The attractiveness of paper-based materials for developing novel fruit and vegetable preservation solutions has grown recently, because of their abundance, low cost, biodegradability, and safety (Cheng *et al.* 2024; Jieying *et al.* 2024; Anubha and Jayarajan

2024; Renard *et al.* 2013). Recent research has focused on overcoming the inherent limitations of conventional paper, namely its low water/grease barrier and lack of active functionalities, through strategies including coating and functional filler incorporation (Yadav *et al.* 2014; Liu *et al.* 2020; Gică 2023; Ehman *et al.* 2023). These limitations remain a central challenge for direct preservation applications. Therefore, the key to development lies in imparting paper with active properties, such as antimicrobial and antioxidant capabilities, enabling intervention in the post-harvest physiology of fruits and vegetables (Guo 2024; D'Aquino *et al.* 2016).

Thymol, a natural phenolic compound prevalent in plants such as thyme and oregano, exhibits significant broad-spectrum antimicrobial activity, potent antioxidant properties, and high safety, demonstrating significant application potential in food preservation, healthcare, and medicinal fields (Boye *et al.* 2020; Hajibonabi *et al.* 2023). However, its high volatility and limited solubility have hindered its direct utilization in food preservation. To address these delivery challenges and enable its integration into paper-based materials, one promising approach is to encapsulate thymol within a Pickering emulsion. Pickering emulsions, stabilized by solid particles, provide an effective system for encapsulating and protecting volatile or insoluble bioactive compounds (Yu *et al.* 2015). In this system, ZP composite colloidal particles, formed *via* antisolvent precipitation and electrostatic deposition, serve as the solid stabilizers. These particles exhibit excellent colloidal stability in aqueous suspension due to the steric hindrance and electrostatic repulsion provided by the negatively charged pectin shell. Moreover, coating paper substrates with such active material-loaded Pickering emulsions has emerged as a feasible method to develop functional packaging with enhanced properties (Li *et al.* 2025). Methods including microencapsulation, electrospinning, and dipping have been explored to effectively deliver thymol for extending the shelf-life of fruits, such as strawberries, blueberries, and apples, with preliminary results demonstrating considerable promise (Boye *et al.* 2020; Munteanu and Vasile 2021; Hajibonabi *et al.* 2023; Ye *et al.* 2024). For instance, Zhong *et al.* (2023) demonstrated that thymol microcapsules effectively slowed the decline of hardness and soluble solids content in strawberries, achieving promising preservation results. Similarly, Ye *et al.* (2024) confirmed that thymol delays fruit softening by influencing cellular metabolism, thereby helping to maintain post-harvest firmness. While these studies underscore thymol's efficacy, its specific integration *via* a Pickering emulsion stabilized by zein/pectin composite colloidal particles and subsequent coating into paper-based materials for stable, controlled release to create functional preservation paper remains an area requiring further exploration.

Herein, this study systematically investigated the preparation of thymol Pickering emulsions, with a focus on the impact of thymol concentration on encapsulation efficiency, stability, antimicrobial activity, antioxidant capacity, and controlled-release properties. Subsequently, the preservation efficacy of thymol Pickering emulsion coated paper on cherry tomatoes was evaluated through simulated storage experiments. The research aimed to provide insights and support for the development of Pickering emulsion coated paper as an innovative fruit and vegetable preservation strategy.

EXPERIMENTAL

Materials

Zein (ZN) and citrus pectin (CP) were purchased from Shanghai Aladdin

Biochemical Technology Co., Ltd.; anhydrous ethanol (Et), sodium hydroxide, agar powder, and n-hexane were sourced from Chengdu Kelong Chemicals Co., Ltd.; thymol (Ty) and sodium chloride were obtained from China National Pharmaceutical Group Chemical Reagents Co., Ltd.; 1,1-diphenyl-2-picrylhydrazyl (DPPH) was purchased from Feijing Biotechnology Co., Ltd.; and medium-chain triglycerides (MCT) were procured from Zhengzhou Sujia Trade Co., Ltd.

Methods

Preparation of thymol Pickering emulsions

Preparation of zein/pectin (ZP) composite colloidal particles was carried out as follows: The composite colloidal particles were fabricated using an anti-solvent precipitation approach. An initial zein solution [4% (w/v)] was prepared by dissolving zein powder in 80% (v/v) ethanol followed by dispersion at 8,000 rpm for 1 min. Concurrently, a pectin solution [4% (w/v)] was obtained by dissolving pectin powder in deionized water at 75 °C. The Zein solution was then added dropwise to an equal volume of the pectin solution under continuous magnetic stirring (1200 rpm) at 75 °C. The mixture was stirred for 30 min at 75 °C to evaporate the ethanol. After cooling, the dispersion pH was adjusted to 4.0 with 0.1 M NaOH, and the original volume was reconstituted with pH-adjusted deionized water.

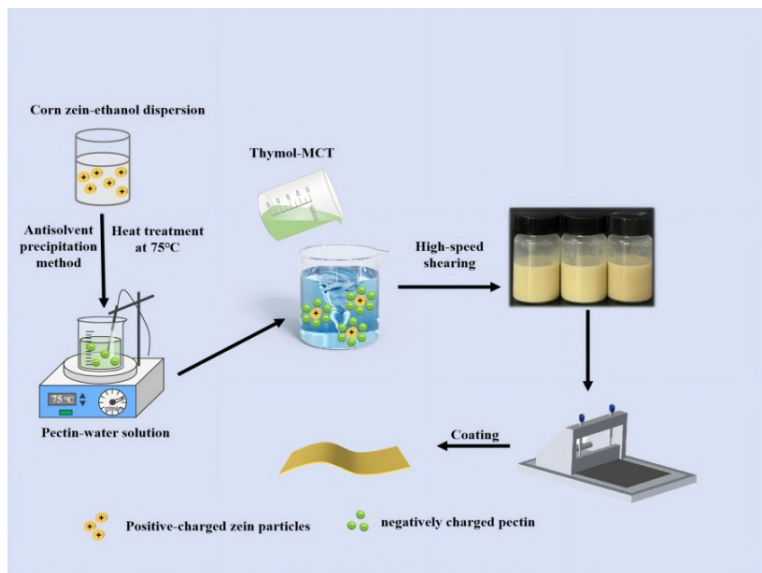


Fig. 1. Schematic diagram of the preparation process of thymol Pickering emulsion

Preparation of thymol Pickering emulsion involved the following steps: Thymol was first dissolved in medium-chain triglycerides (MCT) to form the oil phase. This oil phase was then introduced into an aqueous dispersion of ZP composite colloidal particles at an oil-to-water volume ratio of 2:8. The mixture was homogenized using a high-speed disperser at 20,000 rpm for 4 min to obtain the thymol Pickering emulsion. A series of emulsions were fabricated by varying the thymol mass fraction relative to the total emulsion mass. All prepared thymol Pickering emulsions were stored at room temperature for subsequent use and designated based on their thymol mass fraction (*e.g.*, ZP-Ty-0% and ZP-Ty-1% for 0 wt% and 1 wt% thymol content). A schematic of the preparation process is provided in Fig. 1.

Preparation of functionalized paper

According to GB/T 41515 (2022), a rod coater (C004, China National Pulp and Paper Research Institute Co., Ltd., Beijing, China) was used to apply a coating onto bamboo fiber paper with a basis weight of 100 g/m². A 5-mL aliquot of the thymol Pickering emulsion was coated onto the surface of a circular paper sample (10 cm in diameter) at a speed of 20 mm/s. subsequently, the coated paper was air-dried for 24 h at room temperature prior to further testing.

Characterization of thymol Pickering emulsion

Determination of thymol encapsulation efficiency

To determine the encapsulation efficiency, 2 mL of the thymol Pickering emulsion was mixed with 18 mL of n-hexane and centrifuged at 8,000 rpm for 10 min. Subsequently, 1 mL of the lower emulsion layer was transferred to 9 mL of a 95% (v/v) ethanol solution to extract the encapsulated thymol, followed by a second centrifugation under identical conditions. The supernatant was diluted, and the absorbance at 277 nm was recorded with a UV spectrophotometer (A390, Aoyi Instruments Co., Ltd., Shanghai, China). The concentration of encapsulated thymol was calculated based on a standard curve (Fig. (S1)), and the encapsulation efficiency was derived from Eq. 1. All measurements were performed in triplicate, and the average value was used. Equation 1 is given as,

$$\text{Encapsulation efficiency (\%)} = \frac{C_1}{C_0} \times 100\% \quad (1)$$

where C_0 and C_1 represent the initial concentration of thymol added to the Pickering emulsion and the concentration of encapsulated thymol (μg/mL), respectively.

