



Preparation of chitosan films plasticized by lauric and maleic acids

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ABSTRACT

The energy crisis and environmental concerns have increased interest in natural polymers, and the bio-sourced materials field is experiencing rapid growth. A useful alternative to conventional plastic packaging manufactured from fossil fuels is packaging constructed of biodegradable polymers. Consideration has been given to the instrumental methods for examining modifications to the chemical composition and characteristics of modified chitosan. The molecular weight and the kind of plasticizer present in these materials are the two primary variables influencing their usability and performance. This study set out to physically blend chitosan with two different acids, lauric and maleic, to enhance chitosan cast films' physical and mechanical properties. Different plasticizer ratios appeared to have little effect on the various properties of the chitosan cast films. Examining the obtained films by FTIR implies that chitosan's native structure was unchanged. The films prepared had more flexibility and better solubility than those made with un-plasticized chitosan. It was evident from an analysis of the mechanical properties of the films that both acid plasticizers enhanced the mechanical properties of the chitosan.

1. Introduction

The interest in natural polymers has grown as a result of the energy crisis and environmental concerns, and the field of bio-sourced materials is currently expanding quickly. In this situation, the industry must look for new sources of organic, environmentally friendly, and biodegradable polymers to replace those derived from petroleum. Polysaccharides in this area have enormous potential for use in active and intelligent packaging, smart textiles and biomedical devices, environmental remediation, and other applications. Chitosan is a special cationic polysaccharide with an excellent

affinity for various surfaces and outstanding cosmetic properties, even when left unaltered. It is a naturally occurring cationic copolymer [1]. This biopolymer, which is abundant in nature (the second one after cellulose), holds much promise for various uses. It is a highly renewable, biodegradable, environmentally friendly, and non-toxic polymer. Indeed, chitosan has been successfully used as a scaffold for biomedical applications, water engineering, treatment, the food industry, films, coatings, and construction fields. The functionalization of its chemical structure often enhances its characteristics until it obtains properties equivalent to synthetic products [1]. The development of chitosan-based materials has attracted much attention

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due to their great qualities, such as, nontoxicity, biodegradability, biocompatibility, antibacterial properties, and biofunctional characteristics, not only in the biomedical sector but also in the field of food contact materials. The new or improved properties of chitosan would be obtained through the chemical modification of its structure via the blending or attaching of various chemicals. Therefore, chitosan does not present problems of handling and disposal that may be encountered with some of its synthetic counterparts [2]. Chitosan is a promising material based on its chemical modifications as dye-removing agents and metal ion adsorbents. Recently, the progress on chemical modifications of chitosan has been quite rapid, and we are confident that a more extensive range of applications of chitosan derivatives could be expected shortly [3, 4]. In the plastics sector, plasticizers have long been a popular element [5]. Examples of its numerous applications include packaging, consumer goods, medicines, structures, and construction [6]. However, the industry is moving away from phthalate-based plasticizers and toward bio-based plasticizers due to environmental and health concerns [7]. Low cost per volume, low volatility, diffusivity, low specific gravity, good miscibility, and strong intermolecular interactions between the plasticizer and the polymer resin are all desired properties of plasticizers. A well-plasticized product should be flexible at low temperatures, have a low elastic modulus, a low glass transition temperature, and have good tensile elongation but low tensile strength [8]. Physical blending is a practical and important method for altering chitosan to serve various applications. Chitosan-based films' structural and physical characteristics have been extensively researched for use in biomedical and other applications [9,10]. When polymer chains separate from one another, plasticizers fill the intermolecular spaces between them. This reduces chain retraction and increases free volume, enabling polymer chains to move more freely [11]. The chitosan and plasticizer hydrogen bonding interaction [12,13] regulates

the mechanical and physical characteristics of the films. The physically blended plasticization of extracted chitosan with lauric acid and maleic was carried out in this work. It also focuses on the possible changes in molecular structure and mechanical and water solubility properties to see if they can produce appropriate chitosan films for packaging, which is a potential application for chitosan.

