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Characterization of a Clove Essential Oil Slow-Release Microencapsulated Composite Film and Its Preservation Effects on Blueberry

Yang Li,* Boya Bian, Rongrong Tang, and Kexin Zhang

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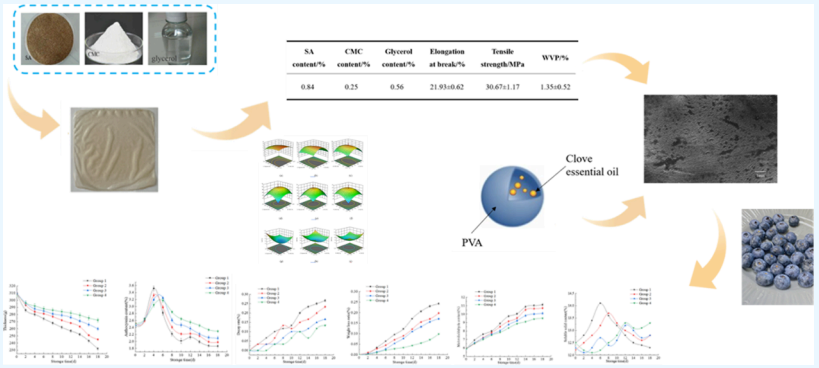

ABSTRACT: In order to extend the shelf life of fruits and vegetables, a sodium alginate-sodium carboxymethyl cellulose composite film loaded with poly(vinyl alcohol) microcapsules was prepared in this paper. The optimal film substrate ratios were obtained after the response surface optimization. Poly(vinyl alcohol) microcapsules were prepared, clove essential oil was loaded into them to investigate the effects of microcapsules on the composite film properties, and the microcapsule composite film with the best overall performance was selected to be applied to blueberry preservation. The results showed that the composite film of 0.84% sodium alginate, 0.25% sodium carboxymethyl cellulose, and 0.56% glycerol presented excellent mechanical properties after adding 1.75% microcapsules. It had a good inhibitory effect on *Escherichia coli*, *Staphylococcus aureus*, and Penicillium and had a DPPH clearance rate of 83.78%. The low-temperature bonded composite film could slow down the respiration rate of blueberry, inhibit browning and water loss, effectively maintain the quality of blueberry, and have a significant preservation effect on the anthocyanin and soluble solid content of blueberry. The clove essential oil slow-release microencapsulated composite film can be used for blueberry preservation.

INTRODUCTION

Due to their inherent functions, fruits and vegetables do not lose their respiration and cellular activity directly after harvesting.[1] Blueberries are grown in large quantities, are highly nutritious, and are a respiratory leapfrog fruit. After picking, blueberries do not lose their respiration and cellular activity directly after picking but continue to perform their basic functions for a period of time due to their own functions. However, the higher temperature in the transportation link will accelerate the degradation of nutrients inside the blueberry, and at the same time, due to the high water content of the blueberry itself although the skin is thin, it is very easy to be affected by the double impact of respiratory heat and the external environment during the storage and transportation period, which leads to the decline of the nutritional value of the blueberry. Therefore, for blueberries after picking, how to treat them to extend the quality of their storage period is particularly important.[2]

At present, for the preservation of fruits and vegetables, commonly used methods are refrigerated low-temperature preservation, air-conditioning preservation, or through a special way, such as the use of ultraviolet-light irradiation sterilization, ozone air-conditioning inhibition of cellular respiration, 1-MCP fumigation, and other measures to achieve the role of anticorrosion.[3−8] In addition, the addition of antioxidant and antimicrobial substances to the film-forming substrate can also produce some antimicrobial and antioxidant properties in the packaging.[9] Al-Hilifi et al. added a whey protein hydrolysate with antimicrobial and antioxidant proper-

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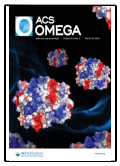

ties to chitosan films for food packaging.[10] Abdalla et al. added Sicilian lemon essential oil with antimicrobial properties to films and coatings from pectin and chitosan for strawberry preservation packaging.[11] Al-Hilifi et al. added natural antioxidant anthocyanins to aloe vera gel coating for freshness packaging of fig fruits.[12] Zhou et al. modified chitosan using glycidyl trimethylammonium, which has antimicrobial properties, and dihydroxy benzaldehyde, a natural polyphenol antioxidant, to prepare quaternate catechol-functionalized chitosan that can be used as a coating material for fruits.[13] Plant essential oils are natural antibacterial and antioxidant substances. Due to the simple extraction process and green, nonpolluting, and wide distribution of raw materials, clove essential oil was chosen as the antimicrobial and antioxidant agent in the composite film.[14] Zhang et al.[15] found that clove essential oil had a certain inhibitory effect on the thiobarbituric acid reactant value and the total volatile saline nitrogen content of soy-brined duck products and extended the shelf life of the products by 2 days, which had a certain antimicrobial and preservation effect. Hasheminejad and Khodaiyan[16] found that, compared with the three groups of chitosan, clove essential oil, and chitosan nanocoating, chitosan nanocoating with 0.15% clove essential oil had significantly lower total yeast and mold counts than the other groups during the storage of pomegranate corms. The total yeast and mold counts of pomegranate corms during storage were significantly lower than those of other groups, and fungal decay was delayed until the 60th day, which effectively protected pomegranates from microorganisms and prolonged the shelf life by 54 days. However, the volatility and poor stability result in a short shelf life. Therefore, it is necessary to use microencapsulation technology to embed clove essential oil to improve the defects and prolong the antibacterial and antioxidant effect.

Microencapsulation technology usually uses polymer materials as the wall material to wrap some easily oxidized and volatile substances into small particles of micrometers or nanometers to achieve the effect of slow release. Zhang et al. studied the freshness preservation performance of a tea polyphenol composite coating film on American redfish fillets and found that several tea polyphenol microcapsule composite coating films, all of which can form a slow-release system of antimicrobial agents, can effectively inhibit the growth of microorganisms in the fillets.[17] Fu and Song used thyme essential oil as the core material and porous starch as the wall material and successfully prepared microcapsules with an excellent slow-release effect by using the sharp pore-coagulation method.[18] Tang et al. investigated the effect of active antibacterial freshness pads on the freshness preservation of grass carp prepared from essential oil microcapsules with β-cyclodextrin as the wall material and bergamot essential oil and celandine essential oil as the core material. The results showed that the freshness preservation mat could effectively slow down the spoilage of grass carp.[19] Poly(vinyl alcohol) (PVA) is a polymer with good biocompatibility, chemical stability, film-forming properties, and mechanical properties.[20] Compared with natural polymers, PVA is less susceptible to external environmental influences and can maintain good properties at low temperatures, so it can be used as the wall material of microcapsules for fruit and vegetable preservation.

Sodium alginate (SA) is a linear polymeric polysaccharide composed of glyoxylate monomers, which has good film-forming properties. It has the effect of slowing down water loss and inhibiting microbial contamination of food.[21,22] Sodium carboxymethyl cellulose (CMC) is a highly polymerized anionic cellulose ether that has good stability.[23,24] Both materials have good film-forming properties, but the mechanical properties and thermal stability of the single film made are poor.[25] A composite film can fill the defects of a single film, improve the film properties, and enhance its application value.[26]

Therefore, this study used PVA to make microcapsules, wrapping the clove essential oil to improve the stability of the essential oil as well as to prolong its action time, then used SA and CMC as the base film, blended the microcapsules with it to make a clove essential oil slow-release microcapsule composite film with antioxidant effects, and applied it to blueberry preservation to investigate its effect on the postharvest quality of blueberry.

MATERIALS AND METHODS

Materials. The blueberries used in the experiment were purchased from Hongqi Township in Harbin, and the variety was "Lanfeng". The blueberries with uniform size, intact fruit powder, and no mechanical damage were selected. *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), and Penicillium were standard strains and produced by Beijing Biological Conservation Center Ltd. PVA, Tween 80, SA, and CMC were analytically pure and purchased from Sinopharm Chemical Reagent Co. Deionized water was prepared by an ultrapure water machine in the laboratory.

