Investigation of the Structural and Physicomechanical Properties of Edible Sodium Carboxymethyl Cellulose Based Bilayer and Composite Films Containing Walnut Oil Emulsion Stabilized with Chia Seed Gum

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Abstract

This study investigated the effects of walnut oil incorporation on the physicomechanical and structural properties of sodium carboxymethyl cellulose-based edible films, with a focus on two methods of oil addition: bilayer and composite configurations. For this purpose, firstly walnut oil Pickering emulsion (10% oil) was stabilized using chia seed gum, which was then incorporated into the formulation of bilayer and composite films. SEM revealed that bilayer film exhibited a more cohesive and homogeneous structure compared to the composite film. XRD analysis indicated a semi-crystalline amorphous structure across all films, with bilayer film displaying slightly sharper peaks than composite film. Moisture content and solubility tests highlighted the hydrophobic influence of walnut oil, with bilayer films exhibiting the lowest moisture content and solubility due to their surface-localized oil layer. Thermal analysis using DSC and TGA demonstrated improved thermal stability and reduced weight loss in bilayer film. Mechanical tests showed that the bilayer film had the highest elongation at break (34.3%) and the lowest tensile strength (3.4 MPa). Color analysis revealed significant changes in chromatic indices, with composite films showing higher saturation and total color difference. These findings underscore the potential of walnut oil emulsion stabilized with chia seed gum, particularly in bilayer configurations, to enhance the functional properties of sodium carboxymethyl cellulose-based films.

Keywords: Chia seed gum, Edible films, Physical properties, Sodium carboxymethyl cellulose, Structural properties, Walnut oil emulsion

Introduction

Food processing encompasses a range of interconnected procedures, encompassing preparatory measures, formulation techniques, production methodologies, and packaging practices. Packaging, an essential component of the food industry, plays a pivotal role in ensuring the quality and safety of food materials, encompassing aspects of preservation and marketing communication (Yan, Hsieh, & Ricacho, 2022). In light of the environmental challenges posed by conventional plastics, extensive scholarly investigations have been undertaken to explore the development of biodegradable films. These films can be classified into two main categories: biodegradable plastics and edible films. Numerous scientific inquiries have explored the utilization of polysaccharides and diverse proteins as viable materials in the fabrication of edible films (Du *et al.*, 2021).

Cellulose is a naturally abundant biodegradable material, and insoluble in water and organic solvents (Chen *et al.*, 2023). Sodium carboxymethyl cellulose, a modified form of cellulose, exhibits desirable characteristics such as biodegradability, transparency, and film-forming properties (Wu & Li, 2023). Moreover, it displays a strong affinity for water and maintains a stable internal network structure, making it a promising candidate for enhancing the performance of composite films. However, like other polysaccharide-based edible films, sodium carboxymethyl cellulose films suffer from a common limitation of weak resistance to water vapor transmission due to their hydrophilic nature (Zhang *et al.*, 2023).

Lipids, primarily composed of triglycerides derived from fatty acids, can be broadly classified as saturated or unsaturated. Walnut oil, a valuable source of omega-3 fatty acids,

offers health benefits by contributing to the prevention of cardiovascular diseases (Rabrenović, Natić, Dabić Zagorac, Meland, & Fotirić Akšić, 2023). The use of lipids in the structure of films can improve some of the physicomechanical properties of films, including increasing the water vapor barrier properties of the films. Given that most edible films have a hydrophilic structure, oils are usually used in an emulsified form in the structure of edible films. In recent years, various studies have been conducted on the effect of oil on the physicomechanical properties of films, and the results of some of these works are presented in Table 1.Pickering emulsions, a specific type of emulsion stabilized by solid particles, do not require surfactants for stability, distinguishing them from conventional emulsions (Low, Siva, Ho, Chan, & Tey, 2020). Recent research has explored the use of various food-grade compounds to stabilize Pickering emulsions, which chia seed gum is one of the notable candidates. Chia, belonging to the mint family, is native to northern Guatemala and southern Mexico. Chia seed gum can make the intestines healthy and improve the functioning of the digestive system (Ramos *et al.*, 2023). Furthermore, the method of emulsion addition, whether as a composite or in a layered manner, significantly influences the properties of the resulting film (Niu *et al.*, 2023).

Therefore, the aim of this study was to use walnut oil in the structure of sodium carboxymethyl cellulose-based films to improve the physicomechanical properties of the films. Additionally, this research explored how the incorporation of walnut oil emulsions (composite and bilayer) affects the physicomechanical and structural properties of sodium carboxymethyl cellulose films.

Table 1- Recent studies on the impact of oil on the physicomechanical properties of films

Film type	Oil type	Finding(s)	Reference
Potato starch	Olive oil	The water vapor permeability was reduced by the addition of oil (1.65×10^{-7} g $(m\cdot h\cdot Pa)^{-1}$. The tensile strength decreased with the incorporation of oil (10.57 MPa).	(Farajpour, Emam Djomeh, Moeini, Tavakolipour, & Safayan, 2020)
Palm starch-chitosan	Extra virgin olive oil	The incorporation of olive oil into composite films enhanced their thermal stability while reducing surface roughness. 2% ($w.w^{-1}$) oil to the film matrix improved the tensile strength (158.1%) and elongation at break (224.6%).	(Hasan *et al.*, 2020)
Mung bean starch-guar gum	Sunflower seed oil	The incorporation of oil into the film matrix led to a reduction in mechanical strength but significantly improved water resistance.	(Lee, Lee, & Han, 2020)
Konjac glucomannan-curdlan	Camellia oil	Elongation at break, dissolution, and water vapor permeability of films containing camellia oil emulsion improved, but tensile strength decreased.	(Chen *et al.*, 2024)
Sodium alginate/guar gum film	Baobab seed oil	2% Baobab seed oil Pickering emulsion improved the water vapor permeability and mechanical properties of the films.	(Yang *et al.*, 2024)

Materials and Methods

Materials

Sodium carboxymethyl cellulose (Figure 1), Tween 80, and glycerol were purchased from Merck, Germany. Walnut oil (0.4 meq kg^{-1} peroxide value) was obtained from Kamjed, Iran, and its profile of fatty acids were as follows: C16:0, 5.8%; C18:0, 3.1%; C18:1, 24.7%; C18:2, 49.6%; C18:3, 15.0%. Also, chia seeds (Figure 1) were purchased from the local market.

