Preparation and characterization of chitosan-citric acid edible films loaded with Cornelian cherry pomace extract as active packaging materials

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ABSTRACT

The development of environmentally-friendly, intelligent and active packaging materials is crucial for the protection of food products and the prevention of environmental pollution. This work aimed to study the development of chitosan films containing an extract form Cornelian cherry pomace extract, a by-product of juice production. Citirc acid was utilized as an alternative acidifier and the effect of β-cyclodextrin incorporation on film properties was evaluated. Compared to chitosan-acetic acid films, the films produced in the present study were found to be more elastic, with a lower moisture content and higher water solubility as well as water vapor permeability. Moreover, the obtained results showed that the increase of β-cyclodextrin concentration from 0.45 to 1.85 % w/v improved the mechanical and water vapor barrier properties of the film. Addition of the Cornelian cherry pomace extracts resulted in alteration of the color of the prepared films as well as improvement of the light barrier properties. Also, the presence of the phenolic compounds in the film matrix enhanced the antioxidant activity of the prepared films.

Keywords: chitosan, citric acid, β-cyclodextrin, cornelian cherry pomace, active packaging materials, SEM

1. Introduction

Food packaging plays a crucial role in the preservation and protection of foods. Plastics, which are cheap, flexible and exhibit good resistance to mechanical stress, are widely used as food packaging materials. However, due to the slow degradation of petroleum-based materials, there is an increasing environmental awareness that has led to the development of biodegradable materials as a natural substitution for packaging (Yu et al., 2023). Biopolymers, such as polysaccharides (e.g. chitosan, alginate, starch), proteins (e.g. gelatin, zein, whey protein) and lipids as well as their combinations, have been utilized for the development of edible films. Among them, polysaccharides are usually used for the preparation of packaging materials due to their good gas barrier; however their mechanical strength and their water vapor permeability still needs to be improved for large-scale applications (Li et al., 2023; Mouzakitis et al., 2022; Yu et al., 2023).

Chitosan is a known film forming, non-toxic, biodegradable, cationic polysaccharide with antimicrobial activity, soluble in aqueous media with a pH value lower than 6. The acidic conditions contribute to the protonation of amino groups of chitosan (NH_3^+), making the polymer positively charged and reducing the interaction between the chains (Nair, Tomar, Punia, Kukula-Koch & Kumar, 2020; Sharmin Rosnes, Prabhu, Böcker, & Sivertsvik, 2022). Different organic and inorganic acids have been examined as dilution media, such as acetic, lactic, citric and hydrochloric acid. The selection of the acid is crucial as it influences the mechanical and moisture permeability properties of the polymer (Chen et al., 2008; Melro et al., 2021). Generally, acetic acid enhances the mechanical properties of the chitosan films compared to other acids due to the development of tighter structure and higher junction density. On the contrary, polycarboxylic acids, such as citric acid (CA), can be utilized also as solvent media and can enhance the elasticity of chitosan films due to the strong interaction of polymers with acids through ionic crosslinking. (Park, Bin, Reis Brod, & Brandini Park, 2002; Qiao, Ma, Wang, & Liu, 2021, Melro et al., 2021, Zhang et al., 2022).

The protection of foods from oxidation is crucial towards the increase of their shelf-life. Chitosan is characterized by low antioxidant activity; this can be overcome by the introduction of pure antioxidant compounds or extracts rich in bioactive compounds, in the film matrix. In this view, Cornelian cherry (*Cornus mas* L.), a traditional red medical fruit of the Mediterranean area, is a good source of different bioactive compounds, e.g. anthocyanins, phenolic compounds, iridoids and organic acids. Mainly three organic acids, namely citric, maleic and tartaric acids, have been identified in Cornelian cherries and their concentration depends on the genotype of the fruit (De Biaggi et al., 2018; Taş & Gundogdu, 2023). Anthocyanins are natural colorants which are sensitive to pH changes (Loukri, Christaki, Kalogiouri, Menkissoglu-Spiroudi & Mourtzinos, 2022). These flavonoids can be utilized for the development of active packaging materials due to their antioxidant activity and also for the preparation of smart packaging materials in order to monitor the freshness of the products based on their color alteration upon pH and gas changes (Zhao, Liu, Zhao & Wang, 2022). However, anthocyanins in the film matrix may not be stable. Cyclodextrins, are cyclic oligosaccharides, which can form inclusion complexes and contribute to their stabilization (Loukri et al., 2022). The presence of cyclodextrin in the film matrix can contribute to the retention of the phenolic compounds during preparation and also to the modification of the mechanical and barrier properties of the films, due to the interaction between the polymers (Bizymis, Giannou & Tzia, 2022;

Higueras, López-Carballo, Cerisuelo, Gavara & Hernández-Muñoz, 2013; Liu et al., 2022).

The use of natural extracts rich in anthocyanins as dissolving media for chitosan is an innovative way to develop novel packaging materials. Considering all the above, the aim of this work was the development of chitosan films using different Cornelian cherry pomace extracts as solvents for chitosan. To the best of our knowledge, Cornelian cherry pomace extracts were used for the first time for the development of active chitosan films. CA, a common food acidifier and antibacterial additive, has been studied as natural crosslinker between biopolymers chains in manner to improve mechanical and barrier properties of their films. In the present study, CA was used as an alternative solubilizer in order to avoid the unpleasant odor of the "conventional" acetic acid. Also, the effect of β-cyclodextrin concentration on the film matrix was examined. Subsequently, the structural, physical and antioxidant properties of the prepared films were evaluated. The results of this study will illustrate the potential of development food packaging materials based on chitosan and cornelian cherry pomace.

2. Materials and methods

2.1. Chemicals

Cornelian cherries were kindly provided by Physis Ingredients (Serres, Greece). Chitosan was purchased from Siveele (Breda, Netherlands) and β-cyclodextrin from Gangwal Chemicals Private Limited Co., Ltd. (Mombai, India). Glycerol, acetic acid and citric acid were supplied by Chem-Lab ANALYTICAL bvba (Belgium) Ultrahigh purity water was produced in the laboratory using a Micromatic Wasserlab system (Spain).

2.2. Preparation of Cornelian cherry pomace extract

Fresh destoned Cornelian cherries were pressed in order to remove the juice with the aid of a slow juicer (SSJ 40441BK, Sencor). The obtained pomace that contained also the peels of the cherries, was then collected and freeze-dried using a HyperCOOL HC8080 freeze-dryer (Gyrozen Co., Ltd., Incheon, Korea) (-80 °C, 0.1 mbar) and then stored at -20 °C until further analysis.

For the preparation of the cherry pomace extract, water or aqueous solutions of β-cyclodextrin at two different concentrations (i.e. 0.45 %w/v and 1.85 %w/v), as the extraction media, were used. The solvent:dry cherry pomace ratio was kept constant at 50 mL/g in all cases. The extraction was carried out with a VCX-130 sonicator (Sonics and Materials, Danbury, USA) working at 130 W and 20 kHz, equipped with a Ti–Al–V sonoprobe (13 mm), at 60 ± 4°C and 90% amplitude. The extraction conditions were selected, based on preliminary experiments. The duration of the extraction was 22 min. Afterwards, the obtained extracts were centrifuged in a bench centrifuge (Hermle Z300K, Germany) at 6,000 rpm for 5 min and then the supernatants were collected. The clear extracts were then used for the preparation of the films.