2. Experimental

2.1. Reagents and Materials

Chitosan was obtained by the deacetylation process of chitin extracted from local shrimp shell waste as described in the literature [14,15]. It had a viscosity average molecular weight of 2.702×10^5 g per mole as determined by the viscosity technique and a deacetylation degree of 80%. The acetic acid ($\text{CH}_3\text{CO}_2\text{H}$; pure $\geq 99\%$; CAS No.: 64-19-7), Lauric acid ($\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$. CAS No.: 143-07-7) and maleic acid ($\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$, MDL Number: MFCD00063177; PubChem ID: 24896549, CAS No.: 99110-16-7) used as plasticizers and acetic acid as a solvent were purchased from Sigma-Aldrich Company and utilized without further treatment. The tris-maleate buffer and sodium maleate buffer make of maleic acid and can be used for the pretreatment of poplar tracheid cell walls for the spectroscopic analysis of lignin.

2.2. Instruments

An FTIR-8101M Shimadzu spectrometer in the $4000\text{--}400\text{ cm}^{-1}$ range was used to investigate the chemical structures of the unplasticized and chemically plasticized chitosan films. The mechanical properties (tensile strength, Young's modulus, and %elongation at break) of the unplasticized chitosan and their plasticizer blend films were measured in the tensile mode (speed 5 mm min^{-1}) with a BTI-FR2.5TN.D14 (ZwickRoell, Germany) mechanical testing machine. The standard test method (ASTM D882-10) for tensile properties of thin plastic sheeting and films was used to determine the mechanical properties of the plasticized and unplasticized chitosan films in the

form of stripes of 20 x 2 mm. This test method covers the determination of tensile properties of plastics in the form of thin sheeting and films (less than 1.0 mm (0.04 in.) in thickness).

2.3. Preparation of the chitosan films

The unplasticized chitosan film was prepared by the solvent evaporation method by dissolving 1.0 g of chitosan in 100 ml of 2% (v/v) acetic acid solution under stirring at ambient temperature for 24 h. Then, it was poured into a leveled Petri dish of 50 mm in diameter. The film was removed from the dish, dried for 12 hours at 45°C, and then stored before determining its structural, physical, and mechanical properties [16]. In the same procedure, plasticized chitosan films with different ratios of various acid plasticizers were prepared, as shown in Table 1.

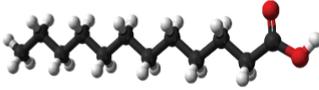
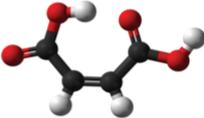
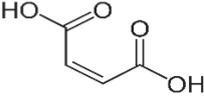
2.4. Film solubility

The amount of dry matter in the film that dissolves in water is used to calculate the solubility of the film. The solubility of the films was evaluated using previously described techniques with some changes [17]. In a nutshell, the films were divided into 2 cm × 2 cm squares and entirely dried before being stored. The films were weighed repeatedly until a stable weight that matched the fully dried films was attained; this weight was then used as the initial dry weight. The films were stirred at 25 °C for 24 hours while submerged in a glass beaker in 50 ml of deionized water. After being taken out of the beakers, the films were dried at 105 °C until they attained a constant weight. This quantity served as the final dry weight. The solubility percentage was calculated using equation 1 [18].

$$\text{Water Solubility (\%)} = \frac{\text{Initial Dry Weight} - \text{Final Dry Weight}}{\text{Initial Dry Weight}} \times 100$$

(Eq: 1)

Table 1. Plasticizers used and their ratio to Chitosan

Plasticizer	Chemical Structure	Chitosan: Plasticizer ratio
<u>Lauric acid</u>	 <chem>CH3(CH2)9CH2COOH</chem>	1:1, 1:2, 1:3, 2:1
<u>Maleic acid</u>	 	1:1, 1:2, 2:1

3. Results and Discussion

3.1. Cast film formation and appearance

The films were easy to peel from the cast Petri dish and simple to handle and treat further. The cast films were transparent, uniform, thin, flexible, and manageable.