Instruments. A desktop blast drying oven (SDH-25055GT) was purchased from Shanghai Island Pure Industrial Co. A digital-display temperature-controlled magnetic stirrer (90-4) was purchased from Shanghai Zhenjie Test Equipment Co. A mass spectrometer (CT3-10K) was purchased from Book Field Corporation. An X-ray diffractometer (X'Pert^3 Powder) was purchased from Panaco, Netherlands. An FTIR spectrometer (Nicolet 6700) was purchased from Thermo Fisher Scientific, USA. A light transmittance and haze meter (WGT-S) was purchased from Shanghai Yidian Physical and Optical Instruments Co. A thickness gauge (D-C11ZXBS) was purchased from Mitutovo, Japan. A scanning electron microscope (JSM-7500F) was purchased from Japan Electronics Corporation. A computerized measurement and control tensile testing machine (LD-05) was purchased from Changchun Mingyue Small Testing Machine Co. A UV−visible spectrophotometer (L6/L6S) was purchased from Shanghai Electric Scientific Instruments Co.

Preparation of Basement Films. SA, CMC, and glycerol were mixed in certain proportions. After stirring for 60 min in a constant-temperature water bath at 60 °C with a force multiplier,[27] the film solution was cast into a 150 × 150 mm square Petri dish and placed in a room-temperature environment to dry for 3 days. The films were uncovered to obtain CMC-SA-glycerol (0.4, 0.3, 0.65%), CMC-SA-glycerol (0.8, 0.3, 0.65%), CMC-SA-glycerol (1.2, 0.3, 0.65%), CMC-SA-glycerol (0.8, 0.1, 0.65%), CMC-SA-glycerol (0.8, 0.5, 0.65%), CMC-SA-glycerol (0.8, 0.3, 0.25%), and CMC-SA-glycerol (0.8, 0.3, 0.95%). The optimal ratio of the basement film was obtained by the response surface optimization.

Characterizations of Basement Films. *Thickness.* According to the test standard of GB/T6672-2001 plastic film thickness,[28] the thickness of the composite films of 10 cm length and 1 cm width was measured at 5 points, and the average value was calculated.

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Mechanical Properties. Referring to the method of GB/T1040.2-2006, the films were cut into standard specimens of 150 mm × 10 mm, and tensile tests were performed with a tensile testing machine.[29] The maximum load and tensile displacement of the specimen at fracture were recorded. The tensile strength and elongation at break were calculated according to eqs 1 and 2, and the average values were taken five times.

$$\sigma_t = \frac{p}{b \times d} \quad (1)$$

$$\varepsilon = \frac{x}{L_0} \times 100\% \quad (2)$$

where σ_t is the tensile strength of the film specimen to be tested (MPa); p is the maximum load (N) of the film specimen to be tested during tensile fracture; b is the width of the film specimen (mm); d is the thickness of the film specimen (mm); ε is the elongation at break of the film specimen (%); x is the displacement occurring at fracture of the film specimen (mm); L_0 is the length of the film specimen (mm).

Optical Properties. Referring to GB2410-2008 and making appropriate adjustments, films were placed at the mouth of the receiver of the transmittance and haze meter for measurement, each group of films was measured once at each of the four corners and the center position, and the average values were taken.[30]

Water Vapor Permeability (WVP). A circle was cut in the film, and a glass vial was filled with 2.0 g of $CaCl_2$ (0% RH). It was placed in a desiccator containing saturated NaCl solution (75% relative humidity) at 20 °C. WVP was calculated according to eq 3.[31]

$$WVP = \frac{\Delta m \times x}{s \times \Delta p \times t} \quad (3)$$

where Δm is the mass of water vapor transmission (g); x is the thickness of the film to be measured (mm); s is the effective area for gas to pass through (m^2); Δp is the pressure difference between the two sides at 22 °C (Pa); t is the interval time.

Basement Film Response Surface Optimization. To further clarify the effects of SA concentration, CMC concentration, and glycerol concentration on the mechanical properties and water barrier properties of composite films and to optimize the preparation process of composite films, the combination test was conducted by the Box−Behnken central combination test based on the previous single-factor test.[32] The three-factor, three-level test setup is shown in Table 1, and the optimal ratio for preparing composite films was obtained by optimizing the composite film preparation process through response surface analysis.

Preparation of Clove Essential Oil Slow-Release Microcapsules. The microcapsules were prepared by the emulsification cross-linking method.[33] We weighed 5 g of PVA particles, dissolved it in 100 mL of deionized water, weighed 2 g of Tween 80 (polysorbate-80) and measured 100 mL of soybean oil, stirred them in a water bath at 50 °C, then added PVA solution drop by drop, continued to stir, emulsified for 30 min, and formed a water-in-oil emulsion. At 55 °C, 0.5 mL of 50% glutaraldehyde was added drop by drop to the emulsion and stirred in a water bath for 10 min, and then, 1.5 mL of hydrochloric acid was added to catalyze the cross-linking reaction, stirred, and centrifuged. The lower precipitate was taken, fully impregnated with 30% clove essential oil, and dried at room temperature to obtain clove essential oil slow-release microcapsules.

Table 1. Factors and Levels of Single-Factor Experiments

	factor		
level	CMC (%)	SA (%)	glycerol (%)
1	0.5	0.15	0.3
0	0.75	0.25	0.6
−1	1.0	0.35	0.9

Characterizations of Clove Essential Oil Slow-Release Microcapsules. *Scanning Electron Microscopy.* Scanning electron microscopy (SEM) was used to observe the morphology of the microcapsules. An appropriate amount of clove essential oil microcapsules was spread evenly on the metal base and sprayed with gold, and the accelerating voltage was 20 kV during the test.[34]

Fourier Transform Infrared Spectroscopy. The raw material of poly(vinyl alcohol) and microcapsules (in a powder form) were stirred and ground with a certain amount of potassium bromide (KBr) powder and compressed into a sheet for the test. The samples were measured using Fourier infrared spectroscopy with a wavenumber range of 4000−500 cm^{-1}, three scans, and a resolution of 2 cm^{-1}.[35]

Measurement of the Slow-Release Property. The release rate test was performed using the weighing method.[36] An alkaline environment (absolute ethanol) and an acidic environment (3% acetic acid solution) were set up. The total weight of clove essential oil slow-release microcapsules and the weighing bottle were measured at 8:00 p.m. every day for 25 days, and the slow-release rate was calculated and plotted in order to study the effect of pH on the slow release microcapsules of clove essential oil.

Preparation of Clove Essential Oil Slow-Release Microencapsulated Composite Films. The 0.75, 1.25, 1.75, and 2.25% microcapsules were mixed with the film solution at room temperature and stirred well. Then, the films were cast into 150 × 150 mm square Petri dishes and placed in a room-temperature environment for 3 days.[37] The films were uncovered to obtain composite films with different microcapsule additions. The resulting dried films were stored and prepared. P1 represents the CMC/SA composite film added with 0.75% clove essential oil microcapsules, P2 represents the CMC/SA composite film added with 1.25% clove essential oil microcapsules, P3 represents the CMC/SA composite film added with 1.75% clove essential oil microcapsules, and P4 represents the CMC/SA composite film added with 2.25% clove essential oil microcapsules.

Characterizations of Clove Essential Oil Slow Release Microencapsulated Composite Films. *Basic Performance Measurement.* The thickness, mechanical properties, optical properties, and WVP of the films were tested according to the test method of the basement film.

Fourier Transform Infrared Spectroscopy. FTIR was tested according to the test method of the basement film.

Scanning Electron Microscopy. PVA essential oil slow-release microcapsule composite films with different mass fractions were cut to a 1 × 1 cm size, and the surface morphology was recorded using scanning electron microscopy.

Antibacterial Ability. *E. coli*, *S. aureus*, and Penicillium are the three most common strains in fruit spoilage. Therefore, these three strains were selected for the inhibition experiment.