2.3. Preparation of chitosan-based films

The chitosan films were prepared following the protocol of Yong, Liu, Kan, & Liu. (2019) with some modifications. In particular, chitosan (2% w/v) was dissolved in a 3% (w/v) CA solution. In order to evaluate the potential of Cornelian cherry pomace extracts to act as chitosan dilution media, citric acid (3% w/v) and chitosan (2% w/v) were added directly in such extracts that were prepared either using aqueous solutions of β-cyclodextrin at two different concentrations (i.e. 0.45 %w/v and 1.85 %w/v) as above mentioned (BE) or water (WE). For comparison purposes, films were also prepared by adding β-cyclodextrin in the final mixture of chitosan and citric acid at the same concentration. A control film was also prepared by diluting chitosan in 1% v/v acetic acid. Each solution was magnetically stirred for 1 h at 40 °C until transparent solutions were obtained. In every case, 30% w/w (based on chitosan content) of glycerol was added as a plasticizer under vigorous stirring to provide film-forming solutions. After filtration, the film-forming solutions were uniformly poured into petri-dishes and dried in an oven at 30 ◦C for 24 h. The prepared films were kept in desiccators with 50% relative humidity at 30 °C until equilibrium. The composition of all these films is provided in **Table 1.**

Table 1. Abbreviated names for the different compositions of films.

Composition of the films	Concentration of chitosan	Type of solvent for chitosan disolution	Type and concentration of acid	Concentration of β-cd
Ch	2 % w/v	Water	1% v/v acetic acid	0
Ch + CA	2 % w/v	Water	3% w/v citric acid	0
Ch+CA+0.45β-cd	2 % w/v	Water	3% w/v citric acid	0.45 %w/v
Ch+CA+1.85β-cd	2 % w/v	Water	3% w/v citric acid	1.85 %w/v
Ch+CA+WE	2 % w/v	Cornelian cherry pomace aqueous extract (WE)	3% w/v citric acid	0
Ch+CA+0.45BE	2 % w/v	Cornelian cherry extract in aqueous solution of β-cd (BE)	3% w/v citric acid	0.45 %w/v
Ch+CA+1.85BE	2 % w/v	Cornelian cherry extract in aqueous solution of β-cd(BE)	3% w/v citric acid	1.85 %w/v

Ch: chitosan, CA: citric acid, β-cd: β-cyclodextrin

2.4. Characterization of chitosan films

2.4.1. Scanning electron microscopy (SEM)

The chitosan film samples for morphological analysis were prepared by partitioning them into longitudinal and cross-sectional pieces, which were subsequently attached to stabs. The morphological properties of the chitosan films (longitudinal and cross-sections) were observed using an FEI Quanta 650 field emission scanning electron microscope (SEM). Prior to analysis, all samples were coated with gold. The images were taken at magnifications of 500x and 3,000x using an acceleration voltage of 1-2 kV under low vacuum conditions.

2.4.2. Structural properties

Attenuated total reflection (ATR) FT-IR spectra were acquired using a 6700 IR (Jasco, Essex, UK) spectrometer equipped with a DLaTGS detector, a high-throughput Single Reflection ATR with diamond crystal, accompanied with the Spectra Manager software (Jasco, Essex, UK). For each spectrum three scans were accumulated in the absorbance mode and recorded at 4 cm^{-1} resolution and 32 scans per sample, covering a range from 4000 to 400 cm^{-1}. Three spectra per sample were recorded and averaged in order to obtain the corresponding spectrum before further pre-processing. The original spectra were corrected with the aid of Spectra Manager software (V.2.15.01, JASCO, Great Dunmow, UK).

2.4.2. Physical properties

2.4.2.1. Thickness

Film thickness was determined using a hand-held micrometer at six randomly selected locations on each film.

2.4.2.2. Color

The CIE color parameters L^* (lightness), a^* (redness), and b^* (yellowness) of chitosan films were determined with a Chroma meter (CR-400, Konica Minolta, Japan) against a white standard color plate ($L^* = 97.59$; $a^* = 0.02$; $b^* = 1.79$) as a background. These values were then used to calculate the overall change in color (ΔE) according to the following equation (Eq. 1).

$$\mathbf{\Delta E = \sqrt{\Delta(\boldsymbol{L}^* - L)^2 + \Delta(a^* - a)^2 + \Delta(\boldsymbol{b}^* - b)^2}} \quad \mathbf{(1)}$$

where L, a, and b represented color values of the film samples.

2.4.2.3. UV–vis light barrier property

The light barrier property of the prepared films was measured by scanning each film with a PC-controlled double beam spectrophotometer (Shimadzu UV1800, Tokyo, Japan). Specifically, films were cut into strips with dimensions of 10 mm x 40 mm and then they were scanned directly at a wavelength range between 200 nm to 800 nm (Zhang, Han & Zhou, 2023).

2.4.2.4. Moisture content and water solubility

The moisture content and water solubility of the films were determined according to the methodology described by Zhang et al. (2022) with slight modifications. In particular, three specimens of each film (2 cm x 2 cm) were initially weighted (W_1) and then they were dried until constant weight (W_2) in an oven at 105 °C for 24 h. The dried films were immersed in 50 mL of ultrahigh purity water. The excess water above the film was carefully scraped away using filter paper. The undissolved films was dried at 105 ◦C for 24 h and they were reweighed (W_3). Finally, the moisture content (MC) and Water Solubility (WS) were calculated according to the equations 2 and 3, respectively. A triplicate of each test was performed.

$$MC(\%) = {(W_1 - W_2)}/{W_1}\ X\ 100 \qquad (2)$$

$$WS(\%) = {(W_2 - W_3)}/{W_2}\ X\ 100 \qquad (3)$$

2.4.2.5. Water vapor permeability

The water vapor barrier property of the films was determined gravimetrically as described previously (Zhang et al, 2019) with some modifications. Films were sealed on a test vessel containing 30 g sufficiently dried silica gel. Then, the test vessel was placed in a desiccator containing distilled water at 20 °C. The weight of the test vessel was recorded every 24 h for 6 days. Water vapor permeability (WVP) was calculated using the following equation (4) (Mouzakitis et al., 2022):

$$WVP = \frac{G*x}{A*\Delta P} \qquad (4)$$

where G is the initial slope of the weight gain of the cell versus time in, x is the film thickness (m), A is the film permeation area (m^2), and ΔP is the water vapor pressure difference between the two sides of the film, i.e. 2339 Pa at 20 °C (Zhang et al., 2019).

2.4.2.6. Mechanical properties

Tensile tests were carried out using a TA.XT plus Texture Analyser (Stable Micro Systems, Godalming, Surrey, UK) (Mouzakitis et al., 2022; Yong et al., 2019). The films were cut into strips (60 mm (length) x 10 mm (width)) which were then analyzed by a texture analyzer at a stretching rate of 60 mm/min The tensile strength and elongation at break of the films were calculated using the following equations (5 and 6):

$$\text{Tensile strength(Mpa)} = {}^{F}/_{x * w} \qquad (5)$$

$$Elongation\ at\ break\ (\%) = {}^{\Delta L}/_{Lo} \qquad (6)$$

where F is the stress of film at break (N), x is film thickness (mm), W is film width (mm); ΔL and L0 are the elongated and original lengths (mm) of the film, respectively.

2.4.2.7. Determination of the antioxidant activity of chitosan films

For the determination of the antioxidant activity of the prepared chitosan films, certain amount of the films (10 mg) were immersed into ultra-pure water for 24 h as described by Zhang et al. (2022). In the prepared solutions, The antioxidant activity of the prepared solution and the original extract was evaluated by examining the scavenging of the free radical DPPH (Loukri et al., 2020). DPPH· solution with no sample addition was used as control. DPPH radical scavenging activity (%RSA) was calculated through the following equation (7):

$$\%RSA=\frac{A_{515}^{t=0}-A_{515}^{t=30}}{A_{515}^{t=0}}\times 100 \qquad (7)$$

2.5. Statistical analysis

The Duncan test and one-way analysis of variance (ANOVA) were used for multiple comparisons by SPSS 29.0 software package. Differences were considered as statistically significant if p-value was < 0.05.

3. Results and discussion

In this study, seven novel chitosan films were formulated to study the effect of citric acid, β-cyclodextrin, and cherry pomace extract on the physicochemical and functional properties of produced films. Different tests were conducted on these films, and the results are presented below.