3.2. FTIR characterization of unplasticized Chitosan films

Figure 1(black) displays the spectrum of the unplasticized chitosan film produced by casting a 2% acetic acid solution after it was removed from the Petri plate and before storage. The distinctive features of the chitosan spectrum in this study are analogous to those in other investigations [19,20]. Pure Cs exhibit characteristic polymer base-state peaks, including those at 1037 cm^{-1} from the vibration of C-O groups, 1562 cm^{-1} from NH bending, and 1654 cm^{-1} from C=O stretching (amide I) $\text{O}=\text{C}-\text{NHR}$. The stretching vibration of free hydroxyl and the asymmetrical and symmetrical stretching of the N-H bonds in the amino groups

are correlated with the peaks between 3610 and 3000 cm^{-1} that are present in all of the films under examination [21]. The bands at 2912 and 2843 cm^{-1} indicate the vibrations of the aliphatic C-H [22].

3.3. FTIR investigation of Cs-lauric acid blended films

Figures 1 illustrate the usual lauric acid peak, which occurs between 2928 and 2844 cm^{-1} [23]. The amide II band for the C-O stretch of the acetyl group is represented by the band at 1654 cm^{-1} , while the band represents the N-H stretch by the band at 1597 cm^{-1} . The linked C-O stretch of the glucosamine residue is represented by the skeletal vibration at 1072 cm^{-1} , and the asymmetric C-H bending of the CH_2 group is indicated by the band at 1377 cm^{-1} [24]. The bands at 2916 cm^{-1} and 2850 cm^{-1} , respectively, reflect the stretching vibrations of CH_2 and CH_3 , whereas the band at 1753 cm^{-1} represents the stretching vibrations of C=O [25,26]. The band between 1750 and 1700 cm^{-1} represents the carbonyl C=O stretching.