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Table 2. Basic Properties of Basement Films

number	thickness (μm)	tensile strength (MPa)	elongation at break (%)	light transmittance (%)	haze (%)	WVP (10^{-6} g m^{-1} s^{-1} Pa^{-1})
T1(0.4, 0.3, 0.65)%	54 ± 0.35	25.22 ± 0.86	16.58 ± 00.83	83.23 ± 0.56	9.58 ± 0.65	1.432 ± 0.011
T2(0.8, 0.3, 0.65)%	59 ± 0.41	29.22 ± 1.28	20.87 ± 1.04	83.97 ± 1.01	8.86 ± 0.74	1.375 ± 0.01
T3(1.2, 0.3, 0.65)%	62 ± 0.55	26.58 ± 1.73	14.25 ± 0.71	81.84 ± 0.87	10.09 ± 0.59	1.383 ± 0.007
T4(0.8, 0.1, 0.65)%	58 ± 0.53	24.21 ± 0.92	12.93 ± 0.65	81.56 ± 0.98	10.01 ± 0.62	1.425 ± 0.006
T5(0.8, 0.5, 0.65)%	60 ± 0.47	28.21 ± 1.25	18.25 ± 0.91	80.83 ± 0.91	11.01 ± 0.73	1.428 ± 0.004
T6(0.8, 0.3, 0.25)%	55 ± 0.61	27.86 ± 0.94	16.78 ± 0.84	81.52 ± 1.12	11.47 ± 0.84	1.39 ± 0.009
T7(0.8, 0.3, 0.95)%	62 ± 0.52	25.49 ± 1.50	19.22 ± 0.96	83.14 ± 1.07	9.62 ± 0.78	1.425 ± 0.01

We prepared an appropriate amount of sterilized saline into three test tubes, labeled as test tube A (*Escherichia coli*), test tube B (*Staphylococcus aureus*), and test tube C (Penicillium sp.). We gently stuck the sterilized inoculation loop into the slant test tube with the strain, scraped the strain to be tested, put it into the sterilized saline test tube, shook the slant test tube, and finally removed the saline with bacteria and set it aside. Then, the composite film was cut into 5 mm discs and irradiated under a UV sterilization lamp for 30 min for sterilization treatment.[38] Afterward, 0.2 mL (10^5 CFU/mL) of the liquid containing the strain in the above tubes was pipetted on an ultraclean bench, and the liquid was evenly spread on the medium plates with a spreading stick and left for 10 min.[39] A piece of the composite film was placed in the middle position of each Petri dish, covered, and inverted; the growth of each strain in the medium was observed until the growth of the inhibition circle was observed, and the diameters of the inhibition circles were measured by vernier calipers. In this way, the antimicrobial effects of the prepared composite films of clove essential oil microcapsules were evaluated. Letters following the diameter of the circle of inhibition in the same column indicate significant differences ($P < 0.05$).

Antioxidant Ability. The antioxidant activity of the composite film solution was reflected by measuring its ability to scavenge DPPH.[40] The anhydrous ethanol group, 2 mL of pure CMC/SA film solution, 2 mL of DPPH standard solution mixed group, and 2 mL of composite film solution mixed with 2 mL of DPPH standard solution were prepared, placed in cuvettes, wrapped with tin foil, and placed in the dark, and the absorbance values were measured by a UV spectrophotometer after 40 min of standing.

Clove Essential Oil Slow-Release Microencapsulated Composite Films Applied to Blueberry Preservation. Four experimental groups were set up, and 20 fresh blueberries of similar sizes were selected for each group. Four different treatment methods were simulated: group 1 is the room-temperature control group, i.e., the blueberries were placed in the room temperature of 25 °C for preservation; group 2 is the room-temperature composite film group, i.e., the blueberries were placed in the room temperature of 25 °C and a piece of essential oil slow-release microencapsulated composite film of 90 × 90 mm was placed on the top of the normal blueberry box for preservation; group 3 is the low-temperature group, in which the blueberries were stored at a low temperature of −4 °C, and group 4 is the low-temperature composite film group, in which the blueberries were stored at a low temperature of −4 °C and a piece of 90 × 90 mm essential oil slow-release microencapsulated composite film was placed at the top of the normal blueberry box. The test period was 18 days, and the quality indexes of these four types of blueberries were tested at the same time point every day during the previous period to study the effects of the four different treatments on the quality changes of blueberries.[41]

Hardness and Anthocyanin Content. The hardness was determined using a texture analyzer, and the anthocyanin content was determined by the UV spectrophotometer method.[42] Three parallel measurements were performed for each test group, and the results were averaged.

Decay Rate and Weight Loss Rate. The decay rate of blueberries can be categorized into four classes, namely, grade 0 (no obvious change in the fruit surface visible to the naked eyes and no obvious change to the touch compared to before), grade 1 (no obvious change in the fruit visible to the naked eyes, but softening to the touch compared to before), grade 2 (fruit performance visible to the naked eyes with creases and depressions, obvious softening to the touch compared to before, and some juice leakage), and grade 3 (fruit visible to the naked eyes with mold spots on its surface).[43]

The decay rate was calculated according to eq 4:

$$\text{decay rate} = \frac{\sum(\text{grade} \times N_{\text{grade}})}{\text{highest grade} \times N_{\text{total}}} \times 100\% \quad (4)$$

where N_{grade} is the number of blueberries of the given grade and N_{total} is the total number of blueberries. The weight loss rate was calculated according to eq 5:

$$\text{weight loss rate} = \frac{w_{\text{before storage}} - w_{\text{during storage}}}{w_{\text{before storage}}} \times 100\% \quad (5)$$

where $w_{\text{before storage}}$ and $w_{\text{during storage}}$ are the blueberry weights before and during storage, respectively.

Malondialdehyde and Soluble Solid Content. The malondialdehyde content was determined by the thiobarbituric acid-UV spectrophotometric method,[44] and soluble solids were measured by a refractometer. Three parallel measurements were set up for each test group, and the results were averaged.

Statistical Analysis. The test data were expressed as the mean ± standard deviation. Response surface models were developed by using Design-Expert 8.0.6 software and plotted by using Origin 2021 and Excel 2022.

RESULTS AND DISCUSSION

Analysis of the Basic Properties and Response Surface Optimization Results of Basement Films. *Analysis of the Basic Properties of Basement Films.* Table 2 shows the thickness, mechanical properties, optical properties, and WVP of the basement films. As shown in Table 2, the transmittance of the substrate film is >80%, which has good optical properties. With the increasing mass fraction of SA, the thickness of the substrate film increased, and the tensile strength, elongation at break, and WVP showed a trend of

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increasing and then decreasing, which was due to the good viscosity and film-forming property of SA, so that the molecules in the composite film were closely connected and the internal voids were filled, which was consistent with the results of Lan et al.[45] With the increase of the glycerol content, the thickness and elongation at break of the base film increased, and the tensile strength and WVP decreased and then increased, which is due to the good internal network structure of carboxymethyl cellulose, which can enhance the internal structural stability of the composite film. This is consistent with the results of Lu and Wang.[46] With the increase of the glycerol content, the thickness, elongation at break, and WVP of the base film increased, and the tensile strength decreased, which was due to the addition of a plasticizer hindering the formation of hydrogen bonds between macromolecules, thus making the film structure loose and changing the barrier properties of the film, which was consistent with the findings of Lu et al.[47]

Analysis of Basement Film Response Surface Optimization Results. The elongation at break (Y_1), tensile strength (Y_2), and WVP (Y_3) of the composite film were used as indicators, and the mass concentrations of SA (X_1), CMC (X_2), and glycerol (X_3) were measured.[48] The mechanical strength affects the usefulness of the film. WVP determines the performance of the film in terms of moisture, water, and oxidation resistance. Considering the characteristics of blueberries, low WVP and high mechanical properties are to be the priority principles.[49] The test results are listed in Table 3.