Determination of emulsion particle size

The stability of the thymol Pickering emulsion was expected to be closely related to the size and distribution of its colloidal particles. Accordingly, the particle size distribution was assessed using a laser particle size analyzer (MS3000E+EV, Malvern Instruments Ltd., Malvern, UK) according to a published method (Zhang *et al.* 2025a). Additionally, optical microscopy (Panthrea L, Motic China Group Co., Ltd., Xiamen, China) was employed for direct visual observation of the particles.

Determination of emulsion zeta potential

Following the ISO 13099-2 (2012) standard, the emulsion zeta potential was measured using a particle charge detector (Litesizer 500, Anton Paar, Austria).

Assessment of emulsion stability

The stability of the thymol Pickering emulsion was evaluated over a 20-day storage period at room temperature. With observations recorded on days 0, 5, 10, 15, and 20, the visual state and colloidal particle size were monitored, and the thymol encapsulation efficiency was measured to assess stability.

Chemical Structure Analysis

The chemical composition of the emulsion and functionalized paper were analyzed using a Fourier transform infrared (FTIR) spectroscopy (Spectrum Two, PerkinElmer, Waltham, MA, USA) with a scanning range of 4000 to 400 cm⁻¹, a resolution of 4 cm⁻¹, and 16 scans.

Determination of Antioxidant Activity

The antioxidant activity of the functionalized paper was assessed *via* the DPPH radical scavenging assay. Briefly, paper samples (20 mm × 20 mm) coated with the test emulsion were mixed with 10 mL of DPPH/ethanol solution and reacted in a shaking incubator in the dark for 12 h at room temperature. After centrifugation at 5,000 rpm for 10 min, the supernatant was collected, and its absorbance at 517 nm was measured to calculate the scavenging capacity according to Eq. 2,

$$\text{DPPH radical scavenging (\%)} = \frac{A_0 - A_i}{A_0} \times 100\% \quad (2)$$

where A_0 and A_i are the absorbance values at 517 nm of the DPPH/ethanol solution without and with the sample, respectively.

Evaluation of Antimicrobial Activity

The antimicrobial activity of the functionalized paper was evaluated against *E. coli* and *S. coccus* according to a previously reported method (Dang *et al.* 2017). The inhibitory efficacy was quantitatively assessed by examining bacterial growth on agar plates.

Evaluation of Sustained-release Performance

To investigate the sustained-release performance of thymol Pickering emulsion, 5 mL of ZP-Ty-2% emulsion, Ty-MCT-2% solution (lacking ZP composite colloidal particles), and Ty-Et-2% solution were uniformly coated onto circular paper substrates with a radius of 10 cm. The resulting functionalized papers were designated as ZP-Ty-2%-P, Ty-MCT-2%-P, and Ty-Et-2%-P, respectively. Subsequently, all samples were conditioned in an environment maintained at $(25 \pm 2)^\circ\text{C}$ and $(50 \pm 5)\%$ relative humidity. Thymol retention in the paper samples ($2 \times 3 \text{ cm}^2$) was monitored at five predetermined intervals: 4 h, 24 h, 48 h, 72 h, and 96 h. Notably, the Ty-MCT-2% solution was prepared analogously to the ZP-Ty-2% emulsion, by emulsifying a thymol-MCT oil phase in anhydrous ethanol (oil-to-ethanol ratio 2:8) under high-speed dispersion (20000 r/min, 4 min), whereas the Ty-Et-2% solution was simply a 2 wt% solution of thymol in anhydrous ethanol.

Evaluation of Preservation Performance of Coated Paper

Pretreatment of cherry tomatoes

Mature cherry tomatoes with uniform ripeness, intact skin, and fresh stems, were selected and surface-sanitized with a 75% ethanol solution. The fruits were divided into three experimental groups: a blank group (unwrapped, BL), a control group (wrapped with plain bamboo fiber paper, CK), and an experimental group (wrapped with ZP-Ty-2%-P functionalized paper). All samples were stored under controlled conditions at 20°C and 50% relative humidity.

Weight loss

Given that moisture loss critically contributes to the quality deterioration of postharvest fruits, the weight loss percentage was evaluated to evaluate the functionalized paper's performance in preventing moisture evaporation, thereby reflecting its preservation ability. During the experiment, cherry tomatoes from all groups were weighed daily, and the weight loss rate was calculated according to Eq. 3,

$$\text{Weight loss rate (\%)} = \frac{M_n}{M_0} \times 100\% \quad (3)$$

where M_n and M_0 denote the cumulative mass loss (g) after n days and the initial mass of the fruit (g), respectively.

Decay incidence

Decay incidence is a critical indicator for evaluating fruit preservation effectiveness. Spoilage is determined by the presence of visible rot on the fruit surface. A decay incidence exceeding 10% generally indicates a loss of commercial and practical value, necessitating the termination of storage. This rate can be calculated using Eq. 4,

$$\text{Spoilage rate (\%)} = \frac{n_0}{n_1} \times 100\% \quad (4)$$

where n_0 and n_1 represent the number of spoiled fruits and the total number of fruits, respectively.

Evaluation of firmness and soluble solid content (SSC) changes

Firmness and SSC are important indicators of fruit maturation and senescence. Monitoring these parameters provides critical insights into the efficacy of the preservation paper. In this experiment, firmness was measured using a texture analyzer (TA.XT PlusC, Stable Micro Systems, Godalming, UK). Several representative cherry tomatoes were randomly selected, and after carefully removing a thin layer of skin with a scalpel, multiple measurements were taken at both the equatorial and bottom regions of each fruit. For the determination of SSC, representative fruits were randomly sampled at predetermined intervals. The fruit flesh was homogenized and filtered to extract clear juice, whose soluble solids content was determined with a handheld refractometer (SW-55T, Guangzhou Speedway Electronic Technology Co., Ltd., Guangzhou, China).

Paper Morphology and Functional Performance

Paper morphology

The surface morphology of the base and functionalized papers was observed using a tungsten filament scanning electron microscope (VEGA 3 SBU, TESCAN, Brno, Czech Republic).

Water contact angle of the paper

The water contact angle was measured with a goniometer (SZ-CAMC33, Suzhou Olonda Instrument Technology Co., Ltd., Suzhou, China) to evaluate surface wettability. A 5- μ L droplet of distilled water was dispensed steadily onto the sample surface using a flat-headed needle. Each sample was tested in triplicate, and the average contact angle was subsequently recorded.

Water vapor transmission of the paper

To evaluate the water vapor transmission (WVT), circular paper samples were mounted and sealed onto vials containing a pre-weighed quantity of anhydrous calcium chloride granules. The film-sealed vials were weighed and placed in a desiccator containing distilled water at 25 °C. The WVT was calculated using Eq. 5,

$$WVT = \frac{24 \cdot \Delta m}{t \cdot A} \quad (5)$$

where WVT, Δm , A , and t represent the water vapor transmission rate of the sample ($\text{g}/(\text{m}^2 \cdot 24 \text{ h})$), the change in mass of the moisture cup (g), the area through which water vapor passes (m^2), and the time difference between measurements (h), respectively.

Statistical Analysis

Data were analyzed using GraphPad Prism 9 software and expressed as the mean $\pm$ standard deviation (SD) from three independent replicates ($n = 3$). Group differences were assessed by one-way analysis of variance (ANOVA), with the threshold for statistical significance set at $P < 0.05$.

RESULTS AND DISCUSSION

Stability and Encapsulation Efficiency of Thymol Pickering Emulsion

Encapsulation efficiency of thymol

The encapsulation efficiency of thymol is closely related to the preservation performance of the functionalized paper. Consequently, the effect of thymol concentration on encapsulation efficiency was investigated, with the results presented in Fig. 2(g).

