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Effects of Three Modified Starches on The Physicochemical Properties of Chitosan-Based Packaging Film

Nguyen Minh Chau[1], Tran Quang Hieu[2], Duong Duc Vuong[1], Huynh Thanh Truc[1], Tran Nhut Hoa[1], Nguyen Thi Ai Van[1], Nguyen Duc Vuong[1]*

[1]*Institute of Biotechnology and Food Tecnology, Industrial University of Ho Chi Minh City 700000, Vietnam, 12 Nguyen Van Bao, Ward 4, Go Vap District, Ho Chi Minh City, Vietnam*
[2]*Basic Sciences Department-Saigon Technology University, Ho Chi Minh City 700000, Vietnam, 180 Cao Lo, Ward 4, District 8, Ho Chi Minh City, Vietnam*

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ABSTRACT

Starch, as a biopolymer, due to its availability and low cost, could be a promising new packaging solution for biodegradable packaging. However, its weak functional properties require measures such as limiting interactions with certain hydroxyl groups and exploring mixtures with other polymers to enhance its effectiveness. In this study, films were prepared from various modified starches (E1412, E1414, and E1420) at different concentrations (2%, 4%, 6%, and 8% w/v), with a combination of 2% chitosan (CH) at different ratios (2:8, 3:7, 4:6, and 5:5 v/v). The impact of these chitosan ratios on important parameters, including water vapor transmission rate, tensile strength (TS), percentage elongation at break (EAB), elastic modulus (EM), and stiffness The transparency of the membrane has been thoroughly inspected. Through protonation, the amino groups of chitosan catalyze the formation of intermolecular bonds, thereby enhancing the tensile strength and water-repellent properties of the starch film. Notably, experimental findings highlighted that the coating containing 4% E1412-chitosan at a ratio of 5:5 (v/v) exhibited the strongest water vapor barrier. Therefore, these composite films have emerged as a promising avenue for developing environmentally friendly packaging solutions in the food industry.

Keywords: Modified starch, Chitosan, Physicochemical properties, Film.

Introduction

The increased awareness of pollution issues has been significantly driven by plastics; they have wide applications in packaging, preservation, transport, and consumption, which makes it almost impossible to find a plastic-free environment. Many studies have been conducted to find alternatives to conventional synthetic plastics, and the creation of eco-friendly materials is one of the key areas that are usually created by mixing biodegradable polymers with different combinations of plasticizers, antioxidants, and antimicrobial agents. In a context where the issue of pollution is increasingly receiving strong attention, human concerns about plastic waste pollution have promoted research into natural, biodegradable materials. increasingly strong. And starch, a natural polymer, thanks to its environmental friendliness, low price and high availability, has strongly emerged as an alternative to develop into a potential packaging material biodegradable. The structure of starch is composed of amylose and amylopectin molecules, and is a linear polysaccharide composed mainly of α-1,4-linked D-glucopyranose units, while amylopectin is a highly branched molecule that is formed by 1,4 and 1,6 bonds from the α-D-glucopyranosyl chains. However, there are some limitations of starch-based polymers such as their tendency to be brittle and sensitive to moisture, so to improve their functional performance, some functional modifications must be made. Certain chemical modifications such as esterification and acetylation can alter the processing properties of starch and the properties of the resulting material. Acetylated starch exhibits slower degradation and reduced gelatinization temperature compared to conventional starch. Acetyl groups will break starch molecular bonds, leading to its structure becoming more flexible and increasing the mobility of the amorphous polymer chain[1]. Films made from modified starch demonstrate improved elongation and reduced water vapor permeability relative to those made from native starch[2]. Although biodegradable starch-based films are highly gas-permeable, they also exhibit significant mechanical strength. By incorporating additives or mixing starch with other polymers, such as polyvinyl, the properties of starch-based materials can be further tuned[3,4]. Chitosan, a linear polysaccharide derived from chitin extracted from the outer shell of crustaceans, is a natural byproduct of the fishing industry. Due to its cationic nature, it can exert antibacterial and antibiotic activity, as well as biodegradability, non-toxicity, biological function and biocompatibility[5]. Research has demonstrated the ability to form films after starch-chitosan fusion. However, the mechanical performance and barrier properties of these sleepers depend on factors such as the rate of deacetylation and the amount of chitosan added to the starch[6]. This study aimed to evaluate the effects of three types of MS at different concentrations and ratios on the physicochemical properties of MS-chitosan films. Specifically, the study will evaluate parameters such as water vapor transmission rate, tensile strength, percent elongation at break, elastic modulus, and opacity values. By clarifying the impact on membrane properties when introducing CH into MS, the study sought to develop MS-chitosan membranes with enhanced physicochemical properties compared to conventional chitosan membranes. This exploration is essential to promote the development of sustainable packaging materials with improved functionality and environmental sustainability.