Table 3. Trial Design and Results

number	X_1 (%)	X_2 (%)	X_3 (%)	Y_1 (%)	Y_2 (MPa)	Y_3 (%)
1	−1	−1	0	16.51	27.09	1.663
2	1	−1	0	14.6	32.58	1.732
3	−1	1	0	15.24	33.17	1.59
4	1	1	0	11.37	22.04	1.688
5	−1	0	−1	17.28	15.2	1.596
6	1	0	−1	17.04	11.33	1.683
7	−1	0	1	14.55	21.25	1.652
8	1	0	1	12.93	28.66	1.724
9	0	−1	−1	21.45	25.96	1.546
10	0	1	−1	23.05	14.73	1.617
11	0	−1	1	18.29	29.51	1.658
12	0	1	1	17.25	32.81	1.524
13	0	0	0	20.54	30.15	1.432
14	0	0	0	21.62	31.02	1.439
15	0	0	0	23.07	30.5	1.43
16	0	0	0	24.5	29.35	1.425
17	0	0	0	18.04	30.38	1.428

The regression equations for elongation at break, tensile strength, and WVP were obtained by fitting the scores in the table using Design-Expert V11 software:

$$Y_1 = 146.74X_1 + 101.95X_2 + 8.95X_3 - 14.6X_1X_2 - 2.93X_1X_3 + 11.33X_2X_3 - 96.43X_1^2 - 209.2X_2^2 - 56.19 \quad (6)$$

$$Y_2 = 71.51X_1 + 159.14X_2 + 46.31X_3 - 25.8X_1X_2 + 5.43X_1X_3 - 13.92X_2X_3 - 44.44X_1^2 - 247.25X_2^2 - 39.83X_3^2 - 29.87 \quad (7)$$

$$Y_3 = 0.01X_1 - 0.03X_2 + 0.04X_3 - 0.007X_1X_2 + 0.02X_1X_3 - 0.07X_2X_3 + 0.12X_1^2 + 0.09X_2^2 + 0.07X_3^2 + 1.34 \quad (8)$$

Their linear correlation coefficients R^2 are all greater than 0.9, indicating that the regression equations fit well, which can confirm that the process parameters obtained from the experimental optimization are reliable and the optimized process can be used as a reference basis.[50]

Figure 1a−c shows the effects of the interaction of three factors, SA, CMC, and glycerol, on the elongation at break of the basement film. It can be seen that the elongation at break is higher when the SA content is fixed, the CMC content is 0.2−0.25%, and the glycerol content is 0.3−0.5%; the elongation at break is higher when the sodium carboxymethylcellulose content is fixed, the SA content is 0.7−0.8%, and the glycerol content is 0.3−0.6%; when the glycerol content is fixed, the SA content is 0.7−0.8%, and with 0.15−0.3% CMC, the elongation at break was higher. Figure 1d−f shows the effects of the interaction of the three factors on the tensile strength of the substrate films. It can be seen that the tensile strength was higher when the SA content was fixed, the carboxymethylcellulose content was 0.2−0.3%, and the glycerol content was 0.5−0.7%; when the sodium carboxymethylcellulose content was fixed, the SA content was 0.65−0.85% and the glycerol content was 0.45−0.7%; when the glycerol content was fixed, the SA content was 0.74−0.9%, and with 0.28−0.32% CMC, the tensile strength was greater. Figure 1g−i shows the effects of the interaction of the three factors on the WVP of the substrate films. It can be seen that when the SA content is fixed, the carboxymethyl cellulose content is 0.17−0.28%, and the glycerol content is 0.3−0.6%, the WVP is smaller; when the CMC content is fixed, the SA content is 0.72−0.84%, and the glycerol content is 0.3−0.71%, the WVP is smaller; when the content of glycerol is fixed, the content of SA is 0.6−0.83%, and the content of CMC is 0.2−0.33%, the WVP is smaller.

The analysis results of Design-Expert software showed that the substrate film preparation process was optimal at a mass fraction of SA of 0.84%, a mass fraction of CMC of 0.25%, and a glycerol content of 0.56%: an elongation at break of 21.77%, a tensile strength of 31.8 MPa, and a WVP of 1.36%. Verification tests were conducted under the optimal preparation process; the elongation at break was 21.93 ± 0.62%, the tensile strength was 30.67 ± 1.17 MPa, and WVP was 1.35 ± 0.52%. The results are basically consistent with the predicted values described above, indicating that the results are reliable.

Characterizations of Clove Essential Oil Slow-Release Microcapsules. *SEM and Infrared Spectroscopy Analysis of Clove Essential Oil Slow-Release Microcapsules.* The scanning electron microscope image of clove essential oil slow-release microcapsules is shown in Figure 2a. It can be seen from the figure that the prepared microcapsules have a distinct spherical structure and no flocculent dispersion around the microcapsules. Figure 2b shows the infrared spectra of PVA raw material and clove essential oil slow-release microcapsules. Comparing the two spectrograms, it was found that the absorption peak of −OH at around 3343 cm^{-1} became narrower, indicating that the number of −OH molecules in the PVA molecule was reduced after cross-linking. In addition, the absorption peak of clove essential oil slow-release microcapsules at 1104 cm^{-1} changed and became sharper compared with that of the PVA raw material. This may be due to the temperature change during the preparation of the clove

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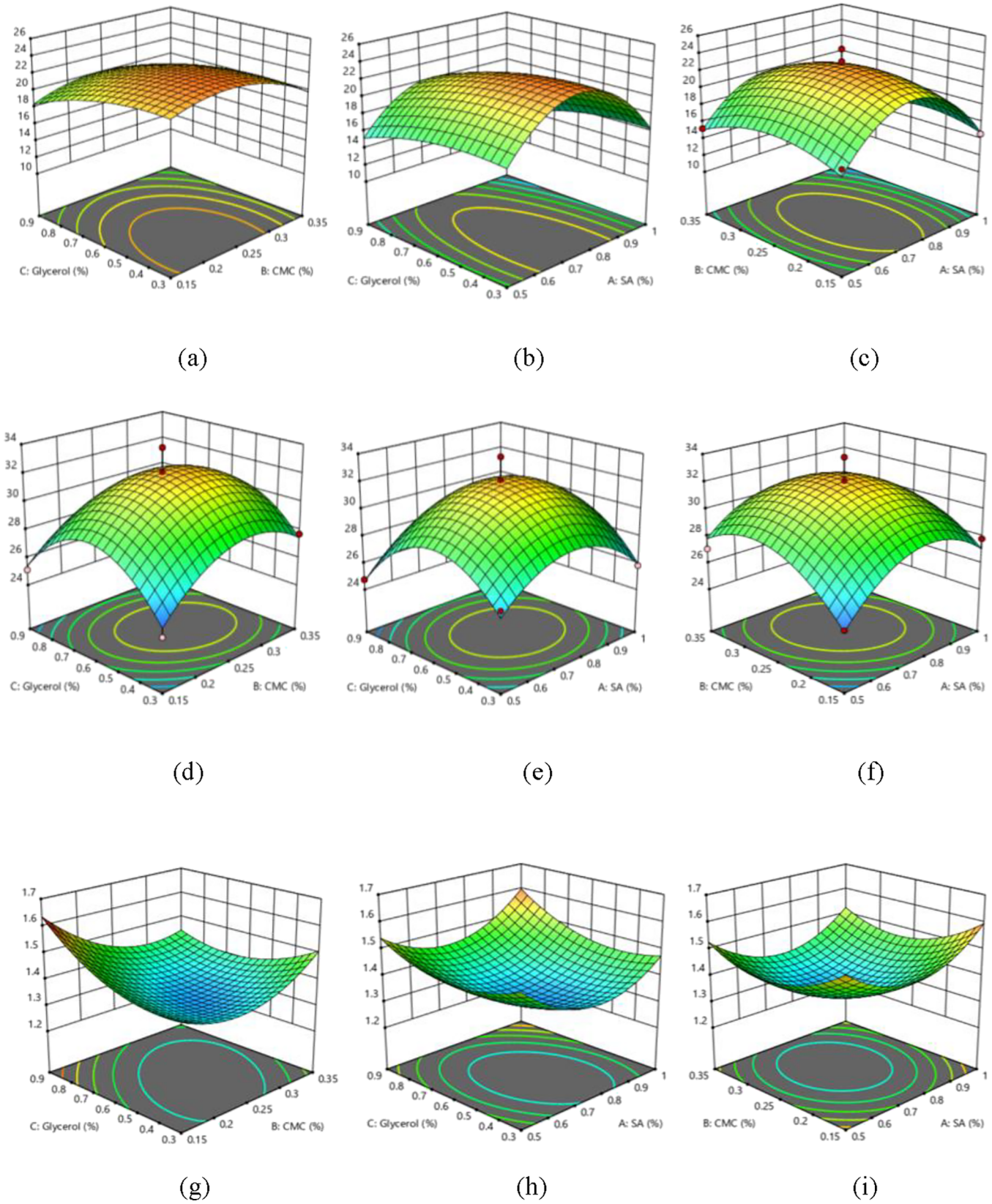

Figure 1. Three-dimensional response surface of the interaction of various factors to the elongation at break(a–c), tensile strength (d–f), and WVP (g–i) of the composite films.

essential oil slow-release microcapsules, which induces the PVA molecules to disorganize and reorganize, making clove essential oil slow-release microcapsules more stable and more compact in structure.[51]