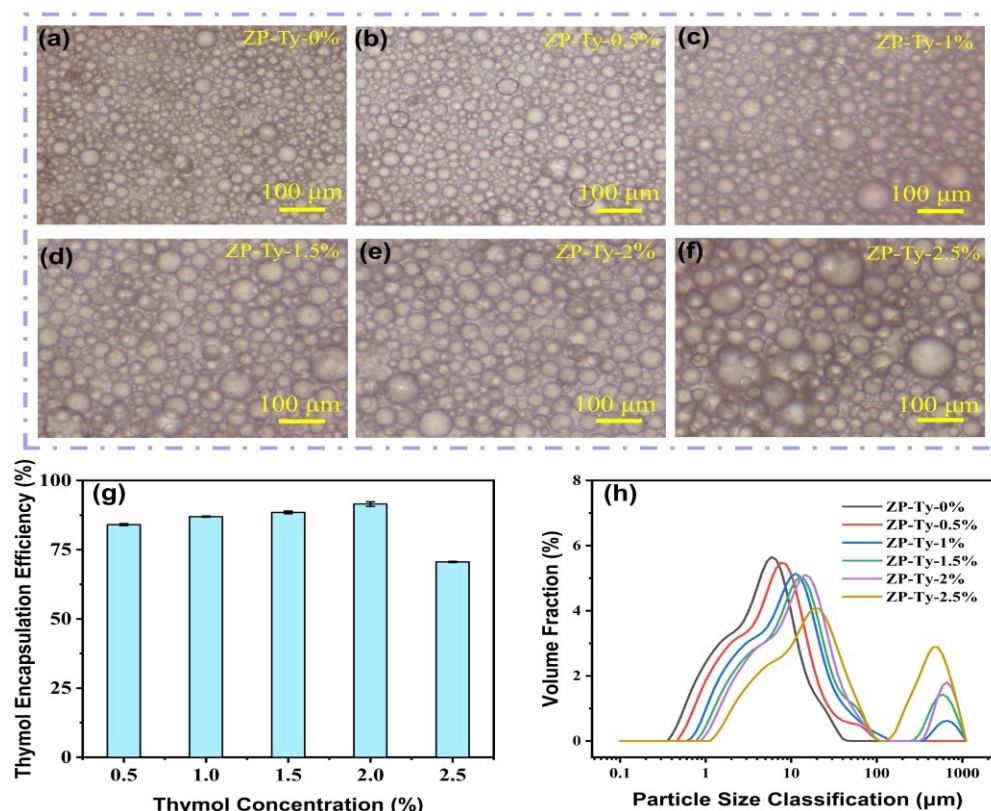


Fig. 2. Optical micrographs of Pickering emulsions with different thymol concentrations (a to f); Schematic of thymol encapsulation efficiency as a function of thymol concentrations (g); Schematic of the corresponding emulsion particle size distribution (h)

As depicted in Fig. 2(g), the encapsulation efficiency of thymol exhibited an initial increase followed by a decrease as the concentration rose from 0.5 wt% to 2.5 wt%. The maximum efficiency of 91.4% was achieved at a concentration of 2 wt%, whereas increasing to 2.5 wt% caused a notable decline to 70.6%. These findings demonstrate that thymol encapsulation efficiency can be enhanced by increasing its concentration within a suitable range, an effect attributable to its chemical structure. Thymol, a hydrophobic phenolic compound (Ferreira *et al.* 2016), contains a benzene ring and hydrophobic C-H groups in its molecular structure that enable it to interact with oily particles in the emulsion. Through hydrophobic interactions, thymol adsorbs onto the carrier surface or becomes embedded within the carrier structure (Zhang *et al.* 2025b), which not only enhances its own encapsulation efficiency but also facilitates the stable encapsulation of the oil phase. However, an overly high thymol concentration can lead to the aggregation of excessive hydrophobic molecules, which disrupts the emulsion interface and results in diminished encapsulation efficiency.

Particle size distribution of the emulsion

Given the expected dependence of stability of Pickering emulsions on particle size, the effect of thymol concentration on this parameter was investigated, as presented in Fig. 2(h). Figure 2(h) reveals a migration of the emulsion particle size distribution toward larger dimensions as thymol concentration rose from 0 wt% to 2.5 wt%, confirming the increase in particle size seen in the optical micrographs (Fig. 2(a to f)). This phenomenon suggests that the introduction of thymol promoted the aggregation or coalescence of emulsion particles to some extent. This could be due to the thymol molecules containing both polar phenolic hydroxyl groups and hydrophobic benzene ring structures. The hydrophobic benzene ring part tends to adsorb onto the surface of ZP composite particles that make up the Pickering emulsion, increasing the hydrophobicity of the particle surface. As the thymol concentration increases, the hydrophobic interactions on the particle surface are enhanced, leading to particle aggregation and the formation of larger aggregates, ultimately resulting in an increase in emulsion particle size (Yang *et al.* 2020).

Stability of the emulsion

The storage stability of the emulsion, a crucial determinant of its application performance, was assessed using the representative ZP-Ty-2% formulation (Fig. 3). Throughout the 20-day storage, the emulsion exhibited a homogeneous macroscopic appearance with no signs of phase separation (Fig. 3(a)). Concurrently, the particle size, as observed in Fig. 3(b), remained predominantly below 100 μm despite a minor increase, confirming the overall stability of the formulation. As displayed in Fig. 3(c), the average particle size of the emulsion increased from 26.9 μm to 36.7 μm as the storage time extended to 20 days, which is consistent with the optical microscope observations (Fig. 3(b)). This gradual increase in particle size is likely driven by time-dependent particle aggregation. The underlying mechanism can be attributed to dynamic changes in the particle surface adsorption layer (Schalow *et al.* 2007). Specifically, the encapsulated thymol may undergo minor redistribution, conformational changes, or partial desorption over time. These processes may weaken the electrostatic or steric repulsive forces between particles, thereby promoting aggregation *via* hydrophobic interactions and leading to the formation of larger aggregates. This minor aggregation and particle growth represent the evolution process towards a more thermodynamically stable state during storage, a phenomenon known as “ripening” (Ravera *et al.* 2021). Additionally, the thymol

encapsulation efficiency was monitored throughout storage. As shown in Fig. 3(d), the encapsulation efficiency decreased from an initial value of 91.4% to 86.9% on day 20. Although a decrease was observed, the minor extent of this loss nevertheless demonstrates the robust stability and thymol encapsulation capability of the developed Pickering emulsion system. This marginal loss can be attributed to the ripening-induced particle aggregation, which reduced the specific surface area available for thymol adsorption, consequently impairing the encapsulation capability. Simultaneously, dynamic changes in the particle surface adsorption layer may induce the desorption of some encapsulated thymol molecules, thereby releasing it into the continuous phase.

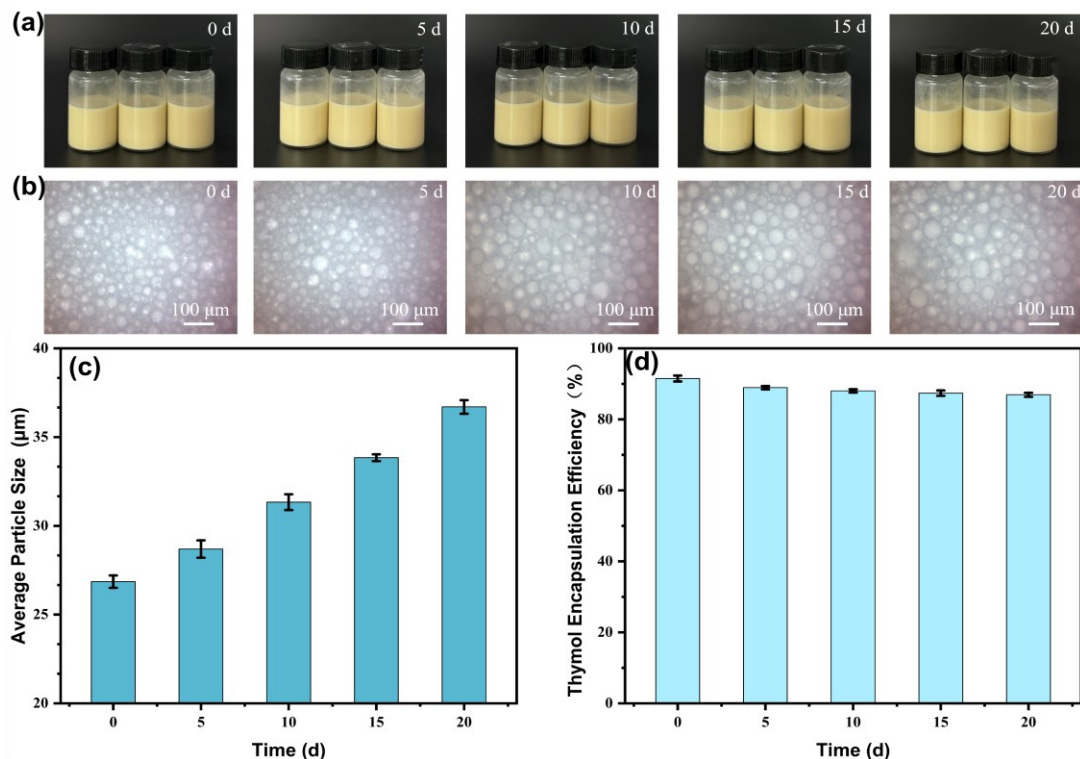


Fig. 3. Macroscopic appearance (a), optical micrographs (b), average particle size (c), and thymol encapsulation efficiency (d) of the emulsions at different storage times