3.1. Structure and morphology of bilayer films

3.1.1. SEM

The study on the inner microstructure of the films could highlight the arrangement of the film components, which may explain the mechanical and barrier properties of the films (Talón et al., 2017). In **Fig. 1** and **2** the surface and cross-section images of the prepared chitosan films are presented. As illustrated in **Figs. 1a and 2a**, the Ch film presented some abnormalities in contrast to other reports (Wang et al., 2019a; Yong et al., 2019). The Ch film, which was prepared with acetic acid, showed a flat surface with small cracks and black spots, which may be related to the permeation of the glycerol (Jiang, Zong, Ma, Chen, , & Li, 2020). Also,in **Fig. 2a**, some damages appeared, which could be attributed to the presence of crystalline and ordered areas in the film matrix (Agarwal, Kóczán, Börcsök, Halász & Pásztory, 2021). In contrast, the replacement of acetic acid with citric acid contributed to a modification of the microstructure of the film. Based on **Figs. 1b and 2b**, the Ch+CA film exhibited a smoother and more compact matrix without any cracks compared to the control Ch film, which is attributed to the strong interaction between chitosan and citric acid (Zhang et al., 2022). As cyclodextrin was introduced in the film, the surface remained smooth without any cracks (**Fig. 1c**). However, as the concentration of the cyclodextrin increased, the roughness of the film was enhanced. In the cross-section, the Ch+CA+1.85β-cd (**Fig. 2d**) showed a rougher surface with small cracks compared to that of the Ch+CA+0.45β-cd film (**Fig. 2c)**. Cyclodextrin can interact with polymers chains and contribute to a more compact structure, as it can fill the gaps in the film matrix. However, the increase of the cyclodextrin concentration can contribute to the development of uneven surfaces with aggregates, due to the non-uniform dispersion of the film components (Bai et al., 2022; Khan, Wang, Shu, Zhang, & Liang, 2023; Zhang et al., 2023).

Based on the **Fig. 1 and 2**, the presence of the extract in the film matrix modified the microstructure of the films significantly. Specifically, the Ch+CA+WE film (**Fig. 1e**) showed a non-uniform surface with cracks compared to the Ch+CA one (**Fig. 1b**) with some aggregates in the cross-section **(Fig. 2f)**, which are related to the low miscibility of the film matrix components. The presence of the extracts in high quantities can modify the microstructure of the film due to limited interaction between anthocyanins and the film components and the aggregation of the extract compounds (da Silva Filipini, Romani, & Guimarães Martins, 2020; Nguyen, et al., 2020; Yang et al., 2022a). However, when β-cyclodextrin aqueous solution extracts were used, the microstructure of the film was improved. Cyclodextrin can develop inclusion complexes with anthocyanins from Cornelian cherry pomace (Loukri et al., 2022) and can facilitate the incorporation of the bioactive compounds in the film matrix (Guan, Li, Zhang & Xue , 2022). The film Ch+CA+0.45BCE showed a smooth and compact structure, which indicates the successfully development of chitosan films with Cornelian cherry pomace extract. However, as the concentration of the β-cyclodextrin increased in the extract, large aggregates were generated on surface and in the crossection, due to the low interaction between film components (Yang et al., 2022c).

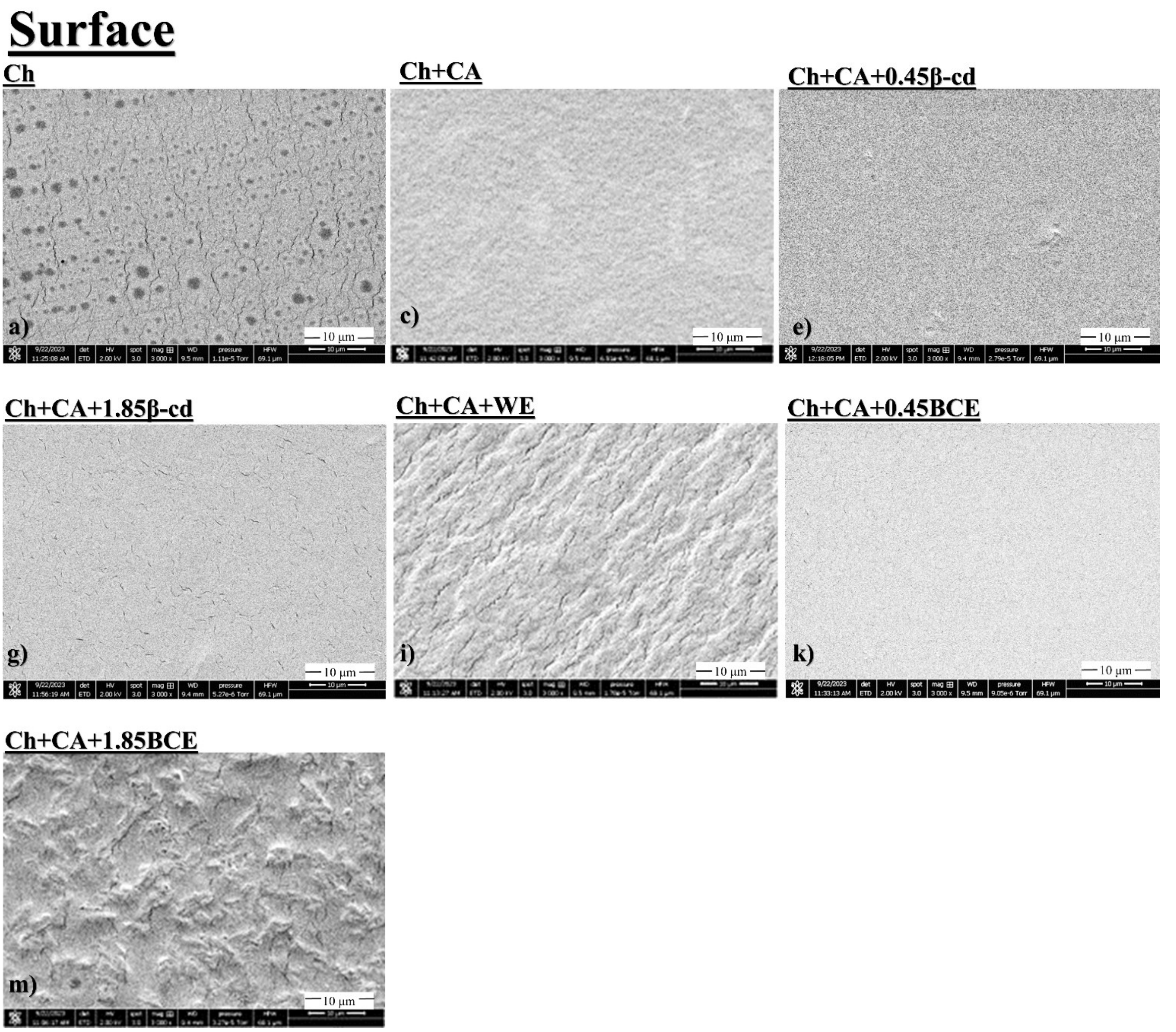


Fig 1. SEM micrographs of surfaces of Ch (a), Ch+CA (b), Ch+CA+0.45β-cd (c), Ch+CA+1.85β-cd (d), Ch+CA+WE (e), Ch+CA+0.45BCE (f) and Ch+CA+1.85BCE films (g).