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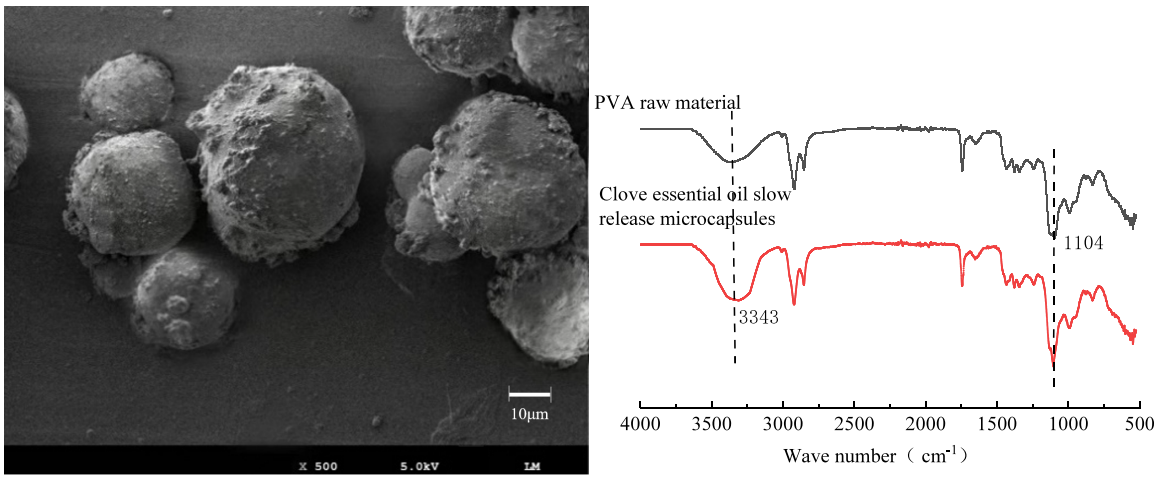

(a)SEM of microspheres (b)Infrared spectra of microspheres

Figure 2. SEM image and infrared spectra of clove essential oil slow-release microcapsules.

Analysis of the Slow-Release Property of Clove Essential Oil Microcapsules. The cumulative release profile of clove essential oil slow-release microcapsules in anhydrous ethanol and 3% acetic acid solution is shown in Figure 3. It can be

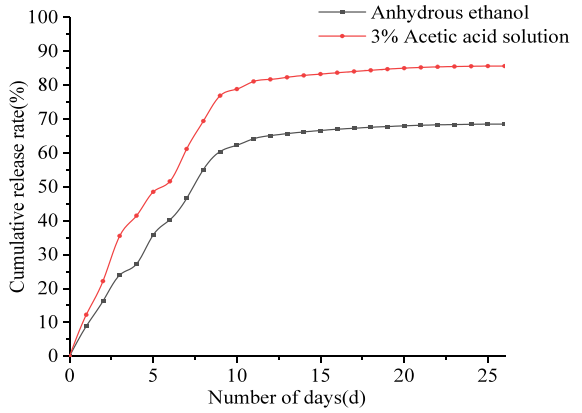

Figure 3. Cumulative release rate of clove essential oil slow-release microcapsules under different environments.

observed that the release of microcapsules is divided into two main phases, the first phase being the rapid release phase for the first 10 days. Lin et al.[52] showed that the volatilization rate of unembedded clove essential oil was much greater than that of embedded clove essential oil under the same environment. Therefore, the main reason for the rapid release may be the rapid diffusion of unencapsulated clove essential oil adhering to the surface of the microcapsules, as well as clove essential oil encapsulated near the surface of the microcapsules. The second phase is the slow release stage. The release rate of the microcapsules slowed significantly after 10 days, indicating that the microcapsules can achieve slow release of the essential oil of clove and achieve the effect of prolonging the release time of clove essential oil. This is in general consistent with the study of Dai et al.,[53] who explored the variation in slow-release properties of composite essential oil microcapsules. In addition, the figure shows that the release rate of microcapsules under an acidic environment was faster than that under an alkaline environment. This may be due to the fact that an acidic environment can cause the microcapsules to swell or partially dissolve, which results in higher diffusivity of clove essential oil encapsulated in the microcapsules.

Characterizations of Clove Essential Oil Slow-Release Microcapsule Composite Films. *Analysis of the Basic Performance of Clove Essential Oil Slow-Release Microencapsulated Composite Films.* The basic properties of clove essential oil slow-release microencapsulated composite films are shown in Figure 4. It can be seen that with the increase of microcapsule addition, the thickness of the composite film is increasing, and the tensile strength and elongation at break show a trend of first increasing and then decreasing; with the microcapsule addition of 1.75%, the composite film has the highest transmittance and haze, and the WVP is the lowest. This is due to the fact that when the microcapsule addition amount reaches 1.75%, a large number of hydroxyl groups on the surface of the microcapsule and the carboxyl and hydroxyl groups on the SA molecule form a hydrogen bonding effect, which makes the microcapsule form a three-dimensional mesh structure between the interface of the microcapsule and SA and strengthens the mechanical properties of the composite film to a large extent.[54] At this time, the microcapsules are distributed more uniformly in the film, which makes the diffusion path of water molecules in the film longer and improves the water-blocking ability of the composite film. When the amount of microcapsules added is too large, the microcapsules produce aggregation in the composite film, which destroys the compatibility between the substrates, resulting in an unstable film structure, increased pores in the film, and increased WVP.[55]

Infrared Spectral Analysis of Clove Essential Oil Slow-Release Microencapsulated Composite Films. Figure 5 shows the FTIR spectra of the composite films with different microcapsule additions and the simple CMC/SA composite film. This spectrogram detects a stronger characteristic peak for SA and CMC found around 3288 cm^{-1}, which is the stretching vibration of −OH and −NH bonds, and the stretching vibration of C−H bonds appears around 2998 cm^{-1}.[56] Moreover, the addition of clove essential oil slow-release microcapsules was found to slow down the amplitude of the stretching response, indicating that the microcapsules have a certain role in promoting tightness between the composite film molecules. With the increase of the addition of

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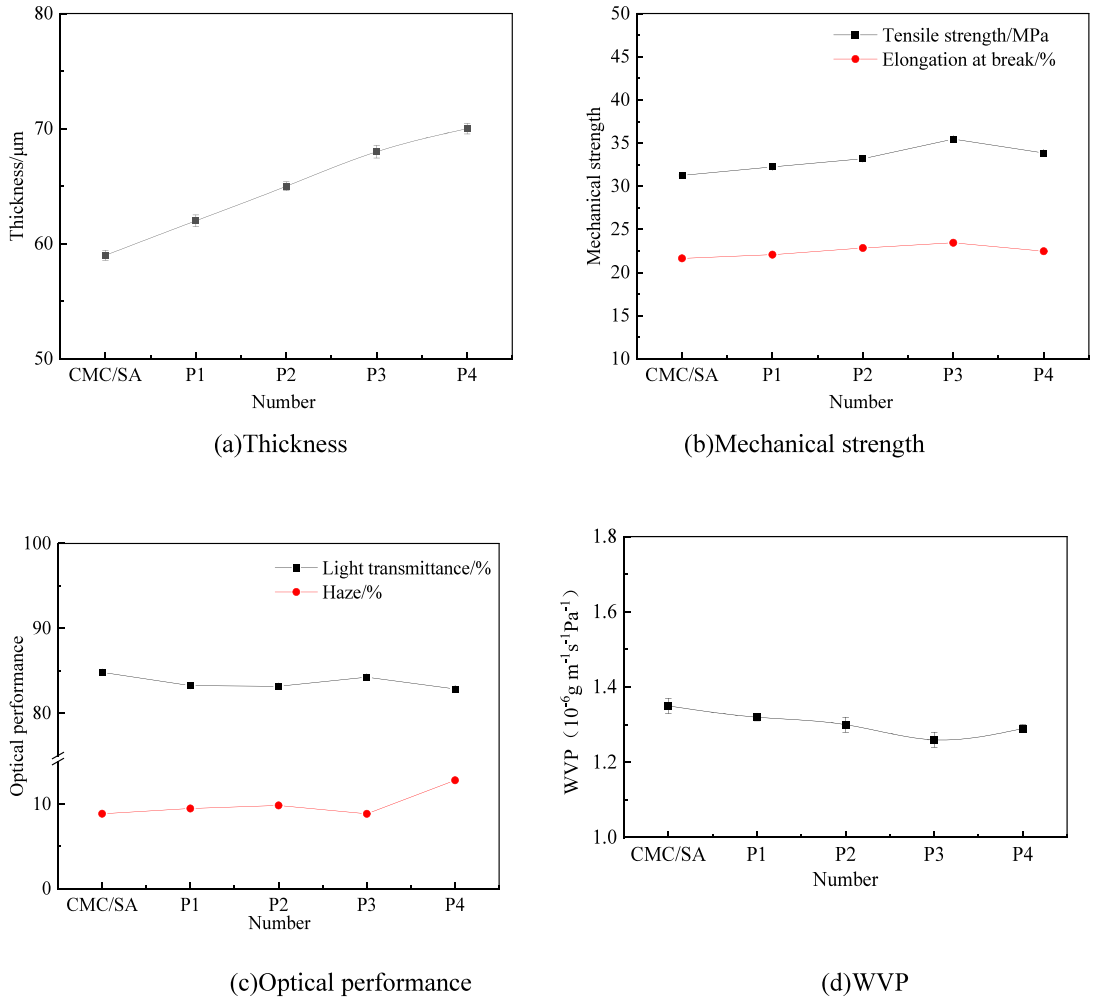