Mechanism of Thymol Pickering Emulsion Formulation

To reveal the formation mechanism of the thymol Pickering emulsion, its chemical structure and surface potential were characterized. As shown in Fig. 4(a), zein, MCT, and thymol shared a characteristic peak at approximately 2959 cm^{-1} , corresponding to C-H stretching vibrations of their alkyl chains, long fatty acid chains, and aromatic rings, respectively (Suriani *et al.* 2009; Beć *et al.* 2021). These hydrophobic groups served as the basis for the encapsulation of the oil phase. The characteristic peak of MCT at 1744 cm^{-1} , attributed to C=O stretching vibration (Verhoef *et al.* 2011), disappeared in the spectrum of the thymol Pickering emulsion, suggesting the effective encapsulation of MCT by the ZP composite particles. Additionally, the characteristic peak of thymol at 1712 cm^{-1} , assigned to the phenolic O-H stretching vibration (Li *et al.* 2018), exhibited significant broadening in the Pickering emulsion spectrum. This broadening suggests the formation of a hydrogen-bonding network between thymol and the zein-pectin composite, which in turn

enhances the stability of the emulsion interface (Asbury *et al.* 2004; Stubenrauch *et al.* 2017; Zhang *et al.* 2024).

As shown in Fig. 4(b), the ZP complex exhibited a zeta potential of -20.7 mV, closely matching that of pectin (-19.3 mV) and contrasting sharply with the positive charge of zein (ZN, +32 mV). This indicates that pectin effectively coats the zein particles, imparting its own characteristic negative charge to the ZP complex. Following the introduction of the oil phase (MCT, with or without thymol), the emulsion exhibited a decreased zeta potential (Fig. 4(c)). This may be attributed to the oriented arrangement of ZP at the oil-water interface, which results in greater exposure of their pectin's negatively charged groups (*e.g.*, carboxyl groups) to the aqueous phase and a consequent increase in surface charge density. Furthermore, as observed in Fig. 4(c), the zeta potential of the emulsion gradually increased from -37.3 mV to -24.3 mV as the thymol concentration rose from 0 to 2.5 wt%. This change in zeta potential can be attributed to the surface adsorption behavior of thymol molecules. Thymol possesses an amphiphilic nature, featuring a polar phenolic hydroxyl group and a hydrophobic benzene ring. The phenolic hydroxyl group can form hydrogen bonds with water molecules, while the benzene ring tends to adsorb onto the surface of the colloidal particles (*e.g.*, ZP composite particles), facilitating the formation of a thymol Pickering emulsion. This interfacial adsorption alters the particle surface and charge distribution, thereby contributing to the observed rise in zeta potential (Ferreira *et al.* 2016).

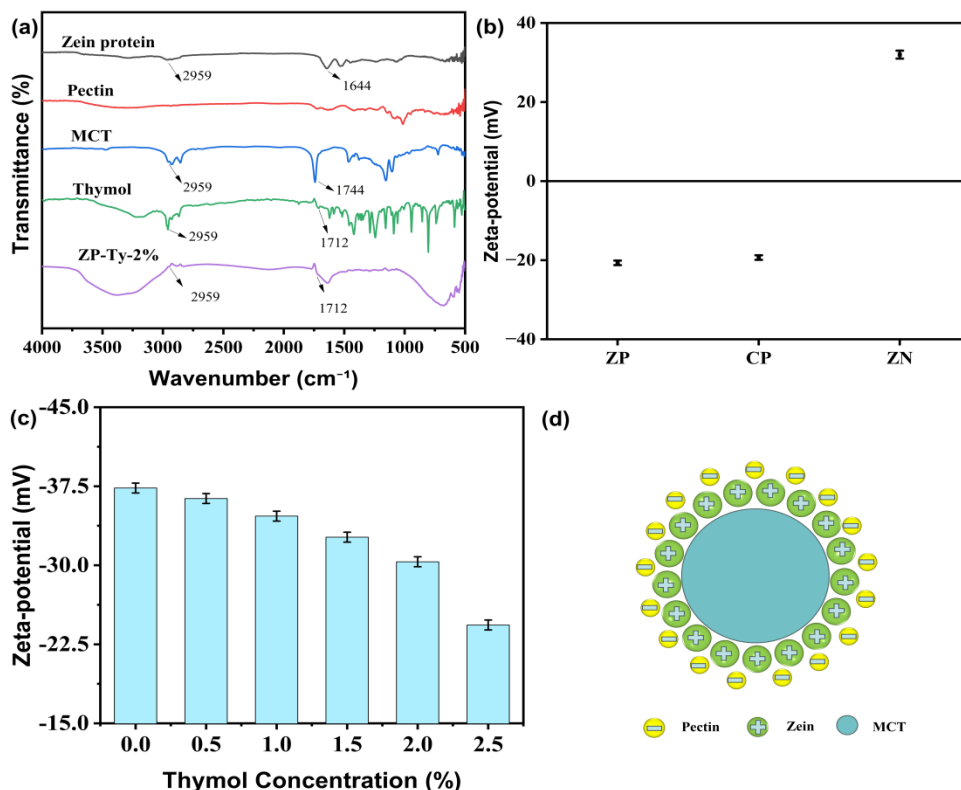


Fig. 4. FTIR spectra of zein, pectin, MCT, thymol, and ZP-Ty-2% emulsion (a); Zeta-potential of ZP, CP, and ZN (b); Zeta potential as a function of thymol concentration curve (c); Mechanism schematic of thymol Pickering emulsion formation (d)

Based on the foregoing analysis, the formation and stability of the thymol Pickering emulsion primarily are attributed to the synergistic action of composite colloidal particles and intermolecular forces. The zein-pectin composite particles adsorb at the oil-water interface, creating a protective barrier that encapsulates hydrophobic active compounds (Fig. 4(d)). Thymol molecules interact with the composite particles *via* hydrophobic interactions, while their phenolic hydroxyl groups form a hydrogen bonding network with the surrounding medium, collectively enhancing the stability of the emulsion. The synergistic effect of these multiple intermolecular forces promotes the uniform dispersion and stability of active components within the emulsion, establishing a foundation for subsequent functional utilization.

Performance of Functionalized Paper

Surface morphology of functionalized paper

The surface morphology of the functionalized paper was first characterized due to its direct impact on barrier properties—a critical factor for preservation. The base paper exhibited a porous, rough fibrous network (Fig. 5(a, b)), whereas the functionalized paper (Fig. 5(c)) displayed a more uniform and smoother surface due to the formation of a thymol Pickering emulsion coating. This coating formation was further confirmed by the particulate structures observed under high magnification (Fig. 5(d)). Microstructural analysis confirmed that the functionalization treatment significantly altered the paper's microstructure.

