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The effect of different molecular weight chitosan on the physical and mechanical properties of plasticized films

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RESEARCH ARTICLE



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ABSTRACT

Packaging materials based on biodegradable polymers are a viable alternative to replacing conventional plastic packaging of fossil origin. The main two factors affecting functionality and performance are the molecular weight and the type of plasticizer used in these materials. The goal of this research was to modify unfractionated plasticized chitosan films to improve the physical and mechanical characteristics of the original unfractionated chitosan films. Chitosan extracted from local shrimp shells was zone-refined to produce five distinct chitosan fractions with molecular weights ranging from 1.089×10^5 to 5.605×10^5 g/mole. The unfractionated and fractionated chitosan films plasticized with 1:3 poly(vinyl alcohol) and 2:1 maleic acid were prepared by casting from their 2% acetic acid solutions. They were examined by FT-IR and were found to be comparable to the native chitosan spectrum, indicating that the primary backbone of the chitosan structure was unaltered. Therefore, the effects of molecular weight fractions and the type of plasticizer on the physical and mechanical properties were investigated. Examining the films' surface topography by atomic force microscopy revealed that increasing the molecular weight of chitosan fractions from 2.702×10^5 to 5.605×10^5 g/mole affects the surface morphology of the chitosan: poly(vinyl alcohol) (1:3) film. This was accompanied by an increase in the surface roughness of the resulting film from 0.953 to 2.82, and for chitosan: maleic acid from 0.509 to 1.62. It was found that the tensile strength and Young's modulus of the cast films decreased and the percent elongation at break of the plasticized fractionated chitosan films was increased, implying that less stiff films were obtained with fractionated chitosan. The outcome of this work suggests that the biodegradable fractionated chitosan blend film is a promising packaging material and that poly(vinyl alcohol) is the most suitable plasticizer for this formulation.

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1. Introduction

Recent years have seen a reappearance of interest in natural macromolecule-based food packaging as a result of environmental concerns and the requirement to use less throwaway packaging materials. Films constructed from polysaccharides are anticipated to be good oxygen barriers due to their highly packed and organized hydrogen-bonded network structure [1]. However, the hygroscopic properties of natural polymers, like chitosan, demonstrate that swelling by water results in a loss of gas and vapor barrier capabilities. The miscibility of the polymers, which is considerably aided by the creation of intermolecular hydrogen bonds between the component polymers, determines the ultimate properties of the films [2-4].

To increase the usability of chitosan, it is typically chemically or physically altered to include desirable properties [5]. A substance called plasticizer makes chitosan more flexible. Plasticizer is a chemical that increases the flexibility of a polymer by reducing the attraction forces between the polymer chains and enhancing the flexibility of the chitosan. Plasticizer

will probably reduce stiffness and strength, but will be more effective when flexibility, shock resistance, and hand or feel for coatings or films are needed [6,7]. Unfortunately, it appears that there is currently no method to completely describe a plasticizer's behavior in terms of any fundamental feature. The behavior of the plasticizer is closely related to the behavior of the base polymer to which it is added, and the polymer itself is highly influenced by its past [4,5].

Plasticizers have long been a popular component in the plastics industry [6], with numerous applications, including automobiles, packaging, consumer goods, pharmaceuticals, building materials, and construction [7]. However, the industry is moving away from phthalate-based plasticizers and toward biobased plasticizers due to environmental and health concerns [8,9]. Desirable plasticizer properties include good miscibility or strong intermolecular interactions between the plasticizer and the polymer resin, low volatility and diffusivity, low specific gravity, and low cost per volume. A well-plasticized product should be flexible at low temperatures, with a low glass transition temperature, a low elastic modulus, and a high tensile elongation but low tensile strength [10].

Physical blending is the most frequently used method for preparing a chitosan-plasticizer solution before making plasticized chitosan films. In this work, a zone-refining fractionation approach was performed for chitosan extracted from shrimp shells to develop new biodegradable films and explore the influence of molecular weight on the final quality of the plasticized chitosan-based films with different plasticizers. The resulting films' physical and mechanical performances were assessed.

2. Experimental

2.1. Materials

Chitosan (Cs) was obtained by the deacetylation process of chitin extracted from local shrimp shell waste as described in the literature [11,12]. It had a viscosity average molecular weight of 2.702×10^5 g/mole as determined by the viscosity technique and a deacetylation degree of 81% poly(vinyl alcohol) (PVA) and maleic acid (MA) were used as plasticizers and acetic acid as solvent, which were obtained from Sigma-Aldrich Company. They were used without further treatment.

2.2. Methods

2.2.1. Chitosan fractionation

Pure chitosan (1% w/v) was solubilized in 400 mL of 2% (v/v) acetic acid solution before being charged into a long glass tube (25 cm long, 5 cm in diameter), divided into five regions, and slowly and gradually frozen in liquid nitrogen. After the whole tube was frozen, each frozen section was cut and placed in a separate beaker. Then, the molecular weight was measured for each thawed fraction [13].

2.2.2. Molecular weight determination

The viscosity method was used to determine the average molecular weight of extracted chitosan and its fractions by dissolving 0.5 g of chitosan in 100 mL of an equal volume of buffer solution (0.15 M ammonium acetate and 0.2 M acetic acid) at 25 °C. The Mark-Houwink-Sakurada equations are known to represent the intrinsic viscosity $[\eta]$ as a function of the viscosity average molecular weight M_v [14].

$$[\eta] = k \times M_v^\alpha \quad (1)$$

where $k = 9.66 \times 10^{-5}$ dm³/g and $\alpha = 0.742$ for chitosan, depending on the solvent and temperature used [15].

2.3. Chitosan film casting

The cast films of unplasticized-unfractionated chitosan (Up-UnFCs) and its plasticized chitosan fractions (P-FCs) were prepared using the solvent evaporation method by dissolving 1 g of chitosan in 100 mL of 2% (v/v) acetic acid solution stirred at room temperature. Then it was poured into a leveled Petri dish of 50 mm in diameter. The film was removed from the dish, and it was dried for 12 hours at 45 °C, and then stored before the determination of its structural, physical, and mechanical properties [16].

2.4. Measurement of the film's surface roughness

Chitosan and plasticized chitosan surfaces were examined in the form of thin films by an Atomic Force Microscope (AFM) model AA3000 Scanning Probe Microscope/Angstrom Advanced Inc. USA. An AFM scans a film surface with a cantilever with a highly sharp tip. The cantilever deflects towards the surface when the tip approaches the surface due to the close-range attractive force between the surface and the tip. However, as

the cantilever gets closer to the surface and the tip makes contact, a growing repulsive force takes control, causing the cantilever to deflect away from the surface.

2.5. Mechanical measurements

The mechanical properties (tensile strength, Young's modulus, and % elongation at break) of the unfractionated chitosan (Un-Cs) and their plasticizer blend films were measured in the tensile mode (speed 5 mm/min) with a Zwick/Roell model BTI-FR2.5TN.D14 (Germany) mechanical testing machine. The ASTM D882-10 standard test method for the tensile properties of thin plastic sheets and films was used to determine the mechanical properties of the plasticized and unplasticized chitosan films (UnP-Cs) in the form of stripes of 20×2 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 in thickness).

3. Results and discussion

3.1. The molecular weight of chitosan fractions

Chitosan, like most synthetic and natural polymers, is inhomogeneous in molecular weight; therefore, many fractionations have been performed to obtain polymer samples having different molecular weight fractions for subsequent studies of physical and mechanical properties.

The feature of viscosity can be used to characterize the polymer molecular weight, which is related to it logarithmically [17]. The viscosity of a substance increases as its molecular weight increases. The viscosity test is a simple approach to see if there is variation in the molecular weights of different chitosan samples. Because a typical sample of chitosan has such a wide range of viscosity, a simple technique to fractionate chitosan based on its viscosity, and thus, its molecular weight is required [13]. Because a normal chitosan sample has such a wide range of viscosity, it is necessary to apply a simple technique to fractionate the chitosan depending on its viscosity and consequently its molecular weight.

Chitosan is usually soluble in an acidic solution due to the salt form of the amino group [11,16]. These tests were done to determine if there was a difference in the solubility of chitosan based on its molecular weight. Without this solubility difference, it would be impossible to fractionate chitosan by solubility based on its molecular weight. After the solution of chitosan was prepared, it was hypothesized that the molecular weight could be easily fractionated using different techniques [18,19]. One of them is the zone-refined fractionation of the chitosan polymer using the freezing-thawing method because it is simple, straightforward, and does not require sophisticated equipment [13]. The fractionations were carried out in a glass tube measuring 25 cm in length and 5 cm in diameter.

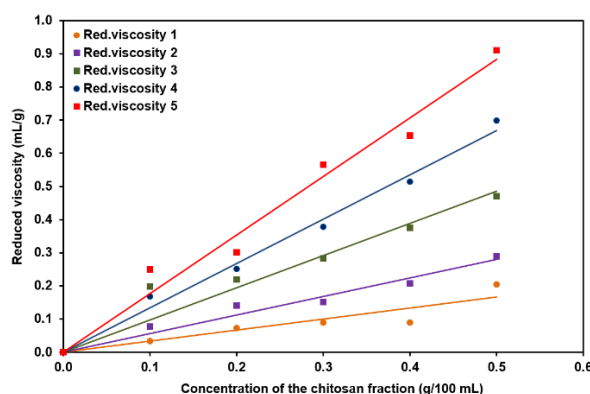
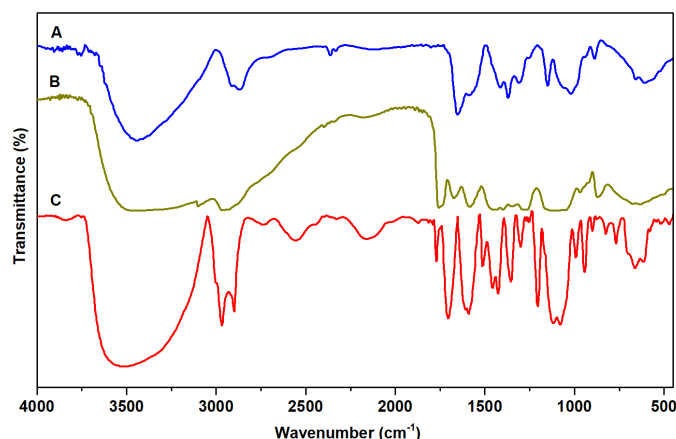
The average molecular weight of the chitosan and its fractions were calculated using the viscosity method. The results obtained are shown in Figure 1 and Table 1. The results imply that the fractionation of chitosan based on molecular weight with a simple freezing and thawing method is easy with the use of simple tools, and its effects are remarkable. The method can then be expanded to fractionate considerably more chitosan.

3.2. FTIR characterization of plasticized chitosan films

Chitosan is a special cationic polysaccharide with a great affinity for various surfaces and outstanding cosmetic properties, even when left unaltered. Physical blending is a useful and significant technique for modifying chitosan to suit different applications. The physical and structural properties of chitosan-based films have been studied frequently for food packing, biomedical, and other applications [20,21].

Table 1. Unfractionated chitosan and its fractions' intrinsic viscosity and molecular weight.

Chitosan fraction code	Intrinsic viscosity [η]	R ²	M _v (g/mole) × 10 ⁵
Unfractionated chitosan, Un-FCs	1.036	0.9723	2.702
Fractionated chitosan A, FCs-A	0.528	0.7978	1.089
Fractionated chitosan B, FCs-B	0.683	0.9913	1.538
Fractionated chitosan C, FCs-C	1.148	0.9105	3.140
Fractionated chitosan D, FCs-D	1.283	0.9281	3.605
Fractionated chitosan E, FCs-E	1.788	0.9498	5.605

**Figure 1.** The linear relationship between reduced viscosity and concentration of various chitosan fractions at 25 °C, where 1: Chitosan fraction-A (FCs-A); 2: Chitosan fraction-B (FCs-B); 3: Chitosan fraction-C (FCs-C); 4: Chitosan fraction-D (FCs-D) and 5: Chitosan fraction-E (FCs-E).**Figure 2.** FTIR spectra of unplasticized and plasticized chitosan. (A) Unplasticized-unfractionated chitosan, Up-UnFCs; (B) Plasticized-unfractionated chitosan, P-UnFCs:PVA (1:3); (C) Plasticized-unfractionated chitosan:Maleic acid, P-UnFCs:MA (2:1).

3.2.1. Unplasticized chitosan film FTIR

The FT-IR spectrum of the unplasticized chitosan film cast from a 2% acetic acid solution after being peeled off the Petri dish and before storage is shown in Figure 2. The chitosan spectrum's distinguishing characteristics in this investigation are comparable to those in earlier reports [22,23]. Pure Cs have base-state peaks that are typical for this polymer, such as those at 1654 cm⁻¹ due to C=O stretching (amide I) O=C-NHR, 1562 cm⁻¹ due to NH bending (amide II) (NH₂), and 1037 cm⁻¹ due to vibration of C-O groups [24-27]. All of the films under study had peaks between 3610 and 3000 cm⁻¹, which correspond to the stretching vibration of free hydroxyl and the asymmetrical and symmetrical stretching of the N-H bonds in the amino groups [28]. The bands at 2912 and 2843 cm⁻¹ indicate the vibrations of aliphatic C-H [29].

3.2.2. PVA plasticized chitosan film FTIR

The FTIR spectra of chitosan: PVA blended films with a ratio of 1:3 are shown also in Figure 2. As noted, the band resulting

from the NH bending (amide II) of chitosan at 1577 cm⁻¹ had less intensity due to the higher ratio of PVA concentration in the blended film, and an increase in the intensity of the CH group was observed at approximately 2912-2939 cm⁻¹ [30,31]. The band at 852 cm⁻¹ was very weak in the pure chitosan spectrum. In contrast, the strength of this band was growing with the addition of PVA. This may be because the reflection of the physical blending and chemical interactions causes changes in typical spectrum peaks when two or more polymers are combined. These findings suggest that chitosan and PVA are well miscible, which is most likely the result of the intermolecular hydrogen bonds that form between the amino and hydroxyl groups in chitosan and the hydroxyl groups in PVA [32,33].

3.2.3. FTIR maleic acid plasticized chitosan film

The FTIR spectrum of the chitosan and maleic acid blend film showed a peak in the region of 3500-2500 cm⁻¹ (Figure 2), which widened due to the carboxyl OH groups of the acid combining chitosan. This suggests that the integration of the two materials simply increased the proportion of hydroxyl

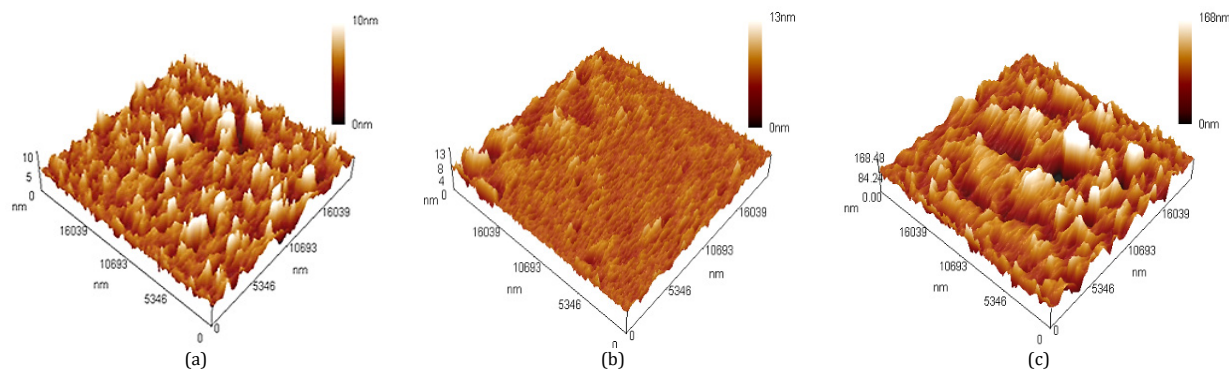


Figure 3. AFM topography images of (a) Unplasticized-unfractionated chitosan, Up-UnFCs, MW = 2.702×10^5 g/mole; (b) Plasticized-unfractionated chitosan, P-UnFCs:PVA (1:3), MW = 2.702×10^5 g/mole; (c) Plasticized chitosan fraction-E, P-FCs-E:PVA (1:3), MW = 5.605×10^5 g/mole.

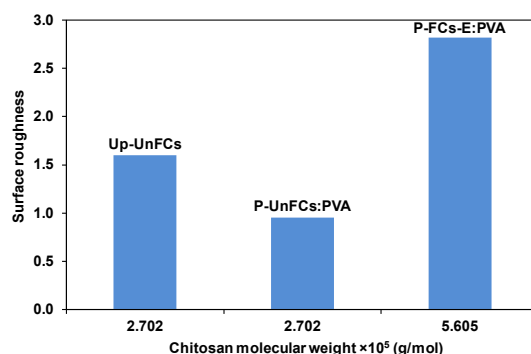


Figure 4. Effect of chitosan molecular weight on the surface roughness of plasticized film with 1:3 poly(vinyl alcohol). Up-UnFCs: Unplasticized-unfractionated chitosan, P-UnFCs:PVA: Plasticized-unfractionated chitosan; P-FCs-E:PVA: Plasticized-fractionated chitosan-E.

groups rather than changed the type of functional groups in the backbone complex [35,36]. The outcome demonstrated that maleic acid successfully interacted with the chitosan amine group. Furthermore, the acid C=O band is present at 1701 cm^{-1} [36]. Similarly, to this, the contribution of the acid C–O bond led to a wider absorption of chitosan C–O at 1180 cm^{-1} . The creation of an amide link between the 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 that are around 1700 and 1750 cm^{-1} , respectively, and stand for free and hydrogen-bonded carboxylic acid groups [37]. 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 [38]. According to a review of the literature on citric acid amides, the cyclic amide analog emerged around 1770 cm^{-1} , but the acyclic amide showed classic absorption of C=O near 1620 cm^{-1} [38]. The cyclic structure cannot exist since there are no peaks in the 1770 cm^{-1} area of the chitosanic acid spectra.

Examining peaks in the range of $563\text{--}675 \text{ cm}^{-1}$ provides more evidence that the native structure of chitosan was unchanged. According to Mima *et al.* [39], these peaks are sharpest for 99 percent deacetylated chitosan and gradually fade away as acetylation increases (amide production), which is the case here because the extracted chitosan used had a degree of deacetylation of about 81%, as mentioned in the material section above. The results of these studies led us to conclude that chitosan and diacid reacted to create an acyclic amide. This is comparable to reports of derivatives of wool-citric acid made using a similar method [40].

3.3. Surface morphology of chitosan films

For high-resolution topographical inspection, the surface concentration of plasticized chitosan fraction particles in the first layer was evaluated using atomic force microscopy (AFM). The root mean square (RMS) roughness of a surface is one of the features that can be utilized to observe topography from the 3D surface morphology of AFM images [41,42].

The influence of some fractionated chitosan molecular weight on the topography and surface roughness of some films prepared by the casting method was also investigated. However, increasing the molecular weight of Cs from 2.702×10^5 to 3.605×10^5 g/mole affects the surface morphology of the FCs/PVA film (1:3), as shown in Figure 3. This was accompanied by an increase in the surface roughness of the resulting film from 0.953 to 2.82, Figure 4, which could be attributed to a slight decline in interaction forces between the high molecular weight of FCs and poly(vinyl alcohol) polymers [43]. This is true for other chitosan fractions plasticized with 2:1 maleic acid, as shown in Figure 5 for their topography images and their measured surface roughness in Figure 6.

Plasticizing the chitosan fraction with maleic acid in a 2:1 ratio seems to behave similarly to PVA, although different values of calculated surface roughness were obtained. However, increasing the molecular weight of Cs from 2.702×10^5 to 3.605×10^5 affects the surface morphology of the FCs/maleic acid (2:1) film, as shown in Figure 5. This was accompanied by an increase in the surface roughness of the resulting film from 0.509 to 1.620, Figure 6, which could be attributed to the declining interaction forces between the high molecular weight of chitosan fraction and maleic acid molecules.