Figure 4. (a–d) Basic properties of composite films.

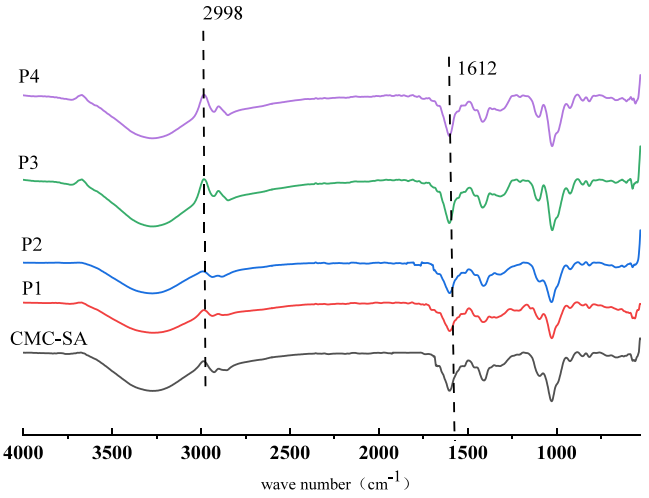

Figure 5. Infrared spectra of composite films.

clove essential oil slow-release microcapsules, there was the appearance of new peaks in the composite film, and the peaks of the films were shifted to some extent. This may be due to the fact that the addition of microcapsules caused a change in the internal molecular groups of the composite film, which has a certain positive effect on the intermolecular action of the composite film, which is consistent with the findings of Wang.[57]

Scanning Electron Microscopy Analysis of Clove Essential Oil Slow-Release Microencapsulated Composite Films. Figure 6 shows the SEM images of the surfaces of the composite films with different microcapsule additions and the simple CMC/SA composite film. It can be seen in the figure that the compatibility between CMC and SA is better, and the surface of the prepared composite film is smoother. The microcapsules could be uniformly distributed on the surface of the composite film after adding the appropriate amount of microcapsules, which was due to the better compatibility between the microcapsules and the film matrix, which was consistent with the results of Li.[58] When too many microcapsules were added, the microcapsules could not be uniformly distributed on the surface of the composite film and agglomeration appeared.

Analysis of Antibacterial Properties of Clove Essential Oil Slow-Release Microencapsulated Composite Films. Clove essential oil is rich in phenolic compounds and aldehydes and ketones, which have strong antibacterial activities.[59] Figure 7 and Table 4 show the inhibitory effects of the simple CMC/SA composite film and clove essential oil microcapsule composite films on three different strains of *E. coli* (a), *S. aureus* (b), and Penicillium (c). It can be seen that the simple CMC/SA composite film had no inhibitory effect on these three strains,

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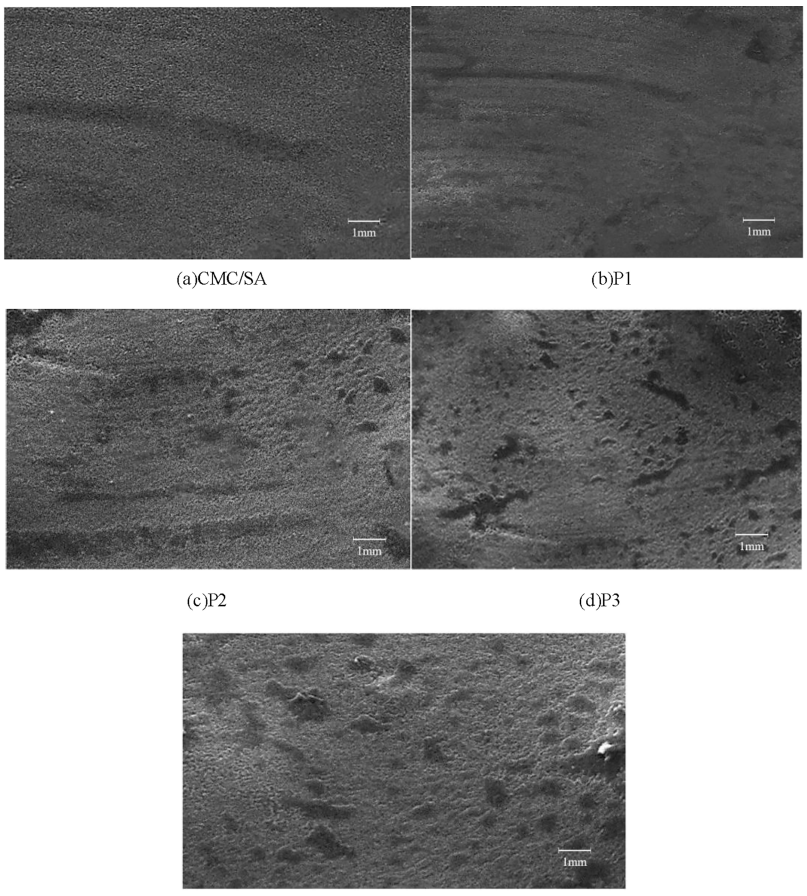

Figure 6. (a−e) SEM images of composite films.

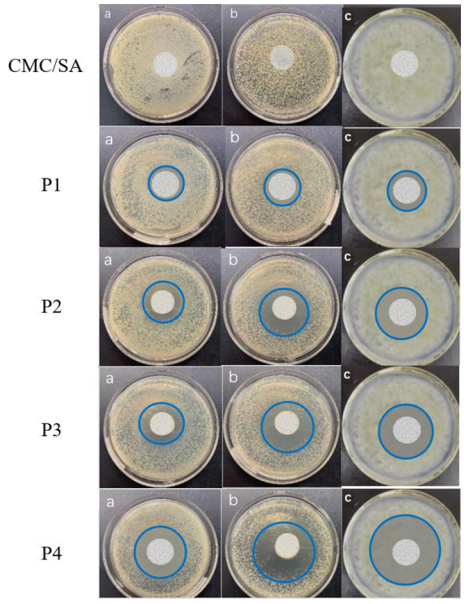

Figure 7. (a−c) Antibacterial effects of composite films.

while the composite film with clove essential oil microcapsules had clear inhibitory circles, which had more significant inhibitory effects on these three strains. From Figure 7 and Table 4, it can be seen that clove essential oil has the strongest inhibitory effect on Penicillium. This is because eugenol in clove essential oil can inhibit the cell wall synthesis of the fungus, leading to cell wall fragility and death. This is consistent with the findings of Shan et al.[60] In addition, the essential oil of clove also had a significant inhibitory effect on *E. coli* and *S. aureus*. This is because eugenol in clove essential oil can inhibit ATP synthesis in bacteria, resulting in an insufficient energy supply and cell death. The inhibitory effect of clove essential oil on *S. aureus* was stronger than that on *E. coli* because eugenol has a better inhibitory effect on Gram-positive bacteria, which is in agreement with the results of Zeng et al.[61] The diameters of the inhibitory circles were larger and the inhibitory effects were better for P3 and P4.