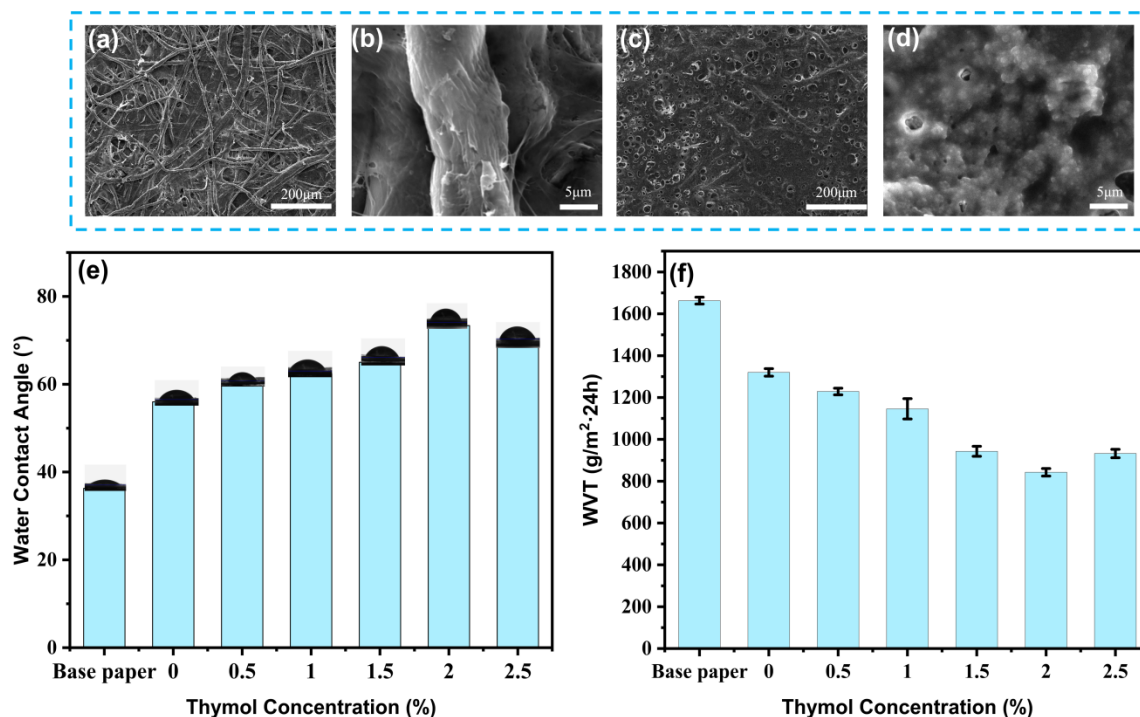


Fig. 5. SEM images of the base paper (a, b) and functionalized paper (c, d); Surface hydrophobicity (e) and water vapor transmission (f) of the base paper and functionalized paper

Water contact angle and water vapor barrier properties of functionalized paper

The hydrophobicity of a material's surface influences its water vapor barrier properties, which consequently affect its preservation performance. Therefore, the water contact angle and the water vapor transmission of the paper were measured, with the results shown in Fig. 5(e, f). The data indicate that applying the Pickering emulsion coating elevated the water contact angle and reduced the WVT of the paper, which can be attributed to the microstructural modifications induced by coating. As the thymol concentration in the Pickering emulsion increased from 0 wt% to 2.5 wt%, the water contact angle of the paper increased initially to a maximum of 73.35° at a thymol concentration of 2.0 wt% before decreasing, a trend mirrored by the WVT, which reached its minimum at the concentration. This observation may be primarily attributed to the thymol encapsulation efficiency within the Pickering emulsion and the concomitant changes in the paper's microstructure. The enhanced hydrophobicity and reduced water vapor permeability of the paper mitigate moisture loss in fruits during storage, thereby improving their preservation performance.

Antimicrobial activity of the functionalized paper

As *S. aureus* and *E. coli* are prevalent pathogenic bacteria, it is crucial for fruit and vegetable preservation materials to possess antimicrobial activity against these two species to ensure human health. Accordingly, the antimicrobial effect of functionalized paper was systematically evaluated *via* the plate counting method (Fig. 6). For *S. aureus* (Fig. 6(a)) and *E. coli* (Fig. 6(b)), as the thymol concentration increased from 0 wt% to 2 wt%, the number of colonies progressively declined, with the inhibition rates reaching 90.9% and 92.4% (Figs. S2 and S3), respectively. Notably, when the thymol concentration was further raised to 2.5 wt%, the colony counts showed a slight rebound, and the inhibition rates for *S. aureus* and *E. coli* decreased to 85.1% and 87.3% (Fig. (S2 and S3)), respectively. The antibacterial rate of the functional paper demonstrated a strong positive correlation with the thymol encapsulation efficiency of the coating emulsion, indicating that its antimicrobial performance is principally governed by the availability of the active antibacterial component.

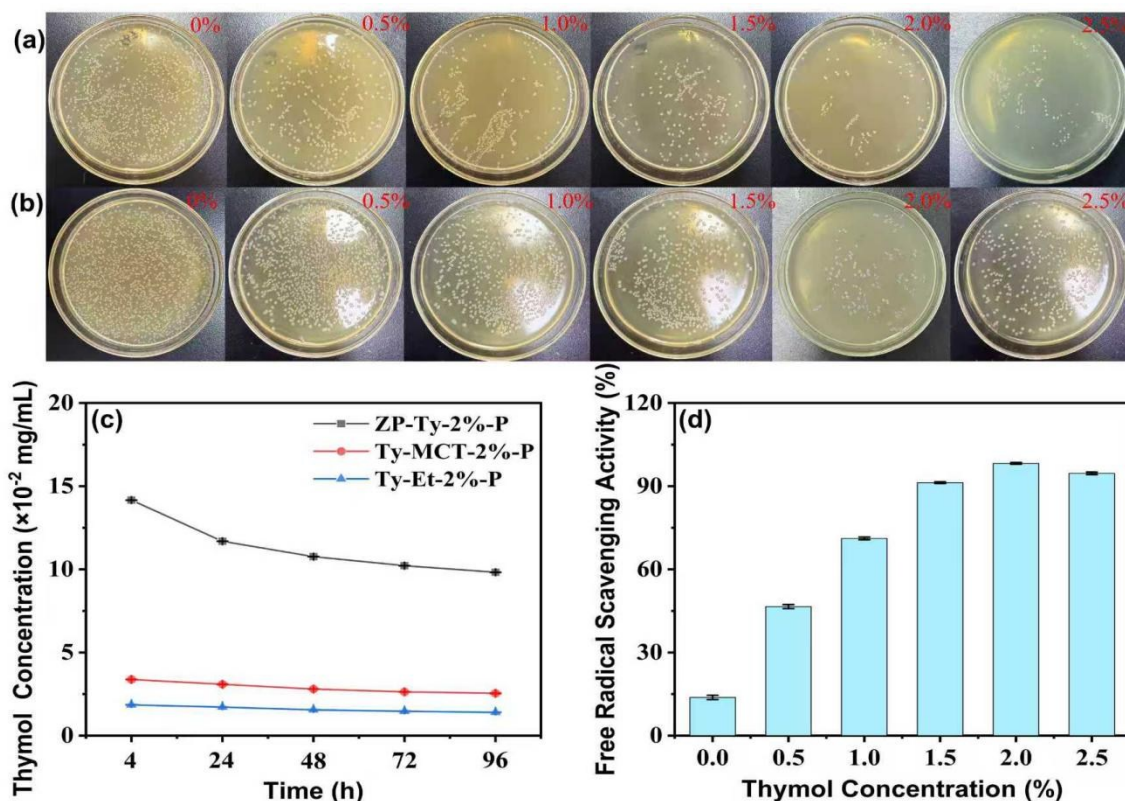


Fig. 6. Antimicrobial activity against *S. aureus* (a) and *E. coli* (b), thymol sustained-release performance (c), and antioxidant activity (d) of functionalized paper coated with emulsions at different thymol concentrations

Thymol sustained-release performance of the functionalized paper

As the thymol sustained-release performance of the functionalized paper is crucial for its application stability, ZP-Ty-2%-P was selected to profile the thymol release behavior (Fig. 6(c)). As seen in Fig. 6, the residual thymol concentration in all functionalized papers gradually decreased over time due to thymol volatilization. Notably, the thymol retention in ZP-Ty-2%-P was significantly higher than that in Ty-MCT-2%-P and Ty-Et-2%-P. This enhanced retention can be ascribed to the effective encapsulation of thymol by ZP composite colloidal particles in the emulsion, leading to a significant reduction in its volatilization.

Antioxidant activity of the functionalized paper

The antioxidant activity of fruit and vegetable preservation materials can effectively delay the oxidative deterioration of the packaged contents, thereby extending shelf life. Accordingly, the antioxidant activity of the functionalized paper was evaluated by its free radical scavenging efficacy, as shown in Fig. 6(d). The results indicated that the free radical scavenging percentage of the functionalized paper gradually rose to 98.2% as the thymol concentration increased from 0 wt% to 2.0 wt%. However, the scavenging percentage declined to 94.6% when the thymol concentration further increased to 2.5 wt%, which is primarily attributed to a decline in the thymol encapsulation efficiency, the essential antioxidant agent (Chen *et al.* 2020), within the emulsion. Collectively, these results confirm the efficacy of thymol as a natural antioxidant for enhancing the paper's antioxidant properties. Given the promising water vapor barrier, antimicrobial and

antioxidant properties of ZP-Ty-2%-P, its potential for practical application in fruit preservation will be the focus of further evaluation.

Preservation performance of the functionalized paper

The preservation performance of the functionalized paper (exemplified by ZP-Ty-2%-P) was evaluated in comparison with a blank group (BL, untreated) and a control group (CK, base paper-treated) by monitoring changes in the extent of decay, weight loss, firmness, and soluble solids content of cherry tomatoes throughout storage. As shown in Fig. 7(a) and Fig. S4, an increase in spoilage was observed with prolonged storage.