Fig. 1. (a) Sodium carboxymethyl cellulose, and (b) chia seeds used in the present work

Preparation of chia seed gum

Chia seeds were hydrated in distilled water with a 1:40 seed-to-water ratio, stirred at 150 rpm for 30 minutes at 25 °C. The gum was separated using cheesecloth, centrifuged at 4000 rpm for 5 minutes, and dried at 50 °C for 10 hours. The dried gum was stored in a plastic container (Fernandes, Romani, da Silva Filipini, & Martins, 2020).

Preparation of walnut oil emulsion with chia seed gum

To create the emulsion, 1 g of chia seed gum powder was dissolved in 200 mL of distilled water. A 10% walnut oil concentration and Tween 80 were mixed into the solution at 600 rpm. Ultrasonication at 700 W for 5 minutes completed the emulsification process (Mirzaee Moghaddam, & Rajaei, 2021).

Preparation of edible films

Sodium carboxymethyl cellulose film

A solution was made by dissolving 1.5 g of sodium carboxymethyl cellulose (CMC) and 1 mL of glycerol in 250 mL of water, heated at 90 °C for 10 minutes. After cooling at room temperature for 30 minutes, bubbles were eliminated through centrifugation at 4000 rpm for 5 minutes. The solution was then poured into plastic molds to form films (Chang, Yu, & Ma, 2009).

Bilayer film based containing walnut oil emulsion

After preparing the CMC solution, it was poured into molds and left to solidify at room temperature for 24 hours. A walnut oil-in-water emulsion was then layered onto the gelatinous film surface, and the bilayer structure was dried at room temperature for 48 hours.

Composite film containing walnut oil emulsion

The prepared CMC solution was combined with a walnut oil-in-water emulsion that exhibited minimal creaming. The mixture was sonicated for 1 minute at 700 W, transferred to molds, and dried at room temperature over 48 hours.

Structural properties of films

To examine structural properties of films, a Scanning Electron Microscope (SEM) (model MIRA 3, Germany) was employed. Surface images were captured at a magnification of 500x, while cross-sectional views were obtained at magnifications of 1.5kx (Mirzaee Moghaddam, & Rajaei, 2021).

X-ray diffraction (XRD) analysis

The X-ray diffraction apparatus (model AW-DX300) was used in the range of 10 to 80 degrees to determine the crystalline structure of the films (Li *et al.*, 2022).

Measurement of moisture content and solubility of films

Film samples (2 cm× 2 cm) were dried at 60 °C for 24 hours, cooled to room

temperature, and weighed. After recording the moisture content, the films were submerged in 25 mL of water for 2 hours, removed, and dried again at 60 °C for 24 hours. Moisture content and solubility were calculated using appropriate formulas (Lim, Tan, & Pui, 2021):

$$W\% = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

where, W_0: The initial weight of edible film, and W_1: The weight of the film after drying.

$$Ws\% = \frac{W_1 - W_2}{w_1} \times 100 \quad (2)$$

here, W_1: Initial weight of dried edible films, and W_2: Weight of dried films after immersion.

Water vapor permeability of films

The examination of water vapor permeability provides insights into the ability of these films to transfer water vapor between the atmosphere and food material in packaged food products. This property significantly influences the susceptibility to spoilage and the shelf life of food items. ASTM 96-95 was employed to measure water vapor permeability. Glass vials were used for conducting this test. Initially, the vials were weighed, and then 15 mL of distilled water were weighed and transferred to the vials. Subsequently, the desired films were cut to the outer diameter of the vials, and placed over vial openings. In the following step, the vial openings were sealed with adhesive. The process of weighing vials was repeated over 72 h at specified intervals. It is noteworthy that the relative humidity of the air was measured during these 72 h (Moore & Akoh, 2017). The water vapor permeability (WVP) was calculated according to Equation (3):

$$WVP = \frac{\Delta W \times FT}{S \times \Delta p} \quad (3)$$

where, ΔW is the weight reduction of the vial (g), FT is the thickness (mm), S is the area (m^2), and Δp is the pressure difference (kPa).

Color characterization

The films' color properties, including luminosity (L*), red-green chromaticity (a*), and yellow-blue chromaticity (b*), were analyzed (Mirzaee Moghaddam, Khosh Taghaza, Barzgar, & Salimi, 2014). Both films and RAL color standards were photographed under controlled conditions with a 14 MP Canon digital camera. Adobe Photoshop was used to extract L*, a*, and b* values, which were calibrated against standard color sheets. These values were applied to calculate the total color difference (ΔE), hue angle ($H°$), and chroma (C) using established equations.

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (4)$$

$$H^\circ = \arctan\left(\frac{b}{a}\right) \quad (5)$$

$$C = \sqrt{a^2 + b^2} \quad (6)$$

where, ΔL, Δa, and Δb are the difference between the color of film samples and the control film.

Thermal properties analysis

Thermal behavior was evaluated through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using a calorimeter. Measurements were conducted from room temperature to 200 °C, with a heating rate of 10 °C per minute (Thakur *et al.*, 2017).

Fourier Transform Infrared (FTIR) analysis

The structural interactions within the film samples were examined through Fourier-transform infrared (FT-IR) spectroscopy analysis. Spectral data were acquired across the wavenumber range of 4000-400 cm^{-1}. Sample preparation was conducted using the KBr pellet method. The films were analyzed using a Fourier Transform Infrared (FTIR) spectrometer, model WQF-510A (Mirzaee Moghaddam, & Rajaei, 2021).