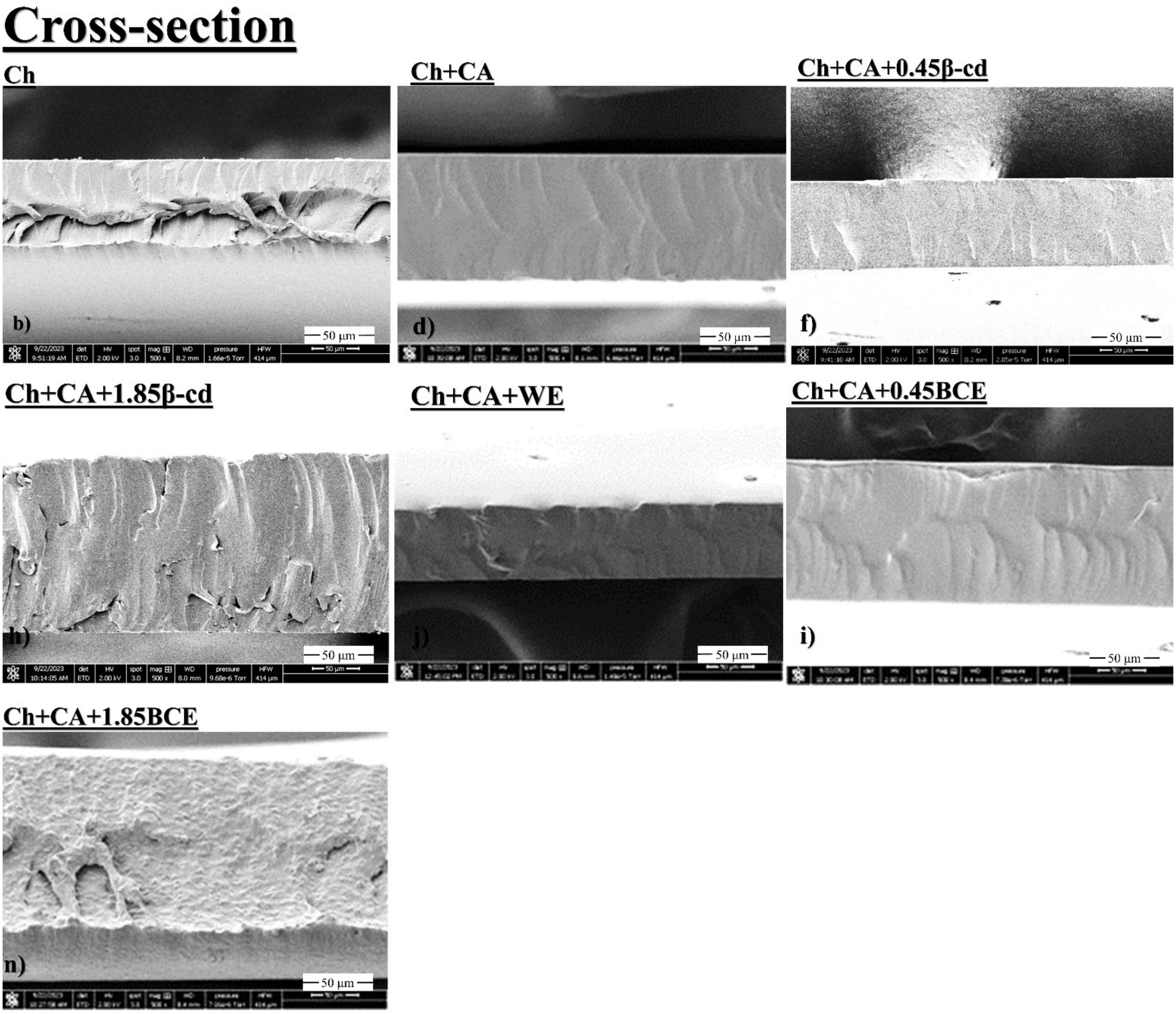


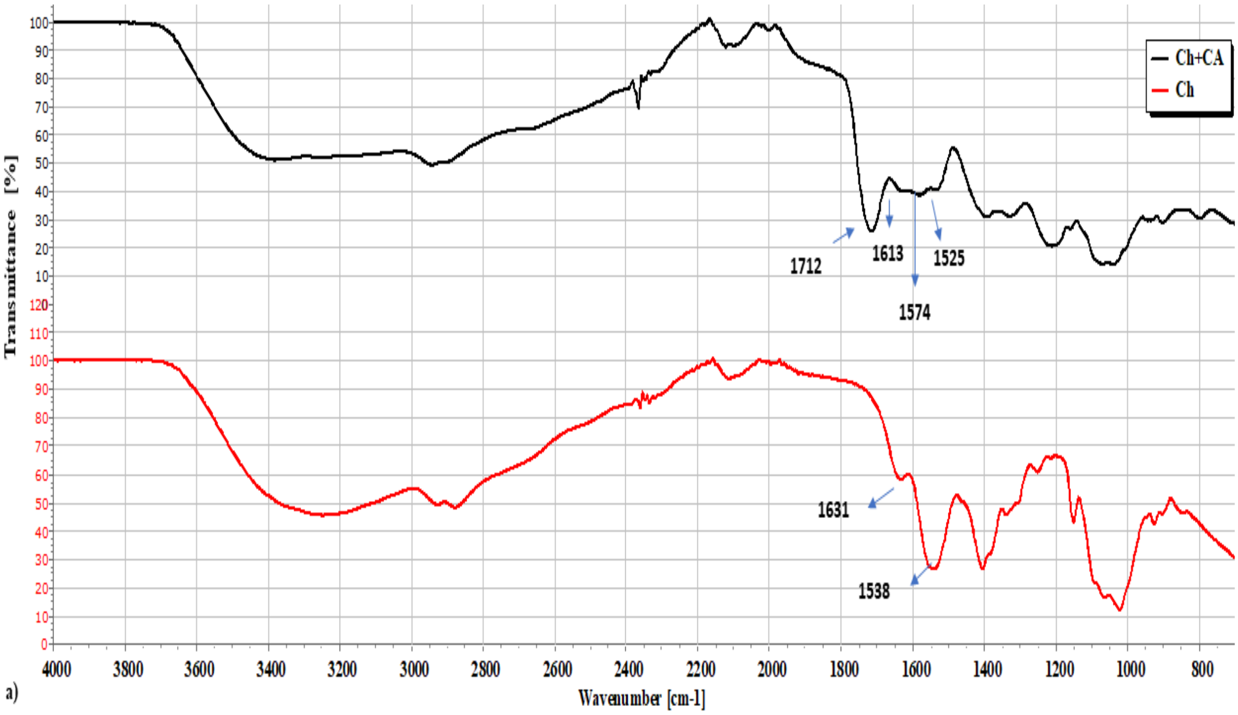
Fig. 2. SEM micrographs of cross-sections of Ch (a), Ch+CA (b), Ch+CA+0.45β-cd (c), Ch+CA+1.85β-cd (d), Ch+CA+WE (e), Ch+CA+0.45BCE (f) and Ch+CA+1.85BCE films (g).