*Corresponding author. E mail: nguyenducvuong@iuh.edu.vn
Tel: + 84946616465

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Materials and Methods

Chemicals/Reagents
Chitosan (> 99.55% purity with a degree of deacetylation of 83%) was purchased from Co., Ltd, Kien Giang Province, Vietnam. Commercial food grade modified starches including Distarch phosphate (E1412), Acetylated distarch phosphate (E1414), Acetylated starch (E1420) supplied by Nam Bao Tin IMEX Co., Ltd, Ho Chi Minh City, Vietnam. All other chemicals were purchased from standard commercial supplies.

Preparation of MS-chitosan film
The film-forming procedure was referenced by the study of Kewang Zheng[7]. In brief, the MS solution of each MS type (E1412, E1414, and E1420) at different concentrations (2, 4, 6 and 8% w/v) was prepared by heating the mixture at 65°C for 10 min. 2% (w/v) chitosan solution was prepared by dissolving 2 grams of chitosan in a 1% (v/v) acetic acid solution. The 2% chitosan solution was evenly mixed with different MS solutions at different ratios (2:8, 3:7, 4:6, 5:5 v/v). The MS-chitosan mixture (35 ml) was cast on the plastic frame (18 x 25 cm) and was allowed to completely dry for 24h at ambient temperature. The MS-chitosan film was used for further analysis.

Mechanical properties measurement
The mechanical properties of the films {tensile strength (TS), percentage of elongation at break (EAB), and elastic modulus (EM)} were evaluated by using the INSTRON tensile testing machine, Illinois Tool Works Inc., USA. The test specimen was prepared according to ASTM D882-09 (10 x 100 mm). The test specimen was subjected to axial tensile force at a fixed speed and distance until the specimen broke to record the data.

Optical properties
The optical properties of the film were determined through the whiteness index and opacity. The color of each film was measured using CHROMA METER CR-400 colorimeter, Konica Minolta Inc., Tokyo, Japan. Each film was recorded for its color at three different positions of the film. The color was expressed according to three values *L**, *a**, and *b**. The whiteness index (WI) of the film was calculated using equation (1) [8].

$$WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \quad (1)$$

The opacity of the sample was determined using a UV-VIS spectrophotometer at a wavelength of 600 nm[9], the opacity is determined using equation (2).

$$\text{Opacity} = \frac{Abs600}{L} \quad (2)$$

where: Abs600 = Absorbance value at 600 nm

L = Film thickness (mm)

Water vapor transmission rate measurement
The water vapor transmission rate (WVTR) was measured according to the ASTM E96-95 standard. In brief, the packaging film was tightly fixed on the top of water containing - porcelain cup with an internal diameter of 3.9 cm. The cup was then placed in the desiccator containing silica gels which were dried at 180°C for 1 h. The cup was recorded for its weight at 1 h intervals for 7 h[10].

Statistical analysis
Each experiment was carried out in thrice replicates. The result was expressed as mean value ± standard deviation. The analysis of variance (ANOVA) and Tukey HSD were applied to compare mean values at the significant level of 5%.

Results and Discussion

Effects of MS concentrations and MS-chitosan ratios on the water vapor transmission rate
The effects of MS concentration and MS-chitosan ratio on the water vapor transmission rate (WVTR) of the composite membrane are depicted in Figure 1. Initially, the WVTR of the normal chitosan membrane was measured to be 66.57 ± 1.53 g/h.m^2, with MS supplementation leading to a significant reduction in WVTR. Notably, membranes with a 5:5 ratio of 4% E412-chitosan, 4% E1414-chitosan, and 4% E1420-chitosan displayed the lowest WVTR values of 29.79, 26.8, and 27.76 g/h.m^2, respectively. Incorporation of chitosan into the

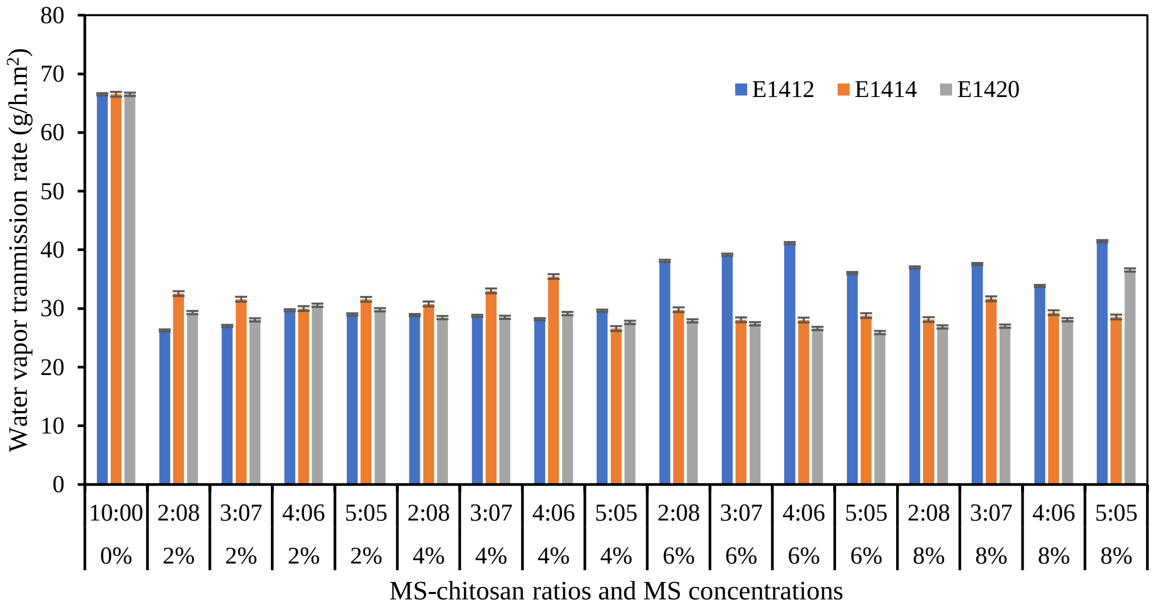

Figure 1: Effect of MS-chitosan ratios (upper values) and MS concentrations (lower values) on the water vapor transmission rate of MS-chitosan film

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MS matrix strengthens the structure of the composite membrane through cross-linking between chitosan and MS, thereby reducing water absorption. This reduction is due to the interaction between chitosan and the amylose and amylopectin structures of MS, leading to the formation of intermolecular hydrogen bonds and thereby improving the water-repellent properties[11]. In addition, the E1414-chitosan membrane has lower water vapor permeability than the E1412-chitosan membrane due to the hydrophobic nature of the acetyl groups, which limits water absorption into the starch granules. Furthermore, increased membrane crystallization rearranges the starch molecules, reducing the interaction between the starch's glucose unit hydroxyl groups and the water molecules. Similarly, the WVTR of E1420-chitosan membrane is lower than that of E1412-chitosan membrane because the hydrophobic acetyl groups weaken the intermolecular forces and reduce the ability to absorb water into starch molecules, ultimately changing the molecular structure of starch[11,12].

Effects of MS concentrations and MS-chitosan ratios on the mechanical properties of composite film

Percentage of elongation at break

Elongation at break refers to the maximum extent to which a film can stretch prior to breaking. This characteristic, which reflects the tensile strength of the film under tension, is a crucial factor in the evaluation of packaging films for food preservation. The greater the elongation, the more flexible and durable the film. Consequently, this is an important consideration when assessing the suitability of packaging films for food preservation. Figure 2 displays the EAB values for different MS concentrations and MS-chitosan ratios. The data reveals that the EAB values of the MS-chitosan films varied. The results show that the films with 6% and 8% MS-chitosan had lower EAB values compared to those with 2% and 4% MS-chitosan. This difference can be attributed to the fact that modified starch is more brittle than chitosan, and a high concentration of MS in the composite film may lead to a decrease in film flexibility[13].

Tensile strength

Tensile strength is the maximum tensile stress that a film can endure, and it is an essential technical parameter for selecting an appropriate film material for fruit preservation. The tensile strength of the film represents its toughness and firmness, and a larger strength value is desirable when applying the film for food preservation.

The effects of modified starch (MS) ratios and concentrations on tensile strength (TS) are depicted in Figure 3. The inclusion of modified starch led to increased tensile strength in the composite film compared to the chitosan film without MS. Experimental data revealed that the TS of the chitosan film was 12.98 ± 1.67 MPa, while films containing MS exhibited higher TS values. Notably, the film with a 6% E1412-chitosan ratio of 3:7 displayed the highest TS of 102.29 MPa, followed by the 4% E1414-chitosan film with a 5:5 E1414-chitosan ratio of 69.54 MPa. Similarly, the composite film with 4% E1420-chitosan at a 5:5 ratio demonstrated the highest TS of 55.09 MPa. The enhanced TS of E1414-chitosan films can be attributed to the interaction between chitosan and MS, where NH_2 groups of chitosan interact with OH^- groups of degraded MS molecules, forming intermolecular hydrogen bonds and thus bolstering the mechanical strength of the composite film.

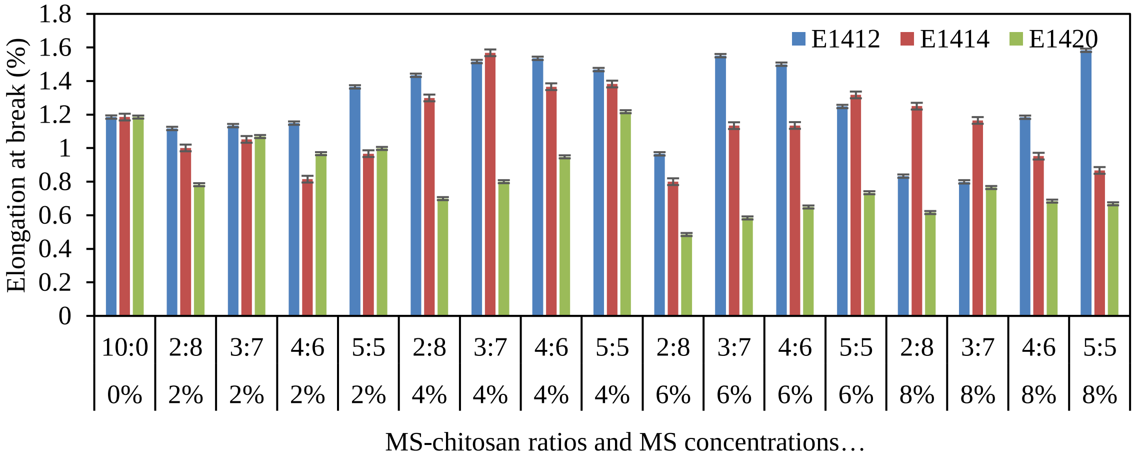

Figure 2: Effects of MS-chitosan ratios (upper values) and MS concentrations (lower values) on the percentage of elongation at break of the composite film

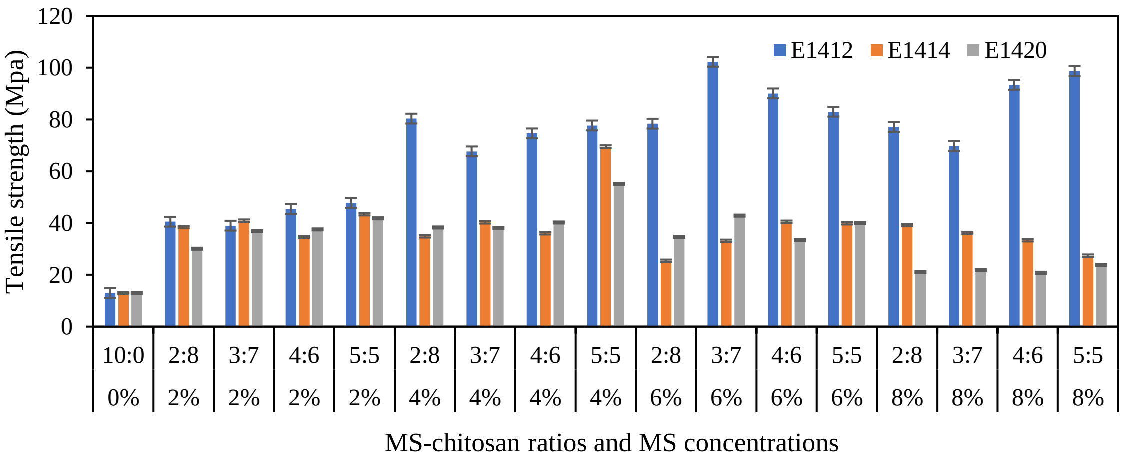

Figure 3: Effects of MS-chitosan ratios (upper values) and MS concentrations (lower values) on the tensile strength of composite film

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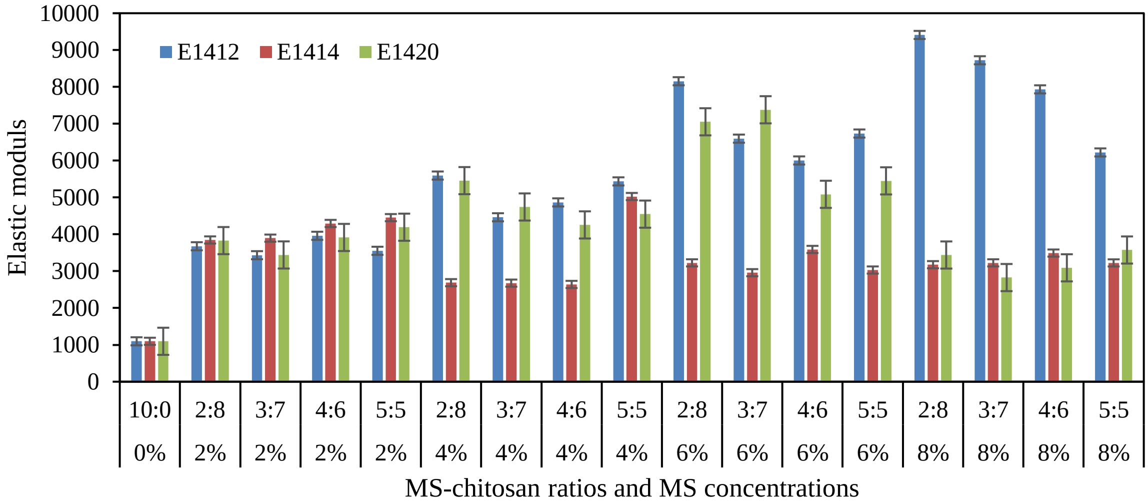

Figure 4: Effects of MS-chitosan ratios (upper values) and MS concentrations on the Elastic Modulus of composite film

Furthermore, as the concentration of modified starch increases in the film-forming solution, the number of OH^- groups also rises, contributing to further strengthening. However, variations in strength may occur at the same modified starch concentration due to the presence of more intramolecular hydrogen bonds than intermolecular hydrogen bonds[14]. In conclusion, the E1412-chitosan film exhibited the highest tensile strength among the three types of MS, possibly attributed to the acetyl groups present in E1414 and E1420 MS, which weaken intermolecular forces by reducing free hydroxyl group[11].

Elastic modulus

The elastic modulus is a fundamental measure of the film's stiffness, which is inversely proportional to the tensile strength and elongation of the film. The lower the elastic modulus, the more flexible the film. The results of the experiments demonstrated that chitosan films prepared by combining different types of MS exhibited an increase in the elastic modulus. This suggests that a higher concentration of MS leads to a decrease in film toughness. The elastic modulus was low at 2% and 4% MS concentrations, indicating that these concentrations were appropriate for film formation.

Effects of MS concentrations and MS-chitosan ratios on the Optical properties of composite film

The color and light transmittance properties of the films are illustrated in Figures 5 and 6, respectively. The values for WI and opacity varied with the amount of starch present and the type of starch used, suggesting that the brightness of the film is influenced by the additive. When modified starch was incorporated, WI decreased, implying that the film had a lower brightness. However, there was no change in opacity. The results of the survey on optical properties showed that when combined with three types of MS, E1412, E1414, and E1420, the CH film tended to increase opacity and decrease WI. Most of the films with added MS had lower opacity and WI values than the control sample, likely due to the change in the concentrations and ratios of CH and MS. Based on previous research, the starch source, concentration, and ratio are critical factors that influence the properties of starch-based edible films. A low opacity value indicates that the film is more transparent and allows light to pass through effectively. This is one of the factors used to assess the aesthetic appeal and consumer acceptability of the film. Although opacity can be affected by film thickness, there was little difference in the average thickness between the pre-prepared films in this study.

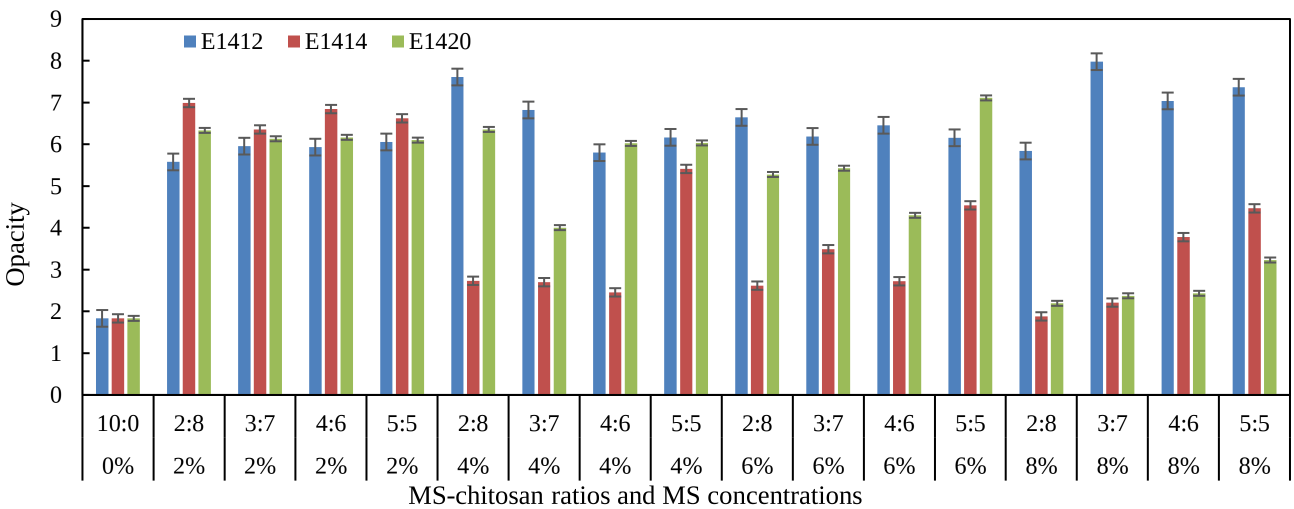

Figure 5: Effects of MS-chitosan ratios (upper values) and MS concentrations on the opacity of composite film

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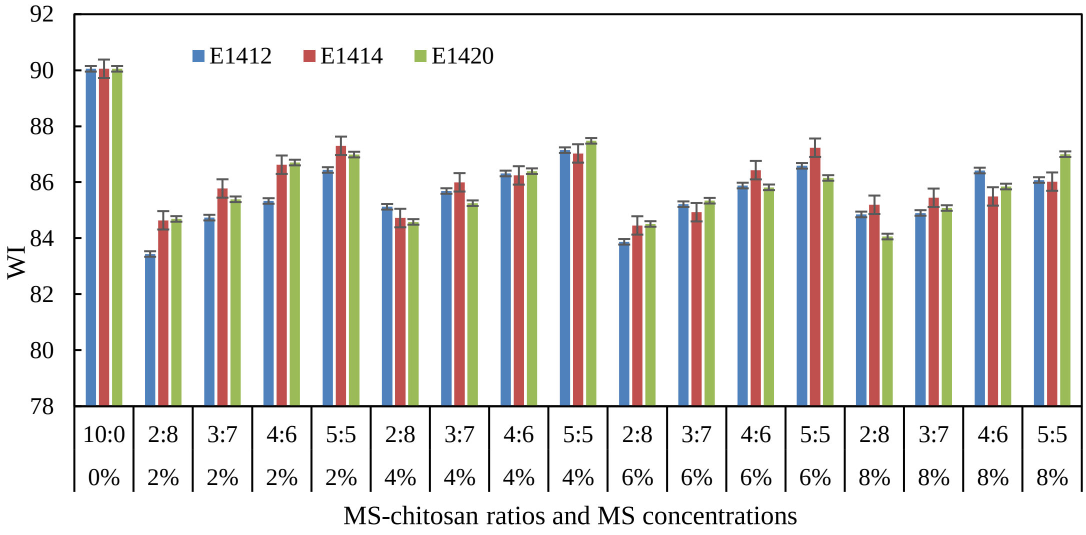

Figure 6: Effects of MS-chitosan ratios (upper values) and MS concentrations on the WI of composite film

The percentage opacity values and WI of the coating films, including the starch-free and chitosan films, are presented in Figs. 5 and 6. The analysis of variance test revealed that there was a significant difference ($p<0.05$) in the opacity value when producing films from chitosan and modified starch. This difference in opacity occurs when the proportion of modified starch in the film increases, compared to chitosan films with a lower opacity index. Chitosan films were more transparent than films made with starch, possibly due to their smoother surface texture and more amorphous structure (X-ray). Cholwasa et al. (2005) also reported similar findings: the addition of chitosan to starch films reduces fading[11].

Conclusion

This research focused on the effect of various concentrations and ratios of modified starch and chitosan on the physicochemical properties of composite films for food preservation. The study utilized three types of modified starch (E1412, E1414, and E1420) and found that combining 2% chitosan with 4% E1412 at a ratio of 5:5 (v/v) yielded the best results in terms of water vapor transmission rate, mechanical strength, film thickness, and optical parameters. These results met the requirements for film preservation and suggest that this composite film could be further utilized in food preservation studies.

Conflict of interest

The authors declare no conflict of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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