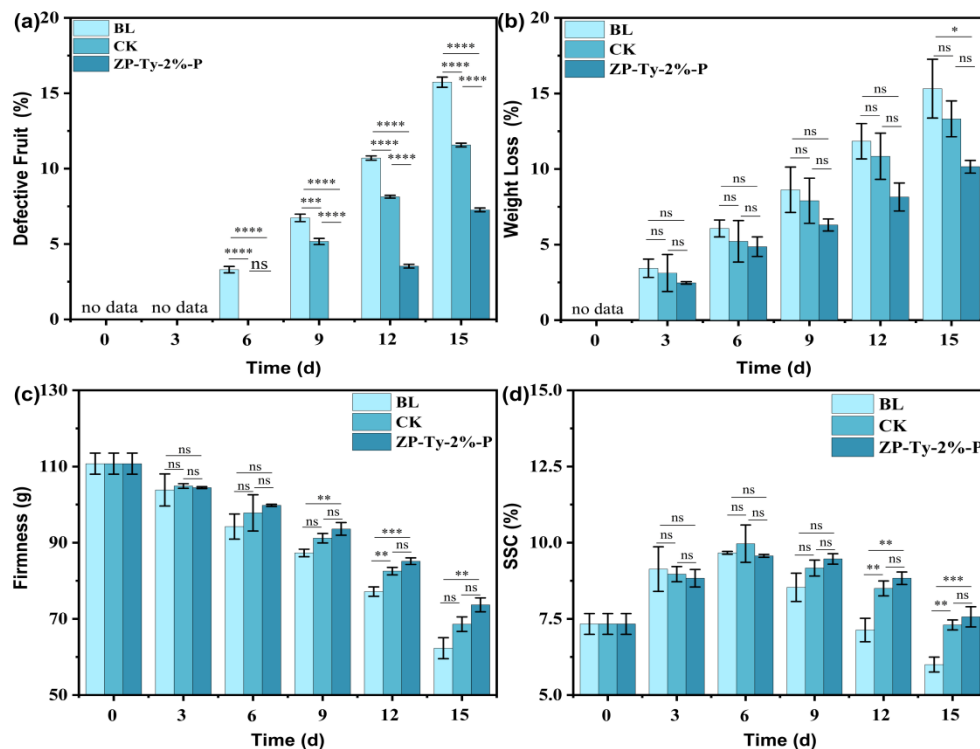


Fig. 7. Changes in spoilage rate (a), weight loss (b), firmness (c), and SSC (d) of cherry tomatoes for the BL (untreated), CK (base paper), and ZP-Ty-2%-P (functionalized paper) groups during storage. Note: Data are presented as mean $\pm$ SD ($n = 3$); * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$, **** $P < 0.0001$; ns, not significant

The spoilage rate of the BL samples increased sharply, reaching 15.7% by day 15. In comparison, the CK samples showed a slower increase yet still attained 11.6% by day 15, indicating that the physical barrier provided by the base paper provides only limited effectiveness in delaying fruit spoilage. Notably, the ZP-Ty-2%-P samples exhibited the slowest increase, attaining only 7.3% after 15 days, which fully demonstrates their excellent preservation performance. This can be attributed to the thymol released from the functionalized paper, which creates an antimicrobial microenvironment that effectively inhibits fruit spoilage (Ranjbar *et al.* 2022).

For the weight loss percentage, Fig. 7(b) reveals a gradual increase across all groups during storage, with the BL, CK, and ZP-Ty-2%-P samples displaying the highest, intermediate, and lowest values, respectively. This trend demonstrates a significant reduction in weight loss from cherry tomatoes by the functionalized paper due to its dual functionality: an effective barrier property that inhibited moisture evaporation, and an

antimicrobial activity that suppressed microbial proliferation, thereby collectively minimizing overall weight loss.

As an important indicator of fruit tissue integrity and maturity (Saladié *et al.* 2007), firmness was monitored during storage. As depicted in Fig. 7(c), a general decline in firmness was observed across all groups over time. Nevertheless, the ZP-Ty-2%-P samples exhibited superior performance in retaining firmness compared to the BL and CK samples. This can be attributed to the barrier layer formed by the Pickering emulsion on the paper surface (Fig. 2(c)), which effectively inhibited moisture evaporation, thereby delaying the fruit softening process (Du *et al.* 2022).

The SSC, a key parameter reflecting the balance between sugar accumulation and consumption in the fruit (Saladié *et al.*, 2007), was monitored throughout storage. As presented in Fig. 7(d), the ZP-Ty-2%-P samples exhibited the most gradual change in SSC and consistently maintained higher levels throughout storage. This can be attributed to the barrier layer formed by the Pickering emulsion on the paper surface, which effectively reduced the fruit's respiratory rate, thereby decreasing the consumption of sugars and other endogenous substances and maintaining higher SSC levels (Ding *et al.* 2024).

In summary, the functionalized paper, benefiting from the formation of a Pickering emulsion barrier and enhanced antimicrobial properties, exhibited a synergistic effect in maintaining the weight, firmness, and SSC of cherry tomatoes, thereby demonstrating its overall preservation efficacy.

CONCLUSIONS

1. This study successfully developed a thymol Pickering emulsion (with a colloidal zein/pectin stabilizer) and corresponding functionalized paper, both of which showed significant effects in preserving cherry tomatoes after harvest. At a thymol concentration of 2 wt%, the encapsulation efficiency reached 91.4%, and the emulsion displayed excellent physical stability and sustained-release performance.
2. The resulting functionalized paper exhibited notable barrier, antimicrobial, and antioxidant properties, with inhibition rates against *S. aureus* and *E. coli* reaching 90.9% and 92.4%, respectively, and a 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging percentage of 98.2%.
3. In preservation tests, the functionalized paper effectively slowed down changes in weight, firmness, and sweetness of cherry tomatoes. After 15 days of storage, the decay rate was only 7.3%, which was significantly lower than that observed in the blank and control groups.
4. The developed functionalized paper offers an efficient, safe, and environmentally friendly approach for postharvest fruit preservation, demonstrating promising potential for future applications.

ACKNOWLEDGMENTS

The authors are grateful for the support from the Yibin City Major Bamboo Industry Research Project "Research and Integrated Demonstration of Key Technologies for the Smart Bamboo Industry" (Project No. YBZD202401) and the Undergraduate Innovation

and Entrepreneurship Training Program (No. CX2025144) at Sichuan University of Science and Engineering.

REFERENCES CITED

- Anubha, Ete, L., and Jayarajan, S. (2024). "Advances in postharvest management of cherry tomato," *BIO Web of Conferences*, N. Kaushik (ed.), 110, article 02012. <https://doi.org/10.1051/bioconf/202411002012>
- Asbury, J. B., Steinel, T., and Fayer, M. (2004). "Hydrogen bond networks: Structure and evolution after hydrogen bond breaking," *The Journal of Physical Chemistry B* 108(21), 6544-6554.
- Beć, K. B., Grabska, J., and Huck, C. W. (2021). "Issues in hyperspectral traceability of foods," in: *Comprehensive Foodomics*, Elsevier, Amsterdam, Netherlands, pp. 258-289. <https://doi.org/10.1016/B978-0-08-100596-5.22848-5>
- Boye, A., Addo, J. K., Acheampong, D. O., Thomford, A. K., Asante, E., Amoaning, R. E., and Kuma, D. N. (2020). "The hydroxyl moiety on carbon one (C1) in the monoterpene nucleus of thymol is indispensable for anti-bacterial effect of thymol," *Heliyon* 6(3), article e03492. <https://doi.org/10.1016/j.heliyon.2020.e03492>
- Chen, J., Yang, J., Ma, L., Li, J., Shahzad, N., and Kim, C. K. (2020). "Structure-antioxidant activity relationship of methoxy, phenolic hydroxyl, and carboxylic acid groups of phenolic acids," *Scientific Reports* 10(1), article 2611. <https://doi.org/10.1038/s41598-020-59451-z>
- Cheng, Z., Li, J., He, G., Su, M., Xiao, N., Zhang, X., Zhong, L., Wang, H., Zhong, Y., Chen, Q., *et al.* (2024). "Biodegradable packaging paper derived from chitosan-based composite barrier coating for agricultural products preservation," *International Journal of Biological Macromolecules* 280, article 136112. <https://doi.org/10.1016/j.ijbiomac.2024.136112>
- D'Aquino, S., Mistriotis, A., Briassoulis, D., Di Lorenzo, M. L., Malinconico, M., and Palma, A. (2016). "Influence of modified atmosphere packaging on postharvest quality of cherry tomatoes held at 20 °C," *Postharvest Biology and Technology* 115, 103-112. <https://doi.org/10.1016/j.postharvbio.2015.12.014>
- Dang, C., Yin, Y., and Pu, J. (2017). "Preparation and synthesis of water-soluble chitosan derivative incorporated in ultrasonic-assistant wheat straw paper for antibacterial food-packaging," *Nordic Pulp & Paper Research Journal* 32(4), 606-614. https://doi.org/10.3183/npprj-2017-32-04_p606-614_pu
- Ding, X., Ma, J., Liu, S., Dong, X., Pan, X., and Dong, B. (2024). "Acid electrolytic water treatment improves the quality of fresh-cut red pitaya fruit by regulating ROS metabolism and phenylpropanoid pathway," *Postharvest Biology and Technology* 207, article 112636. <https://doi.org/10.1016/j.postharvbio.2023.112636>
- Du, Y., Yang, F., Yu, H., Yao, W., and Xie, Y. (2022). "Controllable fabrication of edible coatings to improve the match between barrier and fruits respiration through layer-by-layer assembly," *Food and Bioprocess Technology* 15(8), 1778-1793. <https://doi.org/10.1007/s11947-022-02848-7>
- Ehman, N., Ponce de Leon, A., and Area, M. C. (2023). "Fractionation stream components of wood-based biorefinery: New agents in active or intelligent primary food packaging?," *BioResources* 18(4), 6724-6726. <https://doi.org/10.15376/biores.18.4.6724-6726>