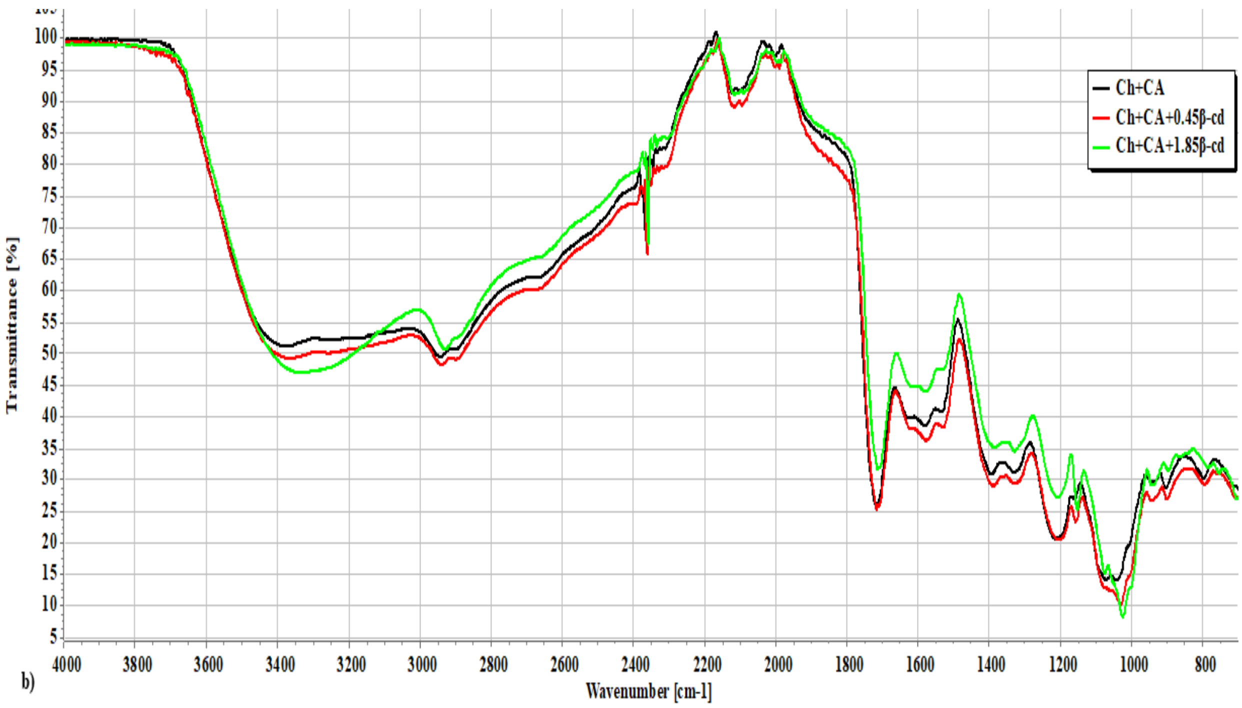
3.1.2. FT-IR analysis

FT-IR analysis was used to investigate the inter and intramolecular interactions between chitosan, citric acid, β-cyclodextrin and bioactives. In **Fig. 3a** the FT-IR spectra of chitosan films, prepared with the usage of different organic acid, is presented.

All samples showed a characteristic peak around 3300-3600 cm^{-1} which is attributed to stretching bonds of O-H and N-H bonds, and the double peak around 2900-2700 cm^{-1}, attributed to C-H symmetric bonds. Furthermore, the characteristic peak at 1631 cm^{-1} observed in the Ch film was attributed to the Amide I bond and the peak at 1538 cm^{-1} to the Amide II. The presence of Amide II bonds suggest that the amino groups of chitosan are in protonate form. The replacement of acetic acid with citric acid resulted in significant changes in the FT-IR spectrum. In particular, the peak of second Amide II had shifted at higher frequencies at 1574 cm^{-1} for Ch+CA spectra, which indicates that the protonated amine groups are limited. Citric acid contains three carboxylic groups with its pKa^1 (3.13) (Lakehal et al.,2019) being lower compared to that of acetic acid (pKa^1 = 4.77). Generally, as the pKa decreases, the interactions of chitosan and the acid increase. Therefore, the peak become broader and shifted at higher wavelength, due to strong interactions. Also, a characteristic peak around 1700 cm^{-1} appeared, which is attributed to the C=O bond of the free carboxylic groups of citric acid. Due to the low volatility of the citric acid, it may not be removed during drying and its characteristic peaks continue to appear in the spectra (Melro et al., 2021; Qiao et al., 2021; Sharmin et al., 2022; Zhang et al., 2022)

In this study, the effect of β-cyclodextrin on the properties of the chitosan- citric based acid film was also evaluated. Based on **Fig. 3b**, no new bands were observed between films with or without cyclodextrin, indicating that no chemical reactions occurred. The increase of β-cyclodextrin concentration from 0.45% w/v to 1.85% w/v seemed to enhance the peaks around 1100 and 1000 cm^{-1}, which is probably related to the stretching bonds of C-O-C. With the increase of cyclodextrin concentration the morphology of the area around 3300 cm^{-1} and also the intensity of the Amide I and II were changed, which may indicate the development of hydrogen bond between chitosan and cyclodextrin (Bai et al., 2022; Zarandona, Barba, Guerrero, de la Caba & Maté, 2020). When the water was replaced with the cherries pomace extracts **(Fig. 3c)**, the characteristic peaks of citric acid and β-cyclodextrin appeared in the FT-IR spectra, without extra peaks. The similarity of the spectra indicates that probably no covalent interaction existed between phenolic compounds and chitosan. Probably the characteristic bands of the phenolic compounds were not observed due to the overlapping into the existing bands or to the small quantity of the phenolic compounds (Agarwal et al., 2021).


Ch+CA
Ch
Transmittance [%]
1712
1613
1525
1574
1631
1538
Wavenumber [cm-1]
a)


Ch+CA
Ch+CA+0.45β-cd
Ch+CA+1.85β-cd
Transmittance [%]
Wavenumber [cm-1]
b)

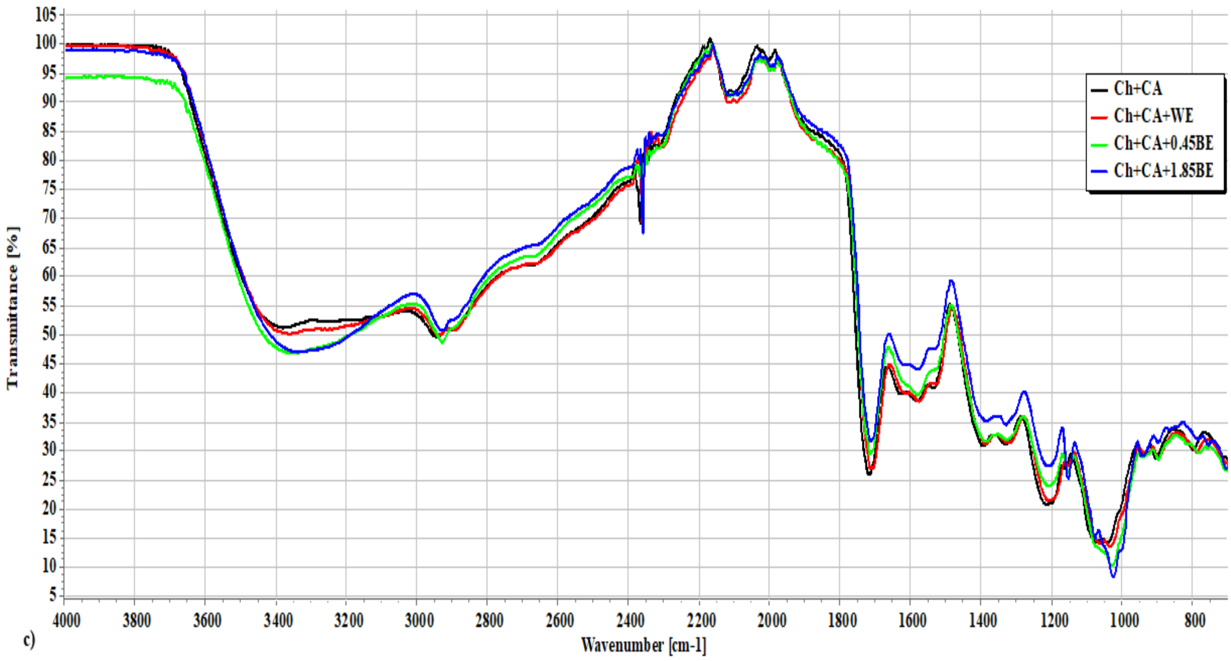


Fig.3. FTIR spectra of chitosan films (a) Ch and Ch+CA, (b)Ch+CA, Ch+CA+0.45βcd and Ch+CA+1.85 βcd and (c) Ch+CA, Ch+CA+WE Ch+CA+0.45BE and Ch+CA+1.85 BE.