Table 4. Diameters of Inhibition Circles of Composite Films

	inhibition circle diameter (mm)		
film	*E. coli*	*S. aureus*	Penicillium
CMC/SA	0.00 ± 0.00^{e}	0.00 ± 0.00^{e}	0.00 ± 0.00^{e}
P1	7.12 ± 0.23^{d}	7.60 ± 0.26^{d}	8.87 ± 0.11^{d}
P2	10.03 ± 0.15^{c}	13.77 ± 0.23^{c}	14.52 ± 0.23^{c}
P3	12.57 ± 0.20^{b}	15.10 ± 0.23^{b}	16.10 ± 0.19^{b}
P4	14.37 ± 0.18^{a}	20.33 ± 0.26^{a}	23.28 ± 0.28^{a}

Analysis of Antioxidant Properties of Clove Essential Oil Slow-Release Microencapsulated Composite Films. As can be seen from Figure 8, the CMC-SA film solution has basically no scavenging ability for DPPH, indicating that the simple CMC-SA composite film has basically no antioxidant ability. When clove essential oil slow-release microcapsules were

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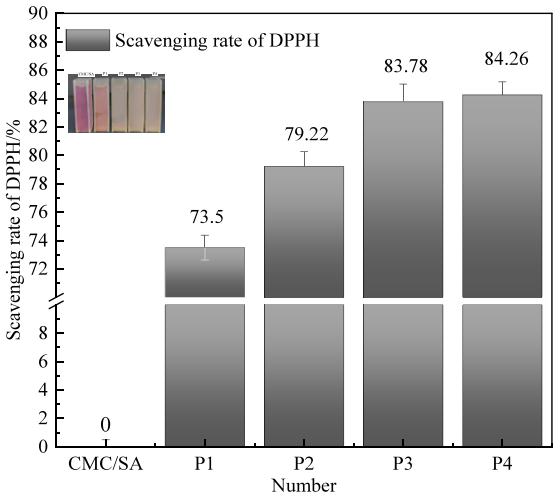

Figure 8. Scavenging ability of clove essential oil microcapsules on DPPH.

added at 1.75 and 2.25%, the scavenging rate of DPPH reached more than 80%, which was due to the fact that microcapsules contained clove essential oil, which itself has a strong antioxidant ability. The antioxidant capacity of clove essential oil is mainly due to the presence of phenolic and terpene compounds, which contain large amounts of eugenol and stilbene. These two compounds are able to prevent free radicals from being generated at the initiation stage of the free-radical chain reaction and are also able to react with peroxidized free radicals to generate more stable substances faster than oxidized substances at the propagation stage of the free-radical chain reaction, which results in the slowing down or blocking of the free-radical chain reaction to achieve the effect of antioxidant. Wang et al.[62] explored the antioxidant capacity of four essential oils and showed that clove essential oil had the strongest DPPH scavenging ability and the strongest antioxidant capacity. Du et al.[63] found that the DPPH radical scavenging rate increased slowly with the increase of clove essential oil concentration. When the mass concentration of clove essential oil was 0.6%, the DPPH radical scavenging rate reached 81.68%, and the DPPH radical scavenging rate basically stabilized after the concentration was further increased. Zhang et al.[64] determined the antioxidant effects of clove and cinnamon essential oils in inhibiting lipid and protein oxidation of ready-to-eat pork chops by a chemical assay, Raman spectroscopy, and sensory evaluation, and the results showed that clove essential oil had higher antioxidant activity than cinnamon essential oil. Moreover, the microcapsules were able to maintain the stability of the clove essential oil and release the clove essential oil slowly to achieve better antioxidant properties, which is consistent with the findings of Ma.[65]

The optimum clove essential oil slow-release microcapsule addition ratio of 1.75% was obtained by analyzing the basic performance, FTIR, SEM, antibacterial properties, and antioxidant properties of the clove essential oil slow-release microencapsulated composite films.

Effect of Clove Essential Oil Slow-Release Microencapsulated Composite Films on Blueberry. *Analysis of Blueberry Hardness and Anthocyanin Content.* Blueberry hardness and anthocyanins are important indicators of the quality of blueberries. Figure 9 shows the curves of the blueberry hardness and anthocyanin content with the number of days under four different treatments.

With the extension of storage time, the original pectin and cellulose were hydrolyzed by enzymes, which disintegrated the cell walls and led to the softening of blueberries; therefore, the hardness of blueberries in all four groups continued to decrease. Since there was a postripening process after picking, the anthocyanin content increased and then decreased. Eighteen days later, the hardness and anthocyanin content of blueberries in the group 2 were higher than those in the group 1. The hardness and anthocyanin content of blueberries in the group 4 were higher than those in the group 3. This is because the essential oil slow-release microencapsulated composite film reduced the respiration rate of blueberries and inhibited the conversion of protopectin to soluble pectin, which was conducive to the maintenance of the higher hardness and anthocyanin content of blueberries, which is in line with the results of the study of Zhao et al.,[66] who applied an edible coated film to the preservation of mango. In addition, the hardness and anthocyanin content of blueberries from groups 3 and 4 were higher than those from groups 1 and group 2. This may be due to the fact that the low temperature inhibited the respiratory strength of blueberries, which was effective in slowing the decline of hardness and anthocyanin content. On

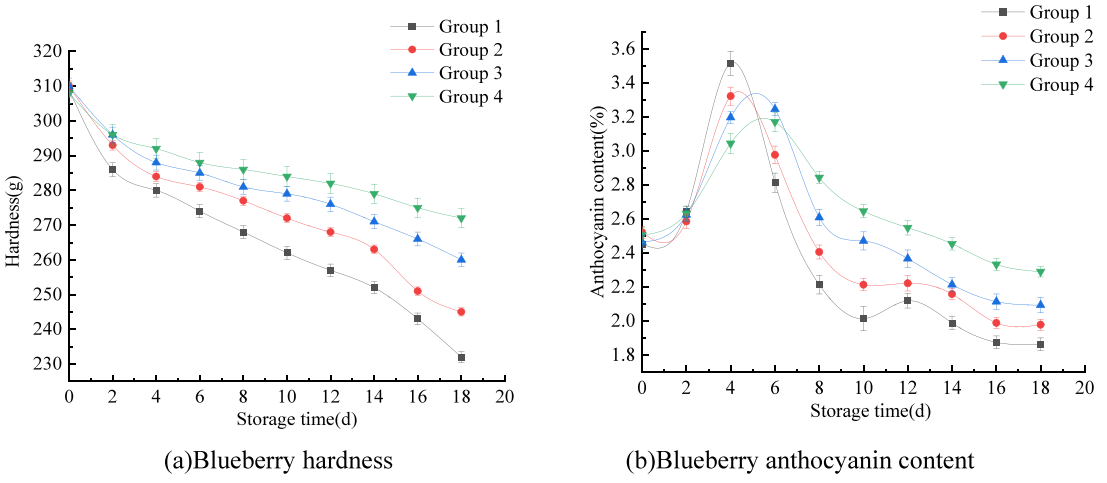

Figure 9. Changes of (a) hardness and (b) anthocyanin content.