Mechanical properties of films

Tensile properties were determined using an STM-20 tensile testing machine (Santam, Iran). Films were cut into 20 mm × 50 mm strips, conditioned at 50% relative humidity for 48 hours, and tested at a grip distance of 30 mm with a speed of 1 mm per second. Ultimate tensile strength and elongation at break were calculated from recorded data (Tajari, Sadrnia, & Hosseini, 2024).

Statistical analysis

Significant differences among various treatments were determined at a 95% confidence level using a completely randomized design through analysis of variance (ANOVA). The means of the data were compared through the Dunnett test using the SPSS software. Additionally, graphs were plotted using Microsoft Excel 2019.

Results and Discussions

Structural properties of films

Examining the structure of the film with SEM

In the present work, chia seed gum particles, which were almost nano-sized, were used to stabilize the emulsion. However, the droplet size of the walnut oil Pickering emulsion stabilized with nanoparticles was in the micrometer range. As can be seen, (Figure 2) nanoparticles form a thick layer when they attach to the surface of the oil droplets, and the nature of the nanoparticles is not known. It should be noted that in the present work, walnut oil Pickering emulsion was used in the structure of the films, and the size of the emulsion droplets used was in the micrometer range. In addition, it is observed, agglomeration of nanoparticles has occurred during the drying stage of the films. Furthermore, as depicted in Figure 2, the control films exhibited smoother surfaces compared to the bilayer and composite films. Additionally, the bilayer and composite films showed a more compact and heterogeneous structure compared to the control films. Moreover, the control films had some level of porosity in the cross-sectional area. Cracks were observed in the cross-sectional area of the composite films. Overall, it can be stated that the bilayer film demonstrated a more cohesive structure compared to the composite film, indicating that the use of walnut oil emulsion in the form of bilayer created a higher level of homogeneity compared to the composite film.

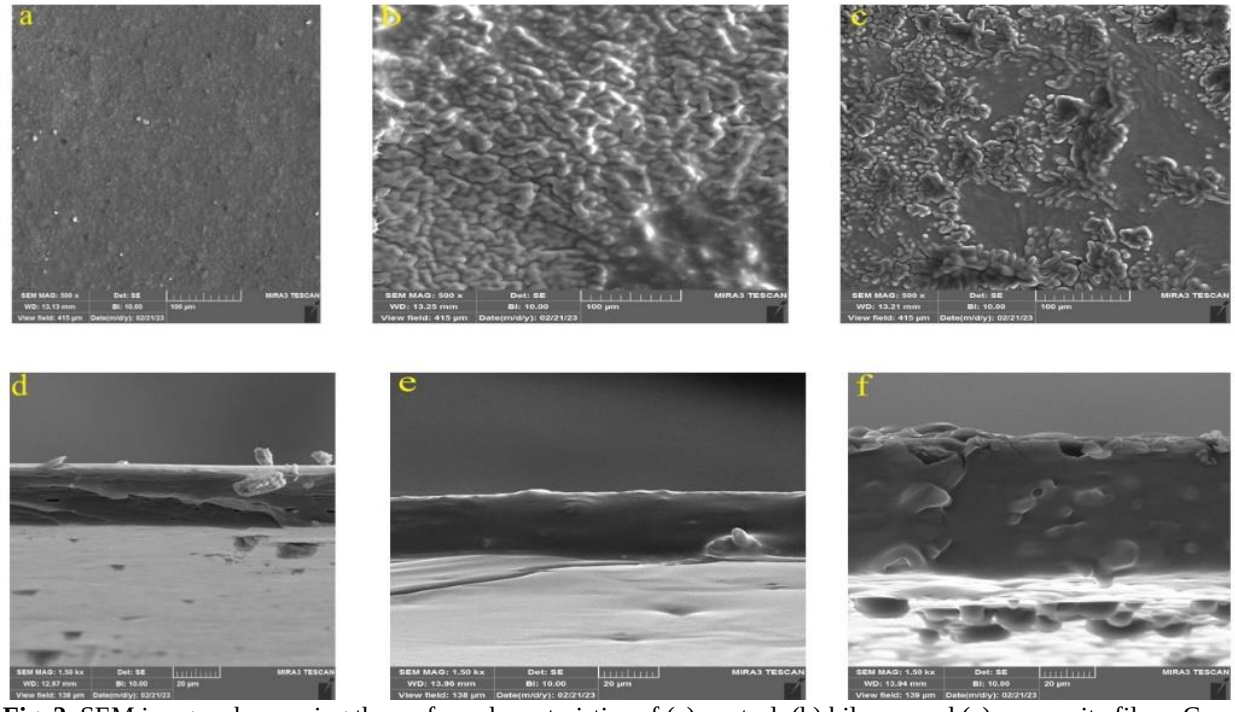

Fig. 2. SEM images showcasing the surface characteristics of (a) control, (b) bilayer, and (c) composite films; Cross-sectional view of (d) control, (e) bilayer, and (f) composite films

In their study, Lee *et al.* (2020) examined the edible mung bean starch film with sunflower oil and stated that the structure of the mung bean starch film without the addition

of sunflower oil was smooth, homogeneous, and crack-free. However, with the addition of sunflower oil to the starch film, the structure became heterogeneous, rough, and exhibited cracks. Tongnuanchan, Benjakul, Prodpran, and Nilsuwan. (2015) investigated an emulsion film based on fish gelatin and palm oil and stated that the gelatin film had a smooth and homogeneous surface, which became rough with the addition of oil. They also observed some cracks or discontinuous areas on the control film and the film containing palm oil. Pereda, Amica, and Marcovich (2012) examined chitosan edible films with olive oil and stated that a smooth and continuous structure was observed on the surface of the chitosan film. In this study, the presence of oil in the film structure led to discontinuities associated with the formation of two phases: lipid and polymer.