3.2. Physical properties

3.2.1. Apparent color and optical properties

The UV- vis light protection of the films has received a great deal of attention in recent years. Exposure to UV–vis light can induce alteration to food properties such as color, taste, nutrition value and enhance oxidation of packaged food (Zhang et al., 2023). Therefore, the light-blocking properties of packaging films are very important for food preservation. The UV-vis spectra of the produced films were presented in **Fig. 4.** The replacement of acetic acid with citric acid, increased the transmittance of the film in a range of 200 to 300 nm, in contrast to findings of other researchers. For example, Uranga, Puertas, Etxabide, DueñasGuerrero& de la Caba. (2019) reported that in a gelatin-chitosan film, citric acid enhanced the UV-Vis blocking properties of the films due to its auxochrome ability. Furthermore, the introduction of cyclodextrin in the chitosan-citric acid based films seemed to affect the transmittance around 280-300 nm. Specifically, the use of low β-cd concentration seemed to enhance the UV-blocking ability of the Ch-CA film. However, the CH, Ch+CA, Ch+CA+0.45βcd and Ch+CA+1.85 βcd showed similar UV-vis spectra. In comparison with all samples, the addition of extract into the film matrix remarkably changed the light transmittance. As shown in **Fig. 4**, the use of the cherry pomace extract in the development of the edible film induced the reduction of the transmittance from 200 to 300 nm, indicating that the light barrier of chitosan-citric acid based films was enhanced. This reduction may be related to the presence of the anthocyanin's benzene rings and the phenolic compounds of the extract (Wang et al., 2019 b; Zhang, Han, & Zhou, 2023). Similar observations could have been obtained probably also using the cherry juice.

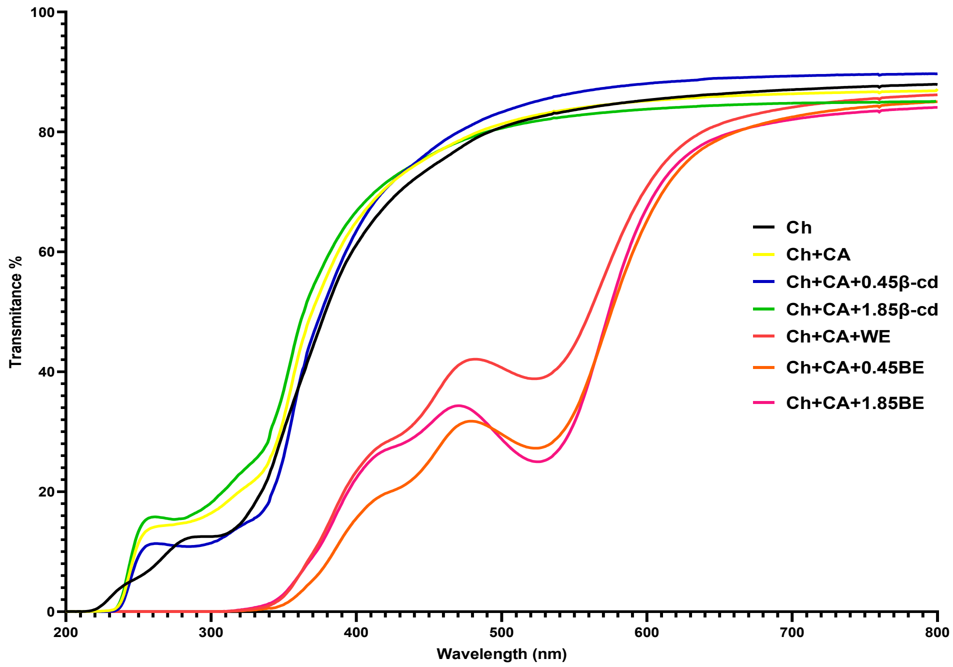


Fig. 4. The ultraviolet–visible light transmittance of the produced chitosan films with or without Cornelian cherry pomace extract.

Color and appearance of an edible film are important properties for the acceptance of the films by consumers. In **Table 2**. the L*, a*, b* and ΔE values for the prepared chitosan films are presented. The films that were prepared in the absence of the cherry pomace extract exhibited lower ΔE values ($p < 0.05$) compared to those prepared with the addition of the extracts, i.e. Ch+CA+WE, Ch+CA+0.45BE and Ch+CA+1.85BE. The higher ΔE values revealed the development of more colored films in accordance with the above mentioned changes of the UV-Vis light transmittance (Wang et al., 2019b). Specifically, the produced films were characterized by a decline of the L* parameter and an increase of the redness of the film. The change of color is linked to the presence of anthocyanins in the extract. The increase of the redness in the produced films may be related to the pH of the solution, as the final pH of the Ch+CA+WE, Ch+CA+0.45BE and Ch+CA+1.85BE film solutions is close to 3. In acidic pH values, anthocyanins presented in flavonyl cation form and the red color is dominant (Loukri et al., 2022; Ma, Ren, Gu, & Wang, 2017). Researchers have observed the development of different colors in chitosan films when they use extracts rich in anthocyanins from different sources. Despite the pH, the development of the final color is depended in the nature and the concentration of the anthocyanins in the plant extract (Kurek et al., 2018; Yong et al., 2019, Yong, Liu, Kan& Liu, 2022). All films showed a smooth surface, besides Ch+CA+1.85BE which showed some defects in the surface, probably due to the development of aggregates. Therefore, the combination Ch+CA+18.5BE was not further examined, as its appearance contrasted with the optical principles of edible films.

Table 2. Color parameters including L*, a*, b* and ΔE and the optical appearance of chitosan in the presence or absence of Cornelian cherry pomace extract.

Sample	L*	a*	b	ΔE	
Ch	91.65 ± 0.20^{d*}	-2.64 ± 0.29^{a}	14.43 ± 0.84^{a}	14.42 ± 0.99^{a}	
Ch + CA	92.34 ± 0.62^{d}	-2.5 ± 0.26^{a}	13.97 ± 2.12^{a}	13.50 ± 2.2^{a}	
Ch+CA+0.45β-cd	91.73 ± 1.02^{d}	-2.70 ± 0.16^{a}	16.32 ± 2.11^{a}	14.54 ± 0.58^{a}	
Ch+CA+1.85 β-cd	92.24 ± 0.54^{d}	-2.48 ± 0.36^{a}	13.89 ± 0.81^{a}	13.76 ± 0.41^{a}	
Ch+CA+WE	67.28 ± 0.96^{c}	27.55 ± 0.87^{b}	31.73 ± 1.58^{b}	50.72 ± 1.92^{b}	
Ch+CA+0.45BE	61.05 ± 2.6^{b}	41.36 ± 0.68^{c}	33.86 ± 1.06^{c}	60.92 ± 2.44^{c}	
Ch+CA+1.85BE	58.38 ± 2.6^{a}	35.32 ± 1.13^{d}	35.40 ± 0.77^{c}	66.82 ± 2.51^{d}	

*Different letters in the same column indicate significant statistical differences between samples (p value < 0.05), according to Duncan's test.

3.2.1. Thickness, moisture content and solubility index

The thickness of the films is an important property, as it significantly impacts various physical characteristics, including opacity, mechanical properties, and water vapor permeability**.** Based on **the results of Table 3**, the thickness of the films was affected by the different treatments, since significant differences were observed (p-value<0.05). The replacement of acetic acid with citric acid increased the thickness of the film. The presence of citric acid, may have enhanced the solid content and the interaction of the polymers, resulting in a denser matrix (Wu et al., 2019). In addition, the introduction of cyclodextrin in the chitosan-citric acid based films was found to enhance their thickness compared to the chitosan-citric acid film (Ch+CA). However, the increase of β-cyclodextrin concentration from 0.45 w/v to 1.85 w/v did not have statistical important effect in the parameter (p-value >0.05). The thickness of the film is connected positively to the content of the polymers which participated in the films' development (Sha, Yuan, Cui, Zhao, & Wang, 2022). Furthermore, the introduction of the cornelian cherry pomace extract in the film increased the thickness of their respectively chitosan-citric acid based films, which is in accordance with previous reports (da Silva Filipini et al., 2020). Phenolic compounds which existed in the extract may interact with chitosan molecules and contribute to the development of a denser matrix (Kadam, Singh & Gaikwad, 2021; Yong et al., 2019). The Ch+CA+0.45BE had reached higher thickness (p-value<0.05) compared to the Ch+CA+WE, probably to the presence of the phenolics compounds and β-cyclodextrin in the film matrix.