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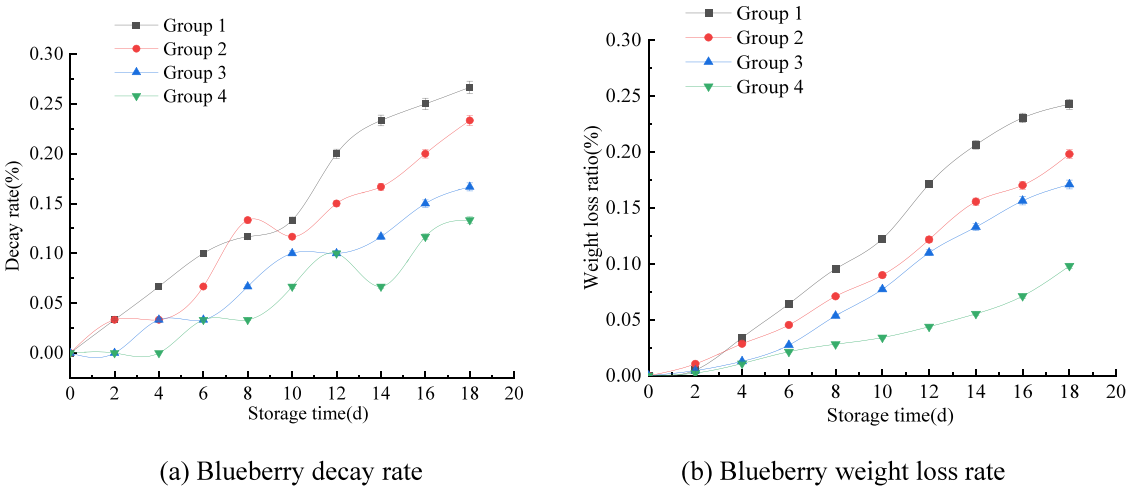
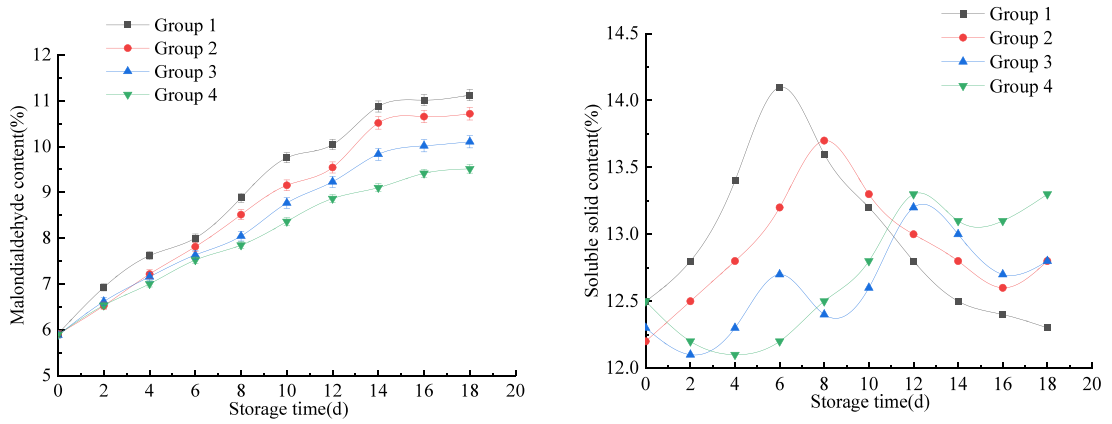


(a) Blueberry decay rate (b) Blueberry weight loss rate

Figure 10. Changes of (a) decay rate and (b) weight loss rate.



(a) Malondialdehyde content (b) Soluble solid content

Figure 11. Changes of (a) malondialdehyde content and (b) soluble solid content.

the 18th day of storage, the hardness and anthocyanin content of group 1 decreased to 232 g and 1.86 mg/g, whereas those of group 4 were 272 and 2.29 mg/g, respectively. This suggests that a low-temperature combination of the essential oil slow-release microencapsulated composite film can have a good retention of hardness and anthocyanin content in blueberries.

Analysis of the Blueberry Decay Rate and Weight Loss Rate. As shown in Figure 10, the decay and weight loss rates of blueberries increased under the four different treatments. The decay and weight loss rates of blueberries in group 3 and group 4 were lower than those in group 1 and group 2. This may be due to the fact that respiration of blueberries was reduced and bacterial growth and multiplication were inhibited under low temperature conditions. The decay and weight loss rates of blueberries in group 2 were lower than those in group 1. The decay and weight loss rates of blueberries in group 4 were lower than those in group 3. This is due to the fact that eugenol, the main active ingredient of clove essential oil, has antimicrobial and antioxidant effects, which can reduce the activity of key enzymes required for respiratory metabolism and block microbial synthetic metabolism, thus playing a bactericidal and anticorrosive role. The clove essential oil slow-release microcapsules in the composite film prolonged the freshness cycle of blueberries by releasing eugenol into the surrounding environment, which is consistent with the results of Zhu and Yu[67] who used eugenol in beef storage to inhibit the increase of bacterial colony counts during storage. The clove essential oil slow-release microencapsulated composite film prevented the entry of external air on the one hand and reduced the oxygen content inside the blueberry tissues on the other hand, which inhibited the respiratory metabolic intensity and water loss and slowed down the senescence of the blueberries, thus effectively prolonging the shelf life of the blueberries. This is consistent with the research results of Zhao et al.,[68] who applied a chitosan composite film to blueberry preservation.

Analysis of the Blueberry Malondialdehyde Content and Soluble Solid Content. The content of malondialdehyde can reflect the degree of cellular damage.[69] As can be seen in Figure 11a, the malondialdehyde content of blueberries from groups 3 and 4 was lower than that of groups 1 and 2. This was attributed to the inhibitory effect of low temperature on peroxidase activity. The malondialdehyde content in group 2 and group 4 was lower than that in the two other groups under the same temperature conditions. This is due to the antioxidant effect of clove essential oil, and the addition of clove essential oil microcapsules inhibited the peroxidation reaction in blueberry cells and suppressed the increase of the

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malondialdehyde content, which is consistent with the results of the study by Li et al.,[70] who applied clove essential oil microcapsules in strawberry preservation. The contents of soluble solids can reflect the taste of blueberries. From Figure 11b, the soluble solid contents of the four groups showed an increasing trend during the first few days of storage. This is because insoluble macromolecules such as cellulose in blueberry fruit were enzymatically dissolved into small soluble sugars, which increased the soluble solid content, which is consistent with the findings of Guo et al.,[71] who used box-type air conditioning for blueberry storage. Moreover, the subsequent decline was due to the respiration of the blueberry fruit itself, which consumed part of the soluble sugars and made the soluble solid content decrease. In the late storage period, the soluble solid content increased in all three groups except group 1, and group 4 had the highest soluble solid content. This is because low temperature can inhibit the respiration of blueberry, and the essential oil slow-release microencapsulated composite film reduces the respiration of blueberry by blocking the entry of O_2, which is consistent with the findings of Lv et al.[72] Both methods were able to reduce the consumption of soluble solids.

CONCLUSIONS

In this paper, composite films were prepared using SA and CMC as the base materials and glycerol as the plasticizer. Taking the elongation at break, tensile strength, and moisture permeability of the composite film as the indexes, 0.84% SA, 0.25% CMC, and 0.56% glycerol were determined as the optimal ratios by response surface optimization. Different mass fractions of clove essential oil slow-release microcapsules were added into the composite film, and the performance of the microcapsule composite film with a mass fraction of 1.75% was found to be superior by analyzing the basic performance, FTIR, SEM, antibacterial ability, and antioxidant ability of the microcapsule composite film. It was applied to the preservation of blueberry. It was found that the clove essential oil slow-release microencapsulated composite film could effectively maintain the quality of blueberry and prolong the storage cycle of blueberry.

Based on the special properties of the clove essential oil slow-release microencapsulated composite film, it is expected to be a potential food packaging film, which provides a new idea for the development of green and pollution-free packaging films.

ASSOCIATED CONTENT

Data Availability Statement

Data are included in the article and Supporting Information or referenced in the article.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c07169.

Eight tables (S1−S8): (S1) data on the cumulative release rate of clove essential oil slow-release microcapsules under different environments, (S2) data on the basic properties of the composite film, and (S3−S8) data on the six indicators of blueberry (PDF)

AUTHOR INFORMATION

Corresponding Author

Yang Li − *College of Civil Engineering and Transportation, Northeast Forestry University, Harbin, Heilongjiang 150040, China*; Email: liya@nefu.edu.cn

Authors

Boya Bian − *College of Civil Engineering and Transportation, Northeast Forestry University, Harbin, Heilongjiang 150040, China*; orcid.org/0009-0002-4549-4430

Rongrong Tang − *College of Civil Engineering and Transportation, Northeast Forestry University, Harbin, Heilongjiang 150040, China*

Kexin Zhang − *College of Civil Engineering and Transportation, Northeast Forestry University, Harbin, Heilongjiang 150040, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c07169

Author Contributions

Y.L. conceived and designed the experiments, performed the experiments, contributed reagents, materials, analysis tools, or data, and wrote the paper. B.B. and R.T. conceived and designed the experiments, performed the experiments, analyzed and interpreted the data, contributed reagents, materials, analysis tools, or data, and wrote the paper. K.Z. performed the experiments, analyzed and interpreted the data, and wrote the paper.

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Notes

The authors declare no competing financial interest.

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