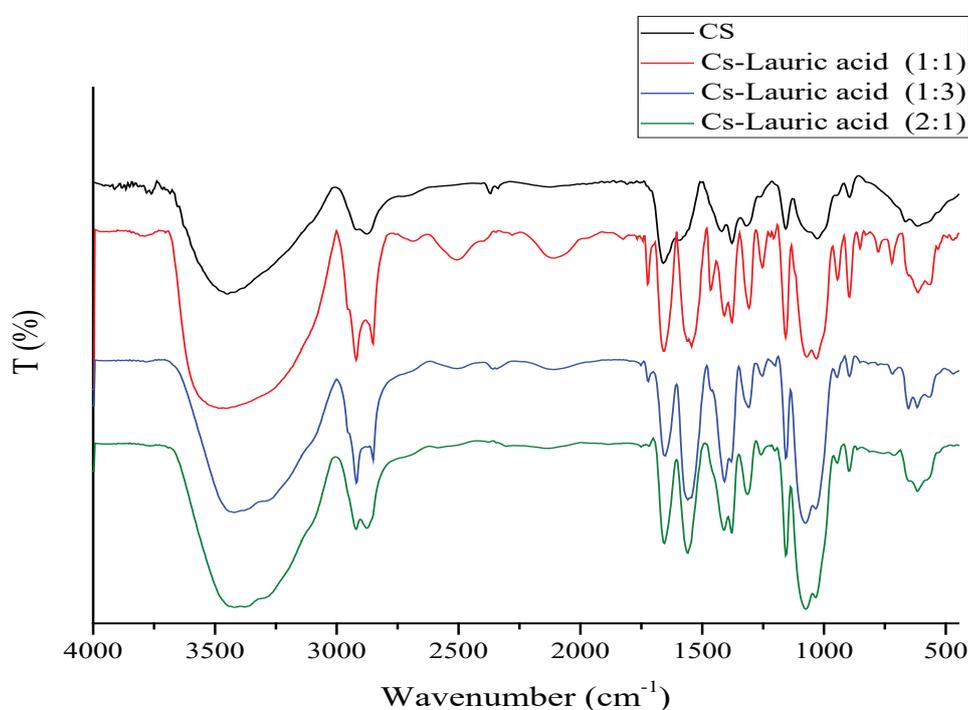


Fig. 1. FTIR spectra of Cs-lauric acid films

3.4. FTIR examination of Cs-maleic acid blended films

The FTIR spectra of the physical blend of chitosan with maleic acid films are shown in Figure 2. The spectra exhibited a peak in the 3500-2500 cm^{-1} , which widened due to the OH groups of both diacids combining chitosan with each diacid individually. This suggests that integrating the two materials raised the proportion of hydroxyl groups rather than changing the type of functional groups in the backbone complex [27,28]. The outcome demonstrated that maleic acid successfully interacted with chitosan's amine group. Additionally, the diacid C=O band at 1701 cm^{-1} [29] is present. Similar to this, the contributions of both diacid C-O bonds led to a wider chitosan C-O absorption at 1180 cm^{-1} . Creating an amide link between maleic acid and the chitosan amine group is responsible for the remaining spectrum alterations.

At 1708 cm^{-1} , the carbonyl C=O stretching

absorption became visible. The literature claims that pure diacid has two C=O peaks around 1700 cm^{-1} and 1750 cm^{-1} , respectively, and stands for free and hydrogen-bonded carboxylic acid groups [30]. The peak at 1750 cm^{-1} vanished after the chitosan reaction, and there were no additional peaks in the 1735 cm^{-1} region, indicating that esterification did not occur. According to a literature review on maleic acid amides, the cyclic amide analog emerged around 1770 cm^{-1} , but the acyclic amide displayed classic C=O absorption near 1620 cm^{-1} [31]. The cyclic structure cannot exist since there are no peaks in the 1770 cm^{-1} area of the chitosantric acid spectra. Examining peaks in the 563–675 cm^{-1} range proves that chitosan's native structure was unchanged. According to Mima et al. [32], these peaks are sharpest for 99 percent deacetylated chitosan and gradually fade away as acetylation increases (amide production), and this is the case here because the extracted chitosan used had about 81% degree of deacetylation.

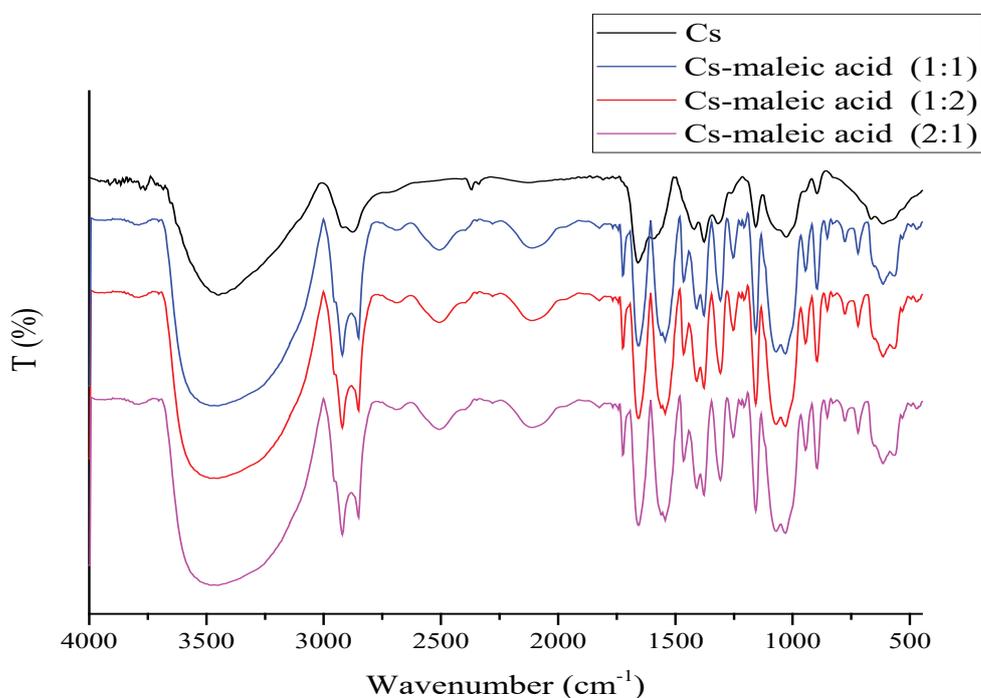


Fig. 2. FTIR spectra of Cs-maleic acid films.