The MC is an important property of composed films, as they are related to the water resistance of the materials. Based on **Table 3**, the Ch exhibited the higher MC compares to other films. The use of the citric acid in the film development reduced (p-value<0.05) the water content of the films. In addition, the introduction of β-cyclodextrin in chitosan-citric acid based films contributed to a significant reduction of the parameter compared to the chitosan-citric acid film (Ch+CA) when incorporated into the higher quantity. The moisture content of the films is controlled by the presence of the hydrophilic groups, which can interact with water molecules (Agarwal et al., 2021). According to (Sha et al., 2022), the increase of concentration of the β-cyclodextrin in pregelatinized cassava starch film contributed to the reduction of water content due to the development of denser matrix. Probably the interaction of chitosan, citric acid, glycerol and β-cyclodextrin, decrease the free amino and hydroxylic groups, thus reducing the interaction with water molecules (Bai et al., 2022). However, the developed films with the use of extracts, reached higher values compared to their respectively without extract chitosan-citric acid based films. Generally, phenolic compounds interact with chitosan and decrease the free sides for the development of hydrogen bounds with water molecules. The increase of the MC may can be attributed to the development of intermolecular bonds among phenolic compounds, hydroxyl and amino groups of chitosan with water molecules (Eze, Jayeoye & Singh, 2022). However, all produced films had significantly lower moisture content compared to the control one.

Table 3. Thicknesses, MC and WS of the produced chitosan films with or without Cornelian cherry pomace extract.

Sample	Thickness (μm)	MC (%)	WS (%)
Ch	69.4 ± 5.4 ^{a}	32.4 ± 0.8^{d}	18.1 ± 1.1^{a}
Ch + CA	121.7 ± 10.1 ^{b}	16.8 ± 1.2^{cb}	18.2 ± 1.0^{a}
Ch+CA+0.45β-cd	149.0 ± 6.4^{c}	15.4 ± 0.9^{b}	20.8 ± 2.6^{a}
Ch+CA+1.85 β-cd	186.1 ± 5.4^{d}	13.1 ± 1.1^{a}	29.0 ± 2.6^{b}

Ch+CA+WE	161.7 ± 15.9[c]	18.1 ± 0.6[c]	18.6 ± 2.6[a]
Ch+CA+0.45BE	185.56 ± 8.6[d]	18.1 ± 0.3[c]	19.8 ± 0.4[a]

*Different letters in the same column indicate significant statistical differences between samples (p value < 0.05), according to Duncan's test.

A significant attribute of a film is WS, which provides information about the water resistance of the films. In contrast to MC, the WS statistically increased only when β-cyclodextrin was used (**Table 3**). Bai et al. (2022) observed that increase of inclusion complex of β-cyclodextrin-epichlorohydrin oligomer with essential oils in chitosan film enhanced WS and decreased MC. This effect attributed to the reduction of the hydrogen bonds and to enhancement of the hydrophilicity (Bai et al., 2022). Films enriched with extract had higher WS compared to the chitosan-citric acid based films without extracts. However, the solubility values did not differ significantly ($p > 0.05$) between treatments. The Ch+CA+0.45BE had the higher WS compared to all treatments. The presence of β-cyclodextrin and phenolics compounds in film matrix may have weakened the intermolecular interaction of the polypeptide chains, making it easier the release of water soluble compounds (Bai et al., 2022; Wang et al., 2019b). The increase of WS of packaging material is favorable for the development of soluble packages for pre-weighted portions of food, which require dilution in water for consumption (da Silva Filipini et al., 2020).

3.2.2. Water vapor permeability

WVP is a crucial property for the application of edible films, as it describes the moisture transport from environment to packaged products. The WVP of edible films are influenced by many factors, such as the thickness, the integrity of the film, the hydrophilicity, the presence of crystalline and the polymeric chain mobility (Zibaei et al., 2021). **Fig. 5** showed the WVP of the produced films. The introduction of citric acid in the chitosan matrix enhanced (p-value < 0.05) the WVP compared to Ch. The use of high quantities of citric acid may have a plasticizing effect in the film properties (Wu et al., 2019). Also, when cyclodextrin was used during the development of the chitosan film, the WVP was remarkably increased compared to the chitosan-citric acid film (Ch+CA). However, increasing β-cyclodextrin concentration from 0.45 to 1.85 w/v, the WVP was significant decreased (p-value<0.05), but the value was still higher compare to acetic film. Sun et al. (2014) reported that the increase of the cyclodextrin inclusion complexes in the chitosan film enhanced the WVP, due to the reduction of intermolecular interactions between polymers and increase the free volumes. A study conducted by Zou et al. (2021) showed that the introduction of a small increase of cinnamaldehyde/β-cyclodextrin complex (0.5% w/v) in high amylose corn starch/ konjac glucomannan film enhanced the WVP, however the further increase of the complex contributed to the reduction of this property. The increase of the interaction of the polymers, contributed to the development of a compact structure with low chain mobility which reduced the diffusion and movement of water (Zou et al., 2021).

Finally, when the extracts were used as solvents, the values of the WVP were higher compare to their compatibly chitosan-citric acid based films. da Silva Filipini et al. (2020) observed when a 10% of solvent substituted by *Syzygium cumini* skins extract, the WVP was significant decreased. However, when the concentration of the extract was increased the permeability of the chitosan films had enhanced due to change the arrangement of the polymers. The presence of phenolic compounds may potentially enhance the breakdown of the network structure and increase the mobility of the polymer chains, thus facilitating the diffusion of water molecules (Sogut & Seydim, 2018).

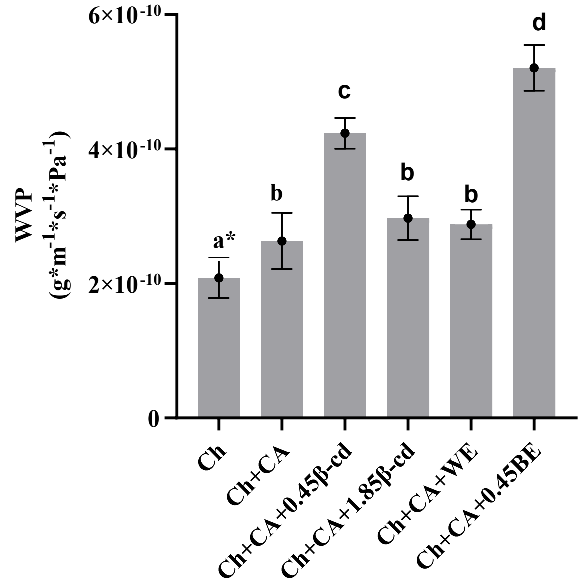


Fig. 5. Water vapor permeability (WVP) of chitosan films with or without Cornelian cherry pomace extract. *Different letters in the same column indicate significant statistical differences between samples (p value < 0.05), according to Duncan's test.

3.2.3. Mechanical properties

The mechanical properties of the films are crucial and play a significant role in evaluating packaging materials for the transportation and storage of packaged foods (Qian, Zhang, Xu & Zhang, 2022). The tensile strength and elongation at break of the blend films are shown in **Fig. 6.** The use of citric acid as dilution media contributed to the decrease of the tensile strength and increase of the elongation. The same trend was observed by others (Melro et al., 2021; Qiao et al., 2021). The strong interaction between chitosan and citric acid contribute to the destruction of interchain and intrachain bonds between polymers. The addition of citric acid in high amounts could lead to residual citric acid, which could act as a plasticizer. The presence of the residual citric acid reduces the packed structure of the film and increases the flexibility of the film (Qiao et al., 2021; Sharmin et al., 2022). The use of the cyclodextrin in film preparation seemed to the influence the mechanical properties of the films. The increase of β-cyclodextrin from 0.45 to 1.85 % w/v enhanced the tensile strength compared to the chitosan-citric acid film (Ch+CA) (**Fig. 6**), due to the enhancement of formation of structure (Sha et al., 2022). Conversely, Bai et al. (2022) observed that an increased presence of the inclusion complex within the film matrix led to a reduction in tensile strength. This reduction occurred due to the weakening of interactions among chitosan molecules. As it can be seen in **Fig. 6**, the elongation at break increased when 0.45 w/v β-cyclodextrin used for the development of the film compared to the chitosan-citric acid film (Ch+CA). However, the further increase of the cyclodextrin concentration at 1.85 % w/v reduced the elasticity. This effect may be related to the filler effect of the cyclodextrin which reduces films stretchability. The increase in cyclodextrin concentration may have enhanced the interaction between polymers and decrease chain movement (Bai et al., 2022; Sha et al., 2022; Yang et al. , 2022b).