- Ferreira, J. V. N., Capello, T. M., Siqueira, L. J. A., Lago, J. H. G., and Caseli, L. (2016). "Mechanism of action of thymol on cell membranes investigated through lipid Langmuir monolayers at the air–water interface and molecular simulation," *Langmuir* 32(13), 3234-3241. <https://doi.org/10.1021/acs.langmuir.6b00600>
- GB/T 41515 (2022). "Coating machine vocabulary," Standardization Administration of China, Beijing.
- Gicü, M. O. (2023). "Physical and surface properties of food packaging paper coated by thyme oil," *BioResources* 18(4), 7333-7340. <https://doi.org/10.15376/biores.18.4.7333-7340>
- Guo, X. (2024). "Research progress of antibacterial and antioxidant packaging materials for meat: A review," *Journal of Food Process Engineering* 47(7), article e14690. <https://doi.org/10.1111/jfpe.14690>
- Hajibonabi, A., Yekani, M., Sharifi, S., Nahad, J. S., Dizaj, S. M., and Memar, M. Y. (2023). "Antimicrobial activity of nanoformulations of carvacrol and thymol: New trend and applications," *OpenNano* 13, article 100170. <https://doi.org/10.1016/j.onano.2023.100170>
- Hu, Z., Chen, C., and Du, L. (2026). "Postharvest suppression of *Staphylococcus aureus* and *Escherichia coli* with softening delay in cherry tomatoes by ultrasonic plasma-activated microbubble water," *Postharvest Biology and Technology* 231, article 113861. <https://doi.org/10.1016/j.postharvbio.2025.113861>
- ISO 13099-2 (2012). "Colloidal systems — Methods for zeta-potential determination — Part 2: Optical methods," International Organization for Standardization, Geneva.
- Jieying, S., Tingting, L., Caie, W., Dandan, Z., Gongjian, F., and Xiaojing, L. (2024). "Paper-based material with hydrophobic and antimicrobial properties: Advanced packaging materials for food applications," *Comprehensive Reviews in Food Science and Food Safety* 23(3), article e13373. <https://doi.org/10.1111/1541-4337.13373>
- Li, J., Xu, X., Chen, Z., Wang, T., Lu, Z., Hu, W., and Wang, L. (2018). "Zein/gum Arabic nanoparticle-stabilized Pickering emulsion with thymol as an antibacterial delivery system," *Carbohydrate Polymers* 200, 416-426. <https://doi.org/10.1016/j.carbpol.2018.08.025>
- Li, D., Mia, F., Chen, J., Liu, Z., Wang, Z., and Wang, Y. (2025). "Pickering emulsions using Pd NP-loaded pH-sensitive carboxylated cellulose nanocrystals for catalytic hydrogenation," *BioResources* 20(2), 3534-3544. <https://doi.org/10.15376/biores.20.2.3534-3544>
- Liu, W., Liu, H., Liu, K., Du, H., Liu, Y., and Si, C. (2020). "Paper as substitute for plastic," *BioResources* 15(4), 7309-7312. <https://doi.org/10.15376/biores.15.4.7309-7312>
- Munteanu, B. S., and Vasile, C. (2021). "Encapsulation of natural bioactive compounds by electrospinning—Applications in food storage and safety," *Polymers* 13(21), article 3771. <https://doi.org/10.3390/polym13213771>
- Ranjbar, A., Ramezani, A., Shekarforoush, S., Niakousari, M., and Eshghi, S. (2022). "Antifungal activity of thymol against the main fungi causing pomegranate fruit rot by suppressing the activity of cell wall degrading enzymes," *LWT* 161, article 113303. <https://doi.org/10.1016/j.lwt.2022.113303>
- Ravera, F., Dziza, K., Santini, E., Cristofolini, L., and Liggieri, L. (2021). "Emulsification and emulsion stability: The role of the interfacial properties," *Advances in Colloid and Interface Science* 288, article 102344. <https://doi.org/10.1016/j.cis.2020.102344>

- Renard, C. M. G. C., Ginies, C., Gouble, B., Bureau, S., and Causse, M. (2013). "Home conservation strategies for tomato (*Solanum lycopersicum*): Storage temperature vs. duration – Is there a compromise for better aroma preservation?," *Food Chemistry* 139(1–4), 825-836. <https://doi.org/10.1016/j.foodchem.2013.01.038>
- Sakthiselvi, T., Paramasivam, M., Vasanthi, D., and Bhuvaneswari, K. (2020). "Persistence, dietary and ecological risk assessment of indoxacarb residue in/on tomato and soil using GC–MS," *Food Chemistry* 328, article 127134. <https://doi.org/10.1016/j.foodchem.2020.127134>
- Saladié, M., Matas, A. J., Isaacson, T., Jenks, M. A., Goodwin, S. M., Niklas, K. J., Xiaolin, R., Labavitch, J. M., Shackel, K. A., Fernie, A. R., *et al.* (2007). "A reevaluation of the key factors that influence tomato fruit softening and integrity," *Plant Physiology* 144(2), 1012-1028. <https://doi.org/10.1104/pp.107.097477>
- Schalow, T., Brandt, B., Starr, D. E., Laurin, M., Shaikhutdinov, S. K., Schauermaun, S., Libuda, J., and Freund, H.-J. (2007). "Particle size dependent adsorption and reaction kinetics on reduced and partially oxidized Pd nanoparticles," *Physical Chemistry Chemical Physics* 9(11), 1347-1361.
- Stubenrauch, C., Hamann, M., Preisig, N., Chauhan, V., and Bordes, R. (2017). "On how hydrogen bonds affect foam stability," *Advances in Colloid and Interface Science* 247, 435-443. <https://doi.org/10.1016/j.cis.2017.02.002>
- Suriani, A. B., Rosazley, R., Sakrani, S., Rusop, M., Rusop, M., and Soga, T. (2009). "Bonding properties of hydrogenated amorphous carbon thin films characterized by Fourier transform infra-red spectrometer," in: *AIP Conference Proceedings*, Shah Alam, Selangor, Malaysia, pp. 437-442. <https://doi.org/10.1063/1.3160180>
- Teng, Z., Luo, Y., Zhou, B., Wang, Q., and Hapeman, C. J. (2021). "Characterization and mitigation of chemical oxygen demand and chlorine demand from fresh produce wash water," *Food Control* 127, article 108112. <https://doi.org/10.1016/j.foodcont.2021.108112>
- Verhoefen, M.-K., Schäfer, G., Shastri, S., Weber, I., Glaubitz, C., Mäntele, W., and Wachtveitl, J. (2011). "Low temperature FTIR spectroscopy provides new insights in the pH-dependent proton pathway of proteorhodopsin," *Biochimica et Biophysica Acta (BBA) - Bioenergetics* 1807(12), 1583-1590. <https://doi.org/10.1016/j.bbabi.2011.09.001>
- Yadav, J., Datta, M., and Gour, V. S. (2014). "Wax coating for paper," *BioResources* 9(3), 5066-5072. <https://doi.org/10.15376/biores.9.3.5066-5072>
- Yang, P., Hu, X., Zi, F., Yang, B., Wang, Q., Chen, Y., and Chen, S. (2020). "Synergistic enhancement of fine-kaolinite-particle hydrophobic agglomeration by combining dodecylamine with octanoic acid," *Minerals Engineering* 155, article 106444. <https://doi.org/10.1016/j.mineng.2020.106444>
- Ye, S., Chen, J., Cao, S., Luo, D., and Ba, L. (2024). "Thymol application delays the decline of fruit quality in blueberries via regulation of cell wall, energy and membrane lipid metabolism," *Food Chemistry* 458, article 140193. <https://doi.org/10.1016/j.foodchem.2024.140193>
- Yu, D., Liu, W., Li, Y., Wang, H., and Li, G. (2015). "Dodecenylsuccinic anhydride Pickering emulsion stabilized by montmorillonite nanoparticles modified with sodium fluoride," *BioResources* 10(2), 2755-2772. <https://doi.org/10.15376/biores.10.2.2755-2772>
- Zhang, R., Ma, Y., Lu, Y., Gao, Y., and Mao, L. (2024). "Structural responses of zein-based oil-in-glycerol emulsion gels during freeze-thawing and heating," *Colloids and*