3.5. Tensile properties of Chitosan films

Especially for single-use packaging when the material is stretched during use owing to continuous wear and tear, flexibility is an important property of plastics. The mechanical properties of synthetic bioplastics must be precisely studied to define their range of uses. Polymer films' strength and elasticity can be determined through mechanical testing. The amount to which the film subjected to the applied pull force reacts is defined by tensile strength measurements. A plasticizer is a substance that, when added to polymer materials, increases their elasticity. This plasticizer is necessary to get around the stiffness of films made with chitosan. The inter-polymer bond between chitosan polymer chains and plasticizers may become brittle and break. The plasticized and unplasticized chitosan films were tested in dry states according to ASTM D882-2010 "Standard Test Methods for tensile properties of thin plastic sheeting and films,"

3.6. Tensile properties of plasticized Cs: lauric acid films

The effect of the addition of lauric acid plasticizer resulted in a decrease of the tensile strength, Young modulus, and % elongation at break with an increasing amount of lauric acid, which was shown in Figures 3, 4, and 5. This leads to the indication that a level of interfacial adhesion may be lacking between chitosan and lauric acid. Adorna et al [33] obtained the same line of results. This happened because too many lauric acid plasticizer molecules were in a separate phase outside the phase of the plasticized blend. This suggests that there may not be enough interfacial adhesion between chitosan and lauric acid. The intermolecular force between the chains is reduced because of the conditions. It is concluded that the decrease in the measured mechanical properties of chitosan plasticized with increasing lauric acid plasticizer amount is in good accord with other reported results [34,35]. Their results were explained due to the plasticizer's effect on the promotion of intermolecular forces, thus lowering the high intramolecular forces inside the plasticized polymer mix chains.

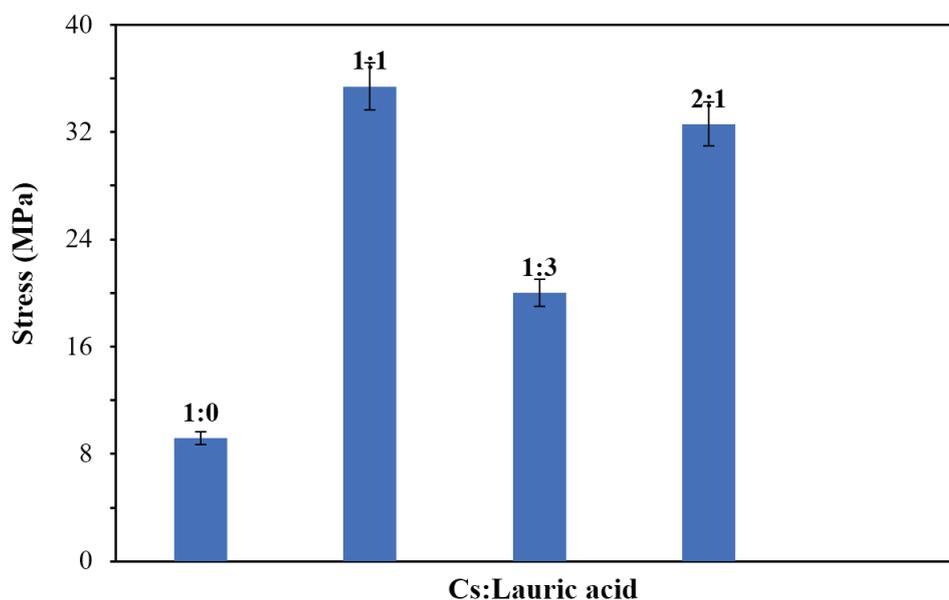


Fig. 3. The effect of Cs: Lauric acid ratios on the tensile strength of plasticized chitosan.