Finally, when extracts were introduced into the matrix, the tensile strength appeared to remain unchanged, while the elongation at break decreased in comparison to the respective chitosan -citric acid based films that did not contain extracts. Nuegen et al. (2020), observed that increasing the *Sonneratia caseolaris* (L.) Engl. leaf extract from to 1 to 3% in chitosan films decreased the elongation at break of the films. Phenolic compounds have the ability to interact with chitosan by forming hydrogen bonds, which result in the formation of aggregates. These aggregates, as reported by Nguyen et al. (2020), subsequently reduced the mobility of polymer chains. Also, the development of crystal forms of phenolic compounds in the film matrix could contributed to the reduction of stretchability (Kurek et al., 2018).

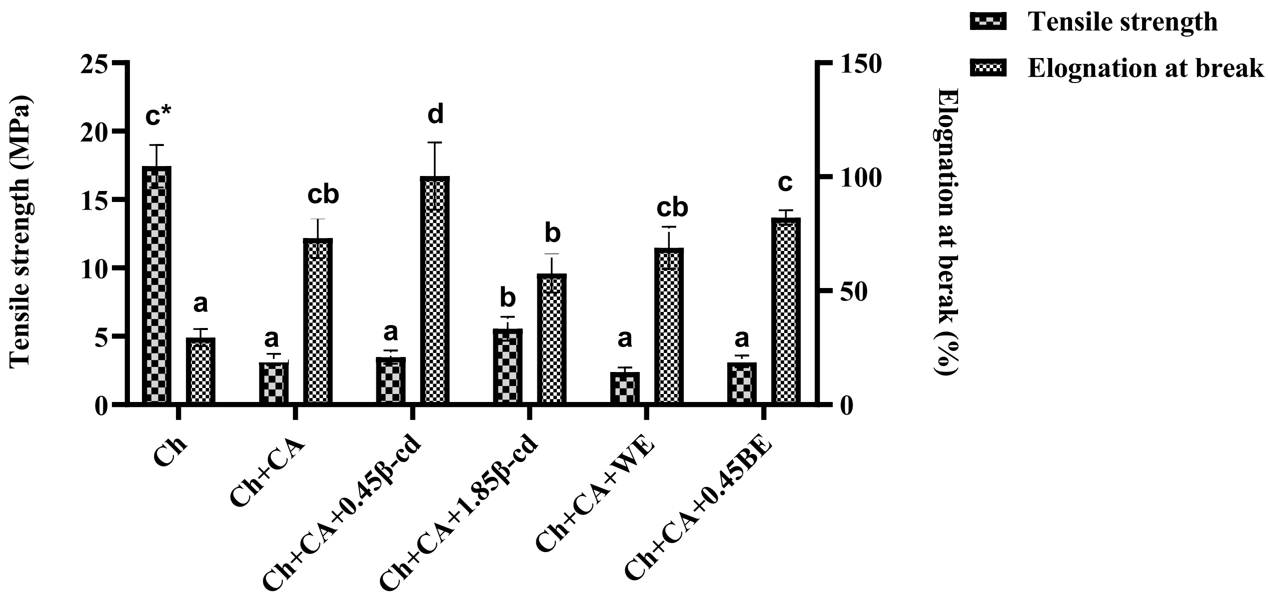


Fig. 6. Tensile strength and elognation at break of chitosan films with or without Cornelian cherry pomace extract. *Different letters in the same column indicate significant statistical differences between samples (p value < 0.05), according to Duncan's test.

3.3. Antioxidant activity tests

Chitosan, apart from its antimicrobial activity, also exhibits antioxidant activity, due to the presence of free amino groups which interact with free radicals (Kurek et al., 2018). The fortification of the edible films with bioactive compounds can enhance the antioxidant and antimicrobial properties of the films and also their preservation role. The antioxidant activity of the prepared films is illustrated in **Fig. 7**. There was no significant difference in antioxidant capacity of the films with or without citric acid ($p > 0.05$). During film formulation, oxidation phenomena and interaction with other components could have occurred, which can reduce the final influence of the citric acid on the antiradical activity of the film (Bonilla, Talón, Atarés, Vargas& Chiralt, 2013). Also, the incorporation of the pure β-cyclodextrin in the film matrix was not found to affect the antioxidant activity of the chitosan-citric acid film (Ch+CA). However, the addition of Cornelian cherry pomace extracts significantly ($p<0.05$) enhanced the antiradical activity of the prepared chitosan-citric acid based films. Indeed, both the aqueous and the b-cyclodextrin extracts that were used for the preparation of the films, showed similar DPPH antiradical activity (WE: 2.55 ±0.22 mMTRE and BE2.96 ±0.28 mMTRE, The Ch+CA+0.45BCE had a higher antioxidant activity compared to Ch+CA+WE, which may be related to the presence of the phenolic compounds and probably to the protective role of β-cyclodextrin during formation. The positive effect in antioxidant activity by incorporation of extracts in the films formulation has been previously reported (da Silva Filipini et al., 2020; Musso Salgado & Mauri, 2019). The development of active films has the potential to protect food systems from oxidation reactions and prolong the shelf-life of food products.

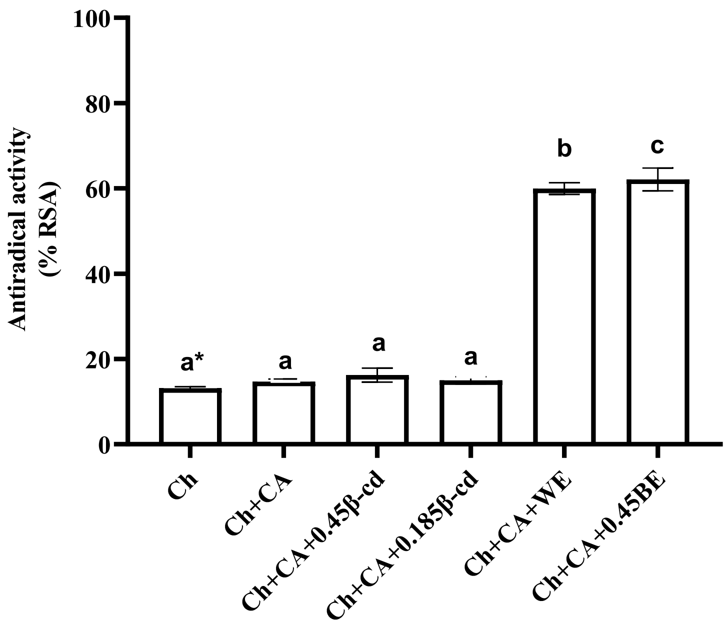


Fig. 7. DPPH antiradical activity of the produced films with or without cornelian cherry pomace extract. Different letters in the same column indicate significant statistical differences between samples (p value < 0.05), according to Duncan's test.

4. Conclusion

Citric acid and β-cyclodextrin were investigated as potential agents for modifying the properties of the films. The combination of bioactive compounds, citric acid and cyclodextrin, contributed to the development of a film with high elasticity, low moisture content, increased solubilization index and antioxidant activity. However, the WVP was higher compared to other films, which hinders the use of the film in products with high water sensitivity. The presence of bioactive compounds in the final mixture modified the color properties, enhanced the light barrier properties and increased the antioxidant properties of the films. The proposed method holds significant potential for developing biodegradable packaging films for applications in the food industry. These materials can be utilized for developing innovative and environmentally-friendly, intelligent and active packaging materials.

Declaration of competing interest

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

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