Surfaces A: Physicochemical and Engineering Aspects 689, article 133747.

<https://doi.org/10.1016/j.colsurfa.2024.133747>

Zhang, J., Liu, J., Yang, Y., Yang, J., and Fang, L. (2025a). "Rosin-aluminum sulphate hybrid emulsion modified by 3-glycidoxypropyltrimethoxysilane (GPTMS) for reducing surface energy of cellulose fibers," *Applied Surface Science* 688, article 162344. <https://doi.org/10.1016/j.apsusc.2025.162344>

Zhang, Y., Boffa, V., Roslev, P., Magnacca, G., and Wang, D. (2025b). "Polyethylene glycol enhanced encapsulation of thymol in metal-organic framework nanocarriers for antimicrobial food packaging," *Food Chemistry* 488, article 144911. <https://doi.org/10.1016/j.foodchem.2025.144911>

Zhong, Q.-X., Zheng, H.-Y., Zhu, Y.-L., Li, J., Chen, H.-C., and Fan, X.-P. (2023). "Preparation of thymol-containing microcapsules and its application in strawberry preservation," *Journal of the Science of Food and Agriculture* 2023, 167-176. <https://doi.org/10.7506/spkx1002-6630-20220426-331>

Zhu, D., Liang, J., Liu, H., Cao, X., Ge, Y., and Li, J. (2018). "Sweet cherry softening accompanied with moisture migration and loss during low-temperature storage," *Journal of the Science of Food and Agriculture* 98(10), 3651-3658. <https://doi.org/10.1002/jsfa.8843>

Article submitted: November 29, 2025; Peer review completed: December 20, 2025;

Revised version received: December 29, 2025; Further revised version received and accepted: December 30, 2025; Published: January 8, 2026.

DOI: 10.15376/biores.21.1.1669-1689

APPENDIX

Supplementary Material

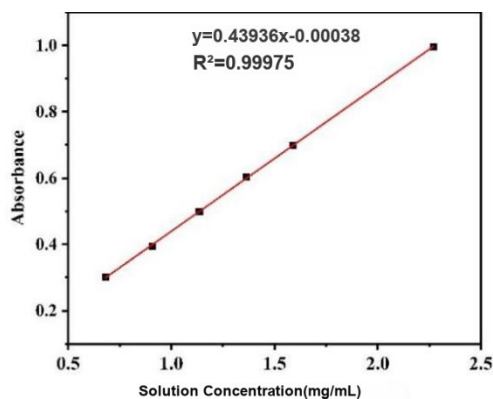


Fig. S1. Standard curve of thymol concentration and absorbance

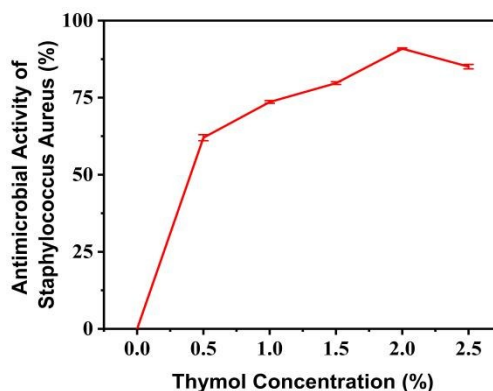


Fig. S2. The antibacterial effect of functionalized paper with different thymol concentrations in Pickering emulsions against *S. aureus*

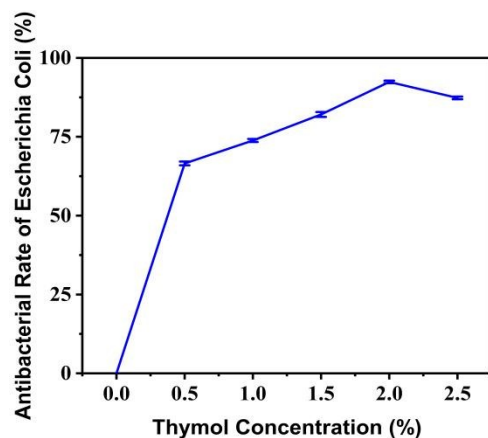


Fig. S3. The antibacterial effect of functionalized paper with different thymol concentrations in Pickering emulsions against *E. coli*

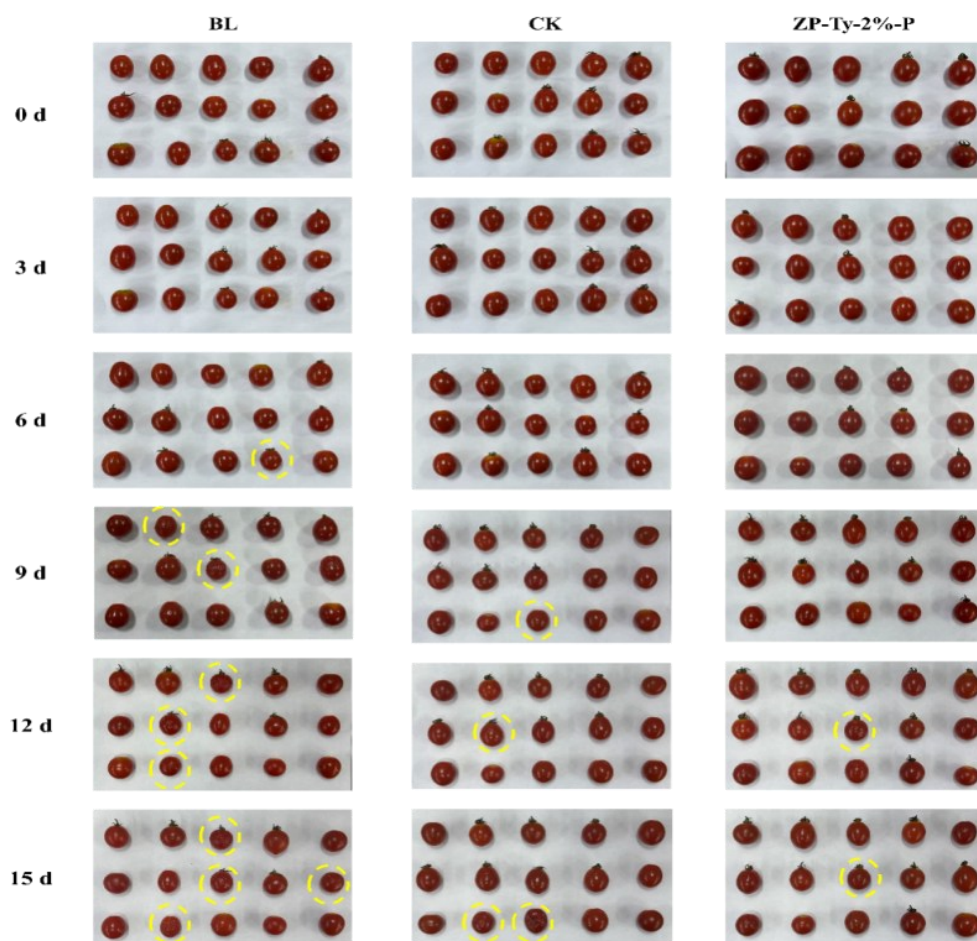


Fig. S4. Photos of BL, CK, and ZP-Ty-2%-P samples at different times during storage