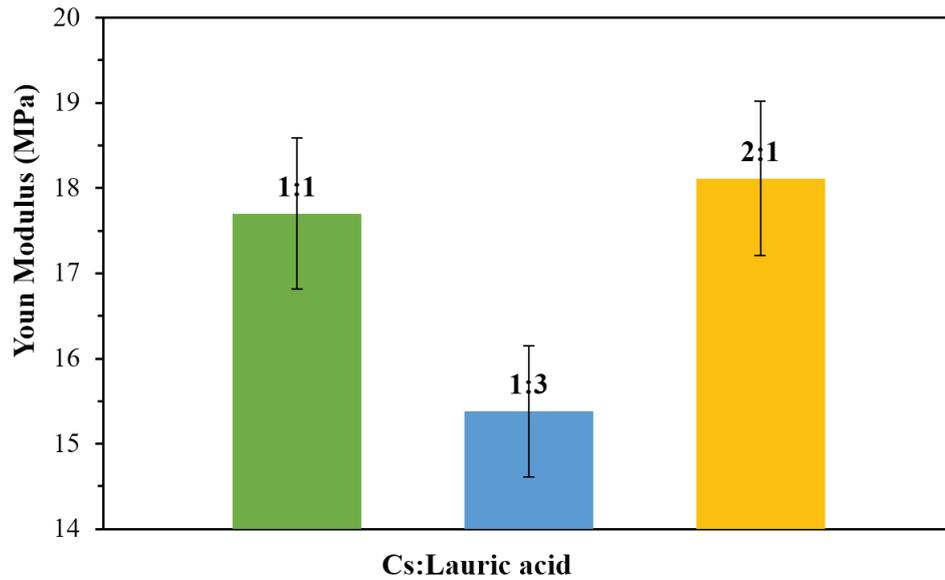


Fig. 4. The effect of Cs: Lauric acid ratios on the Young modulus of plasticized chitosan.

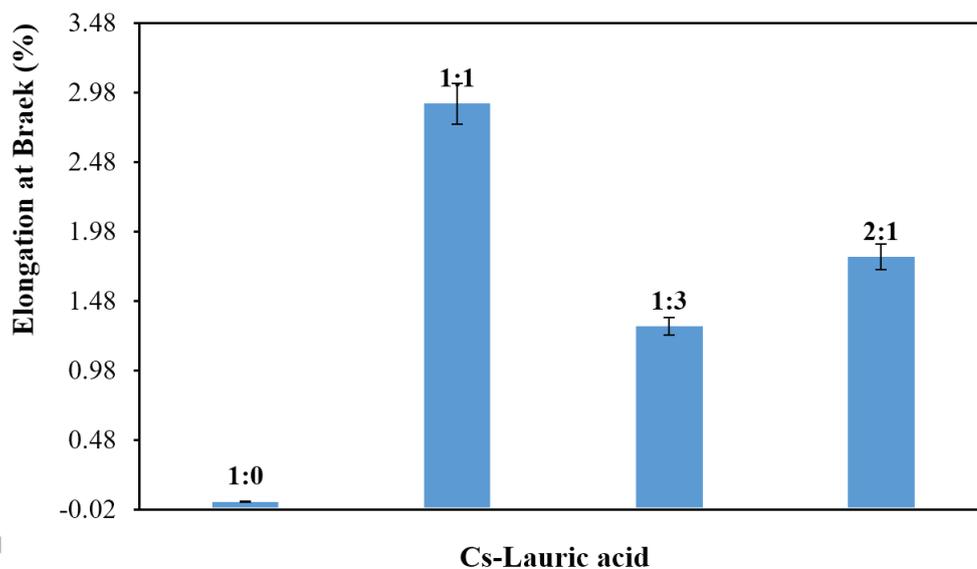


Fig. 5. The effect of Cs: Lauric acid ratios on the % elongation at break of plasticized chitosan.

3.7. Tensile properties of plasticized Cs: maleic acid films

Figures 6, 7, and 8 showed the effect of different ratios of chitosan: maleic acid plasticizer on the mechanical properties of the chitosan-based blended films, i.e., tensile strength, Young modulus, and %elongation at the break, respectively. It can be observed that Cs: maleic acid films with a ratio of 2:1 showed higher stress at maximum load and Young's modulus

than those by (1:2) cross-linked by maleic acid, accompanied by an increase in the %elongation at break as well. This is because there is an excess of cross-linking bridges, resulting in lower chain stiffness and higher extendibility.