X-ray diffraction (XRD)

The XRD results of the different films can be observed in Figure 3. In the control film, the 2θ angle equals 21.85 degrees, whereas in the bilayer and composite films, the 2θ angle is equal to 20.5°. In control and composite films, broad and non-sharp peaks were observed, indicating the lack of crystallization in these films.

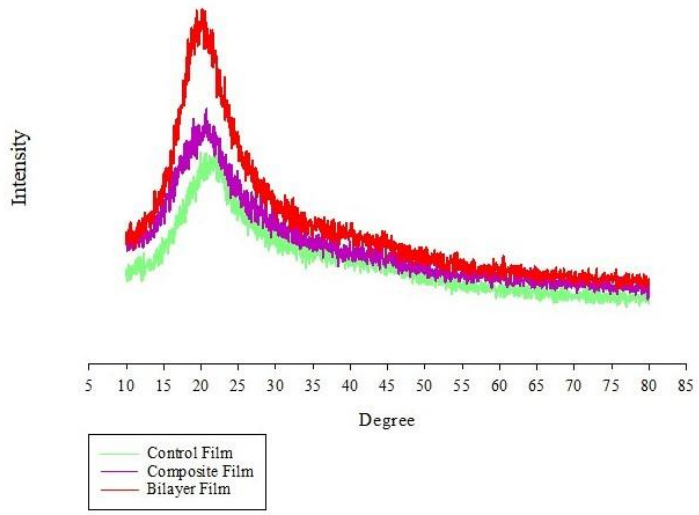

Fig. 3. X-ray diffraction results of control, composite, and bilayer films

The addition of emulsion to the composite film did not induce crystallization in this film. The intermolecular interactions between the components of the composite network restrict the movements of molecular segments and hinder the crystallization process. However, the 2θ angle of 20.5 degrees in the bilayer film was slightly sharper compared to the composite film. Niknam, Ghanbarzadeh, Ayaseh, and Hamishehkar (2019) investigated the effects of different vegetable oils on the microstructure and physicochemical properties of plantain films and stated that the plantain gum film (control film) exhibited a typical semi-crystalline amorphous structure, lacking strong or sharp peaks, indicating no crystallinity. Furthermore, the addition of corn, canola, and olive oil did not have a significant impact on these films. Valenzuela, Abugoch, and Tapia (2013) examined a chitosan-based edible film with quinoa protein and sunflower oil and stated that the combination of quinoa protein and chitosan showed sharp peaks, indicating intermolecular interactions between

the two polymers. Additionally, the combination of chitosan, quinoa protein, and sunflower oil exhibited broad and smooth peaks, indicating that the addition of sunflower oil to the film created a less crystalline structure.

Physical properties of films

Moisture content of edible films

Edible films often come into contact with moist food items, making it vital to evaluate their moisture content. Films with low water resistance tend to dissolve rapidly, which can lead to increased migration of their components into the food matrix, thereby diminishing their protective functionality.

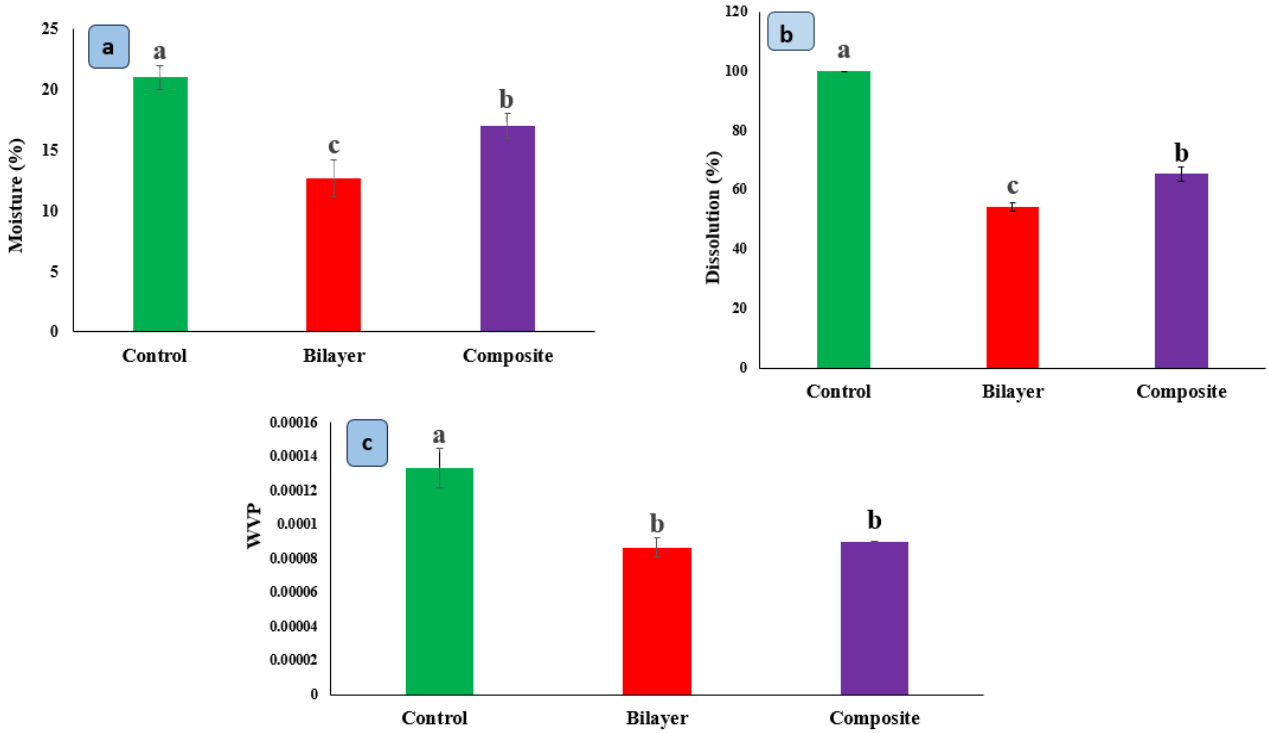

Fig. 4. (a) Moisture content, (b) solubility, and (c) water vapor permeability of control, composite, and bilayer films

However, water-insoluble films may be advantageous for maintaining product integrity, while solubility before consumption can be beneficial in some scenarios. As illustrated in Figure 4a, significant differences ($p < 0.05$) were observed in the moisture content among the control, bilayer, and composite films. The control film displayed the highest moisture content, whereas the bilayer film exhibited the lowest. The incorporation of walnut oil into the bilayer film structure appeared to reduce its moisture content more effectively than when incorporated in a composite configuration. Similar findings were reported by Niknam *et al.* (2019), who studied the influence of various oils on plantain-based films. They observed that adding oils reduced moisture levels, attributed to the interaction between oil molecules and the hydroxyl groups in plantain, which decreased hydrophilicity. Conversely, adding glycerol increased moisture absorption. This behavior underscores the hydrophobic nature of oils, which improves water resistance in hydrocolloid films. Comparable results were found by Aydogdu, Radke, Bezci, and Kirtil (2020), who noted that moisture content in guar gum-orange oil films decreased with higher orange oil concentrations, attributing the effect to phenolic interactions with hydroxyl groups.

Dissolving edible films

Figure 4b shows significant differences ($p < 0.05$) in solubility among the control, bilayer, and composite films. The control film exhibited the highest solubility, while the bilayer film demonstrated the lowest. Reduced solubility in bilayer and composite films was due to the presence of oil, which created a hydrophobic barrier. Amal, Kasim, Khaled, Lucia, and Ioan (2011) similarly found that the solubility of egg-white protein films decreased with increasing olive oil and oleic acid concentrations. The lower solubility of bilayer films compared to composite films (Figure 4b) was likely due to the surface localization of oil in bilayer films, forming a water-repellent layer. In contrast, in composite films, oil was uniformly dispersed throughout the structure.

Film permeability to water vapor

The results of the film's water vapor permeability can be observed in Figure 4c. The control film exhibited higher water vapor permeability compared to the bilayer and composite films. Additionally, no significant difference ($p > 0.05$) was observed between the bilayer and composite films. The results indicated that the addition of walnut oil, due to its water-repellent properties, to sodium carboxymethyl cellulose film, which has high water affinity, resulted in a decrease in water vapor permeability. This section's findings demonstrated that the addition of oil can reduce water vapor permeability, but the method of oil addition to the film (composite or bilayer) did not have any effect on water vapor permeability. Xiao *et al.* (2016) investigated the effect of the melting point of palm oil on the water vapor permeability of gelatin-palm oil emulsion films and stated that all films containing palm oil exhibited significantly lower water vapor permeability compared to pure gelatin films.

Color evaluation

The color properties of the films are depicted in Figures 5a-f. Brightness (L*) showed a significant reduction ($p \leq 0.05$) in bilayer and composite films compared to the control, with bilayer film retaining greater brightness than composite film (Figure 5a). The addition of walnut oil emulsion influenced chromatic indices: the red-green index (a*) increased, reducing green tones, with composite films showing a higher a* value than bilayer films (Figure 5b). The yellow-blue index (b*) also rose with walnut oil inclusion, with composite films exhibiting higher values (Figure 5c). Hue angle and chroma, as shown in Figures 5d and 5e, also varied significantly ($p \leq 0.05$). Composite films displayed higher hue angles and chroma, indicating more pronounced color intensity. The total color difference (ΔE) was greater in composite films than in bilayer films (Figure 5f). The appearance of the films is shown in Figure 5g. The appearance of the films clearly shows the greater color difference of the composite film compared to the bilayer film, which is in line with the ΔE results. Farajpour *et al.* (2020) observed that adding olive oil to potato starch films reduced brightness and increased yellowness, aligning with findings for walnut oil films. Galus (2018) examined isolated soy protein-based edible films under the influence of rapeseed oil and stated that an increase in rapeseed oil resulted in a reduction in brightness and a darker film. Additionally, with an increase in rapeseed oil in the isolated soy protein film, the b* index increased due to the bright yellow color of rapeseed oil. The hue angle and chroma increased with increasing rapeseed oil concentration, indicating increased saturation with increasing rapeseed oil concentration.

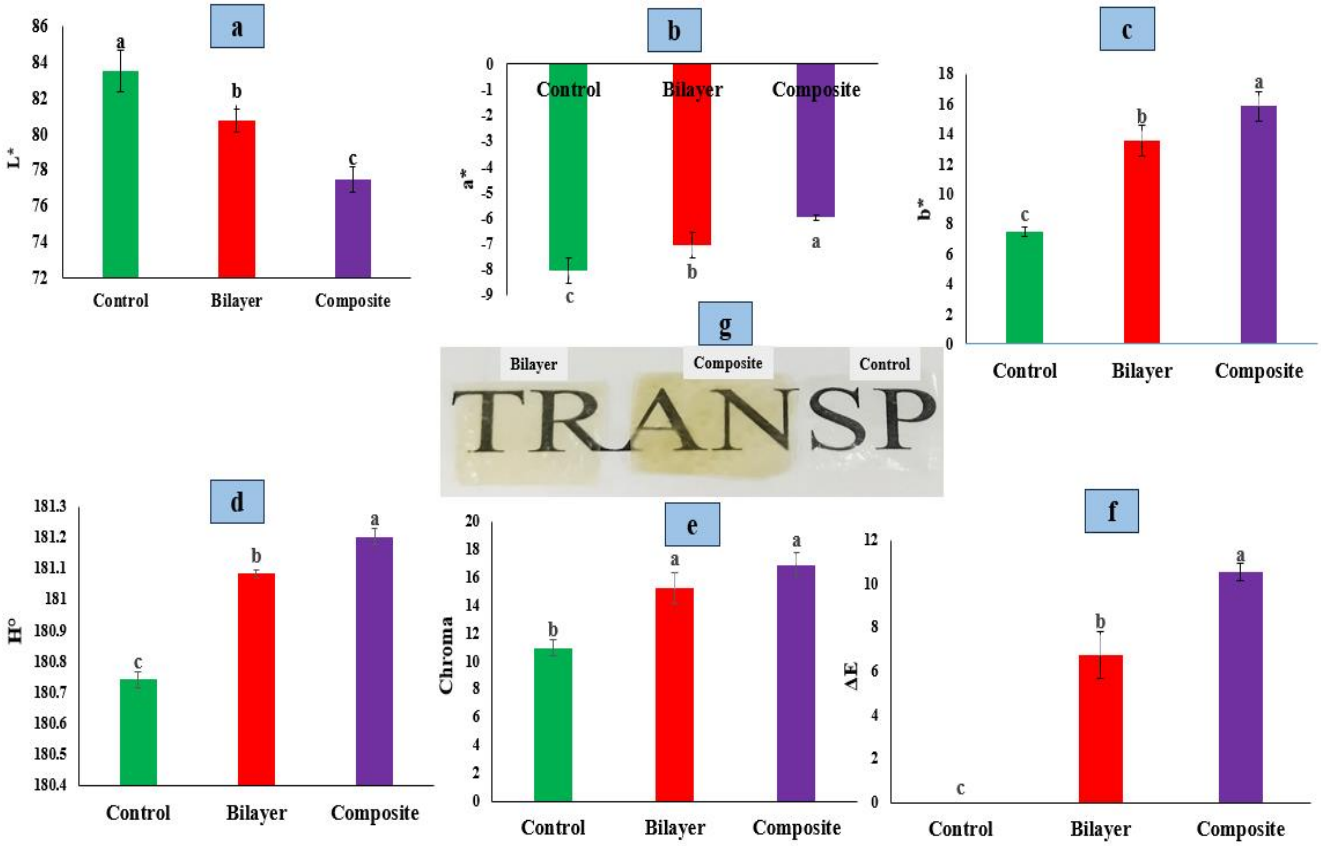

Fig. 5. (a) L*(b) a*(c) b*(d) hue angle, (e) chroma, (f) ΔE, and (g) appearance of control, composite, and bilayer films

Thermal properties of films

Thermal behavior of the films was analyzed using differential scanning calorimetry (DSC) (Figure 6a). The control film showed a single melting peak at 94.32 °C, associated with the crystalline structure of sodium carboxymethyl cellulose. Composite and bilayer films exhibited higher melting peak temperatures at 104.99 °C and 117.64 °C, respectively. The increase in melting point with oil incorporation suggests enhanced crystallinity, particularly in bilayer films, as confirmed by XRD analysis. This increase may result from interactions between the lipid phase and the film matrix, strengthening the structure. Ma *et al.* (2012) observed similar trends with gelatin films containing olive oil, where the lipid phase increased the melting point and crystallinity.

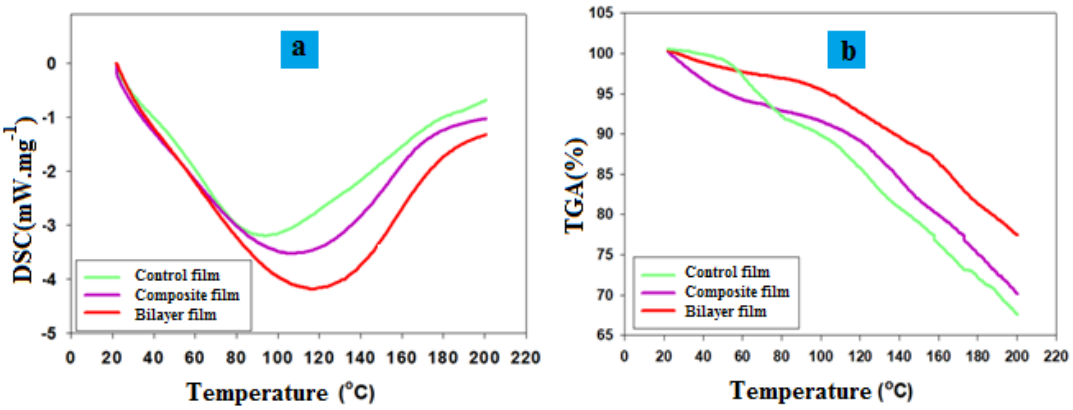

Fig. 6. Results of: (a) DSC and (b) TGA of control, composite, and bilayer films

The TGA curves of the control, bilayer, and composite films are shown in Figure 6b. From Figure 6b, in the case of all three film samples (control, composite, and bilayer), weight loss was observed up to the temperature of 200 °C. The weight loss of edible films at low temperatures is mainly due to the evaporation of volatile components of the film such as water. But at high temperatures, the weight loss can be due to the destruction of the chemical structures of the film components. The weight loss due to evaporation was higher in the control film (23%) compared to the composite and bilayer films. Additionally, the composite film had a higher weight loss (7%) compared to the bilayer film, which was consistent with the moisture content results. Bhatia *et al.* (2023) examined the effect of rosemary essential oil on the physicochemical properties of composite edible films based on sodium alginate and casein. In their study, a peak was observed from room temperature to 120°C, which was attributed to the evaporation of water and the presence of rosemary essential oil in the film.

Fourier transform infrared spectrometry (FTIR)

FTIR spectra of different films based on sodium carboxymethyl cellulose are shown in Figure 7. Some similar peaks were observed in all three control, bilayer, and composite films due to the presence of sodium carboxymethyl cellulose polysaccharide (Figure 7). For example, a broad peak in the region of 3500 cm^{-1} was observed in the spectra of all three types of films, which was related to the stretching vibration of O-H groups. Also, the peak 1026 cm^{-1} observed in the spectra of all three types of films is related to the stretching vibration of the C-O-C group and the bending vibration of the C-O-H group due to the 1→4 glycosidic bond, which was considered as a characteristic of polysaccharide compounds.

However, additional peaks unique to the bilayer and composite films were observed, indicating the influence of emulsion components on the film structure. For example, the peak at 791 cm^{-1} related to C-C bending vibrations, suggests the integration of non-polysaccharide components in the emulsion, likely arising from the additives used to modify film properties. The peak around 3000 cm^{-1} is assigned to the stretching vibration of CH= groups, which highlights the presence of unsaturated bonds introduced by the triglycerides in walnut oil. The oil acts as a plasticizer or hydrophobic agent, altering the film's mechanical and water-barrier properties. Peak at 1740 cm^{-1} corresponds to the C=O stretching vibrations of the carbonyl group in triglycerides, further confirming the presence of walnut oil. The peak at 1169 cm^{-1}, associated with bending vibrations, was related to CH_2 groups, and the peak at 667 cm^{-1}, also linked to bending vibration, was indicative of cis groups. Additionally, the FTIR spectra revealed peaks at 1595 cm^{-1} and 1415 cm^{-1}, attributed to the symmetric stretching of the carboxylate ($-COO^-$) groups of uronic acid.

These peaks are indicative of the anionic nature of chia seed gum, which contributes to its emulsifying and stabilizing properties in the films. The presence of uronic acid and its functional groups enhances electrostatic interactions within the film matrix, promoting cohesive film formation and potentially improving mechanical strength (Mohammadi, Mirabzadeh, Shahvalizadeh, & Hamishehkar, 2020; Vargas, Albors, Chiralt, & González-Martínez, 2009). The observed trends suggest that the inclusion of walnut oil and chia seed gum in the emulsion significantly alters the chemical environment and molecular interactions within the bilayer and composite films. These modifications likely improve their barrier, mechanical, and optical properties compared to the control film. The distinctive FTIR peaks validate the integration of these components into the film structure and highlight their synergistic role in enhancing film functionality.

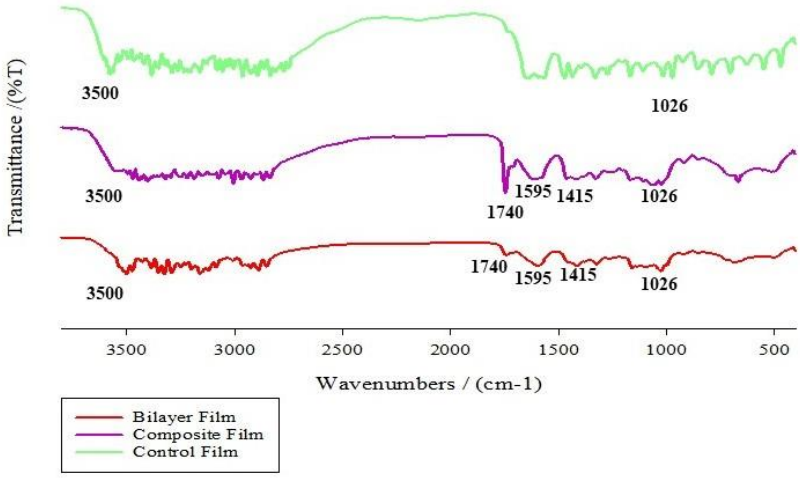

Fig. 7. FTIR spectra of control, composite, and bilayer films

Mechanical properties of edible films

According to Figure 8a, the elongation (strain) at break in the control, composite, and bilayer films showed a significant difference ($p \leq 0.05$). The bilayer film exhibited a higher elongation at break compared to the control and composite films. It can be concluded that walnut oil played the role of a plasticizer in the structure of the bilayer film and, with limited penetration into the sodium carboxymethyl cellulose layer, increased the elongation of the film compared to the control film. In the case of the composite film, the presence of oil in the film structure likely excessively weakened the intermolecular forces, resulting in a reduction in elongation. Additionally, the presence of oil droplets in the film structure could lead to the formation of a heterogeneous and discontinuous structure, which could result in cracks at those points. Mohammadi *et al.* (2020) and Vargas *et al.* (2009) obtained similar results in their studies. These researchers stated that adding oil to the film creates a heterogeneous and discontinuous structure, which consequently reduces the percentage of elongation at the breaking point of composite.

The ultimate tensile strength results of the different films are shown in Figure 8b. The control film exhibited a significant difference ($p \leq 0.05$) compared to the bilayer and composite films. However, no significant difference ($p > 0.05$) was observed between the bilayer and composite films. The tensile strength between the bilayer and composite films decreased with the addition of walnut oil

emulsion. The addition of the emulsion to the film likely replaced some of the polymer-polymer interactions with emulsion-polymer interactions, resulting in a decrease in the strength of these films. Javanmard and Golestan (2008) investigated the effect of olive oil and glycerol on a casein-based edible film and stated that the addition of oil and glycerol to the film reduces the tensile strength. The reduction in tensile strength with increasing glycerol content may be attributed to an increase in the distance between protein molecules. Additionally, the incorporation of lipids in protein films leads to a decrease in tensile strength upon fracture. This can be explained by the fact that the protein phase has higher tensile strength compared to the lipid phase.

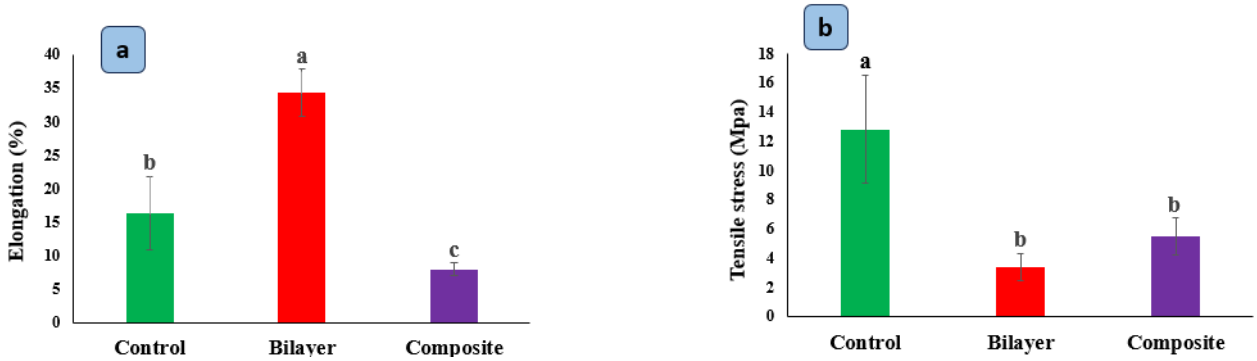

Fig. 8. Results of (a) elongation at break, and (b) the ultimate tensile strength of the produced edible films

Conclusion

This study explored the incorporation of walnut oil into sodium carboxymethyl cellulose-based edible films using composite and bilayer approaches, focusing on their structural, physical, thermal, and mechanical properties. The findings revealed that the method of oil incorporation significantly influenced film characteristics. Structurally, bilayer films exhibited greater homogeneity and cohesion compared to composite films, as observed through SEM and XRD analyses. The bilayer configuration also enhanced moisture resistance and decreased solubility, likely due to the surface localization of oil forming a hydrophobic barrier. Physically, bilayer films displayed lower moisture content and solubility than composite films, underscoring their potential for food applications requiring moisture resistance. Thermal analysis indicated improved thermal stability and increased melting points for oil-incorporated films, particularly in bilayer structures, suggesting enhanced crystallinity due to interactions between the lipid phase and the film matrix. Mechanically, bilayer films demonstrated higher elongation at break, likely due to the plasticizing effect of walnut oil. However, both composite and bilayer films exhibited reduced tensile strength compared to the control, attributed to disrupted polymer-polymer interactions. These results highlight the bilayer film's superiority in combining desirable physicomechanical properties, making it a promising candidate for edible coatings and food packaging applications. Future research should explore optimizing oil concentrations to balance mechanical strength and flexibility while investigating interactions with various food matrices. Additionally, scaling up production and assessing the films' biodegradability, sensory attributes, and compatibility with active compounds such as antioxidants or antimicrobials could further expand their applications in the food industry.

Authors Contribution

A. Nahalkar: Methodology, Data acquisition, Data pre and post processing, Statistical analysis, Software services,

Visualization, Text mining
A. Rajaei: Technical advice, Conceptualization, Methodology, Validation, Text mining, Review and editing services
H. Mirzaee Moghaddam: Supervision, Conceptualization, Methodology, Validation, Text mining, Review and editing services

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بررسی خواص ساختاری و فیزیکومکانیکی فیلم‌های خوراکی دولایه و کامپوزیتی حاوی امولسیون روغن گردو تثبیت‌شده با صمغ دانه چیا بر پایه سدیم کربوکسی متیل سلولز

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چکیده

این مطالعه اثرات ترکیب روغن گردو بر خواص فیزیکی و مکانیکی و ساختاری فیلم‌های خوراکی مبتنی بر سدیم کربوکسی متیل سلولز را با تمرکز بر دو روش افزودن روغن بررسی کرد: پیکربندی‌های دولایه و ترکیبی. بدین منظور ابتدا امولسیون جمع‌کننده روغن گردو (۱۰ درصد روغن) با استفاده از صمغ دانه چیا تثبیت شد و سپس در فرمولاسیون فیلم‌های دولایه و کامپوزیت گنجانده شد SEM نشان داد که فیلم دولایه ساختار منسجم و همگن‌تری را در مقایسه با فیلم کامپوزیت نشان می‌دهد. تجزیه و تحلیل XRD یک ساختار آمورف نیمه‌کریستالی را در تمام فیلم‌ها نشان داد، با فیلم دولایه که قله‌های کمی تیزتر از فیلم کامپوزیت را نشان می‌دهد. آزمایش‌های محتوای رطوبت و حلالیت تأثیر آب‌گریز روغن گردو را برجسته می‌کنند، با فیلم‌های دولایه که به دلیل لایه‌های روغن موضعی سطحی، کمترین میزان رطوبت و حلالیت را نشان می‌دهند. تجزیه و تحلیل حرارتی با استفاده از DSCو TGA بهبود پایداری حرارتی و کاهش وزن را در فیلم دولایه نشان داد. آزمایش‌های مکانیکی نشان داد که فیلم دولایه دارای بیشترین کشیدگی در هنگام شکست (۳۴/۳٪) و کمترین استحکام کششی (۳/۴ مگاپاسکال) است. تجزیه و تحلیل رنگ تغییرات قابل‌توجهی را در شاخص‌های رنگی نشان داد، با فیلم‌های کامپوزیتی که اشباع بالاتر و تفاوت رنگ کل را نشان دادند. این یافته‌ها بر پتانسیل امولسیون روغن گردو تثبیت‌شده با صمغ دانه چیا، به‌ویژه در پیکربندی‌های دولایه، برای افزایش خواص عملکردی فیلم‌های مبتنی بر سدیم کربوکسی متیل‌سلولز تاکید می‌کند.

واژه‌های کلیدی: امولسیون روغن گردو، خواص فیزیکو مکانیکی و ساختاری، سدیم کربوکسی متیل سلولز، صمغ دانه چیا، فیلم‌های خوراکی

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