This result was also in agreement with Reddy and Yang [36] and Thessrimuang and Prachayawarakorn [37]. They reported using an acid plasticizer caused by excess cross-linking, which led to an increase in tensile strength, and this was the case here.

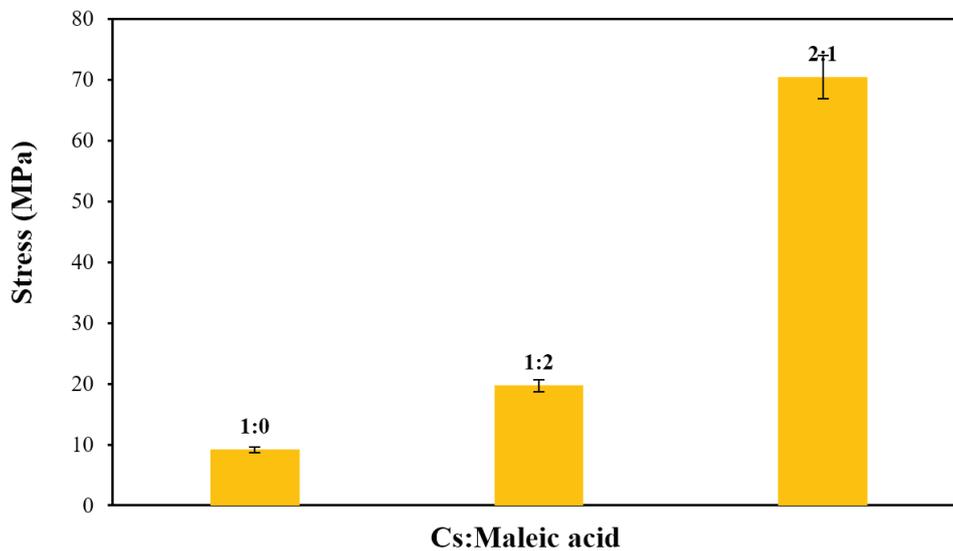


Fig. 6. The effect of Cs: Maleic acid ratios on the tensile strength of plasticized chitosan.

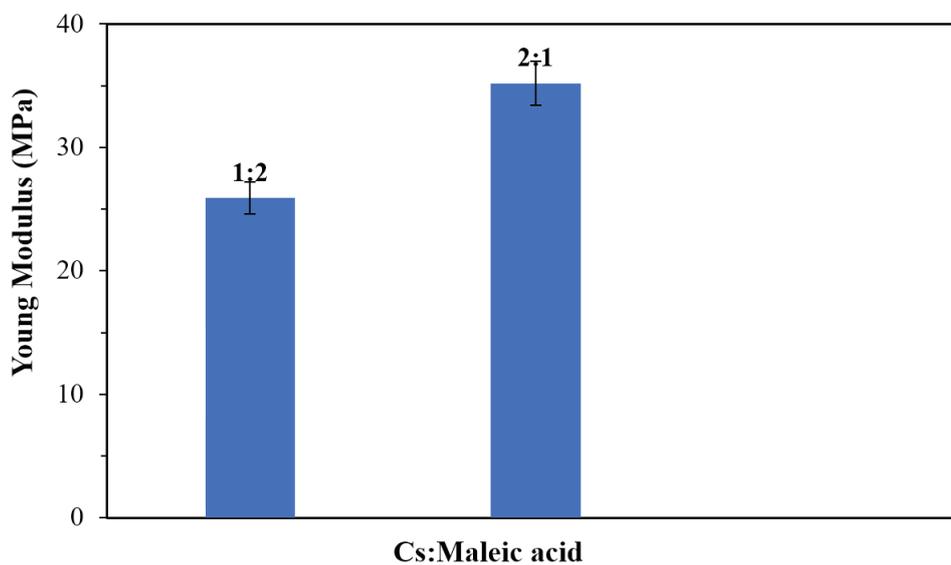


Fig. 7. The effect of Cs: Maleic acid ratios on the Young modulus of plasticized chitosan.

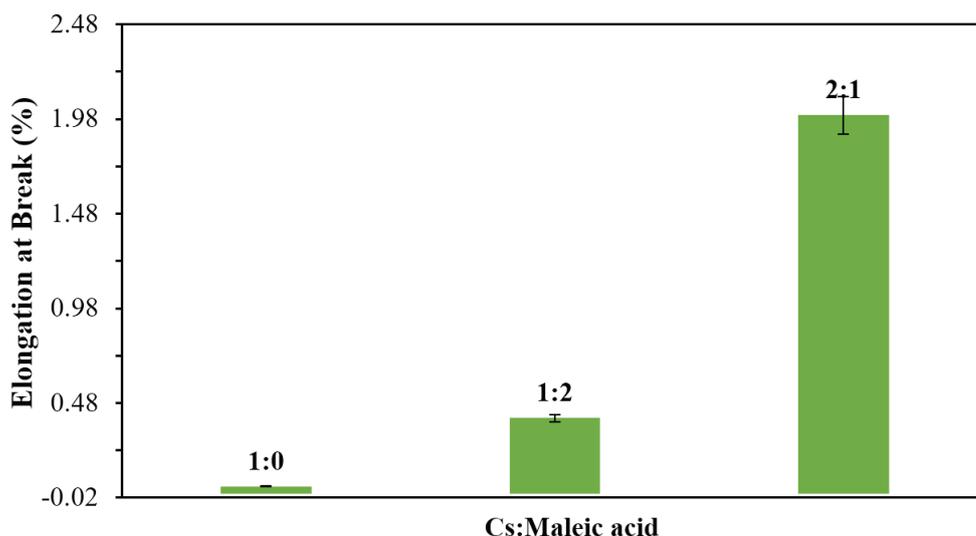


Fig. 8. The effect of Cs: Maleic acid ratios on the % elongation at break of plasticized chitosan.

3.8. Solubility of plasticized and un-plasticized Chitosan films

As measured by the film water solubility of chitosan films with various chitosan: plasticizers ratios (w/w), the impact of various plasticizers on the water barrier qualities of the materials was studied. The solubility of films in water was measured in triplicate. According to the type of plasticizer and its relative ratio, the films' water solubility increased, as shown in Table 2. This might be explained by the plasticizers' higher hydrophilicity than chitosan. By adjusting the kind and proportion of each plasticizer used in the production of those films, the solubility of chitosan/plasticizer films and blends may be controlled, opening up a wide range of industrial

applications. While it may be necessary for certain materials to be insoluble in specific applications to ensure the dependability and durability of the implemented product, film solubility may occasionally be desired before consumption. It will therefore rely on how each plasticizer is used when preparing the sample [38,39].

It may be worth mentioning here that the chitosan films always turned rubbery when submerged in water, but they never retained their structural integrity because the soluble plasticized portion of the film interfered with the structure. However, the type and concentration of the plasticizer can be adjusted to modify the solubility of the film, making it necessary for more potential applications.

Table 2. Solubility of some plasticized chitosan

Cs-Plasticizer	Ratio	SW 1 (%)	SW 2 (%)	SW 3 (%)	SW 4 (%)
Cs	0:0	2.1	2.8	3.3	3.9
Cs-Lauric acid	1:3	10.25	12.8	16.2	26.5
Cs-Maleic acid	2:1	2:1	48.7	53	55

The soluble plasticized part of the chitosan films interferes with the structure, which may be worth highlighting here. Despite usually turning rubbery when submerged in water, they never maintained their structural integrity. However, the kind and amount of the plasticizer can be altered to change how soluble the film is, necessitating it for more applications.

4. Conclusions

The purpose of this research was to examine how the types of mono and di-acid plasticizers affected the molecular structure, solubility, and mechanical characteristics of chitosan cast films. To improve some of the physical and mechanical qualities of the resulting plasticized cast plasticized chitosan films, the characteristics of the original chitosan film were evaluated in conjunction with those of the other films. The instrumental techniques used to study changes in the chemical structure and properties of modified chitosan have been considered. Every plasticizer tested showed enhanced mechanical performance, and regardless of the kind or quantity utilized, they all demonstrated the typical plasticizer action of increasing elongation and decreasing film stiffness. Data demonstrating the possibility of using modified chitosan in food packaging as sustainably as possible have been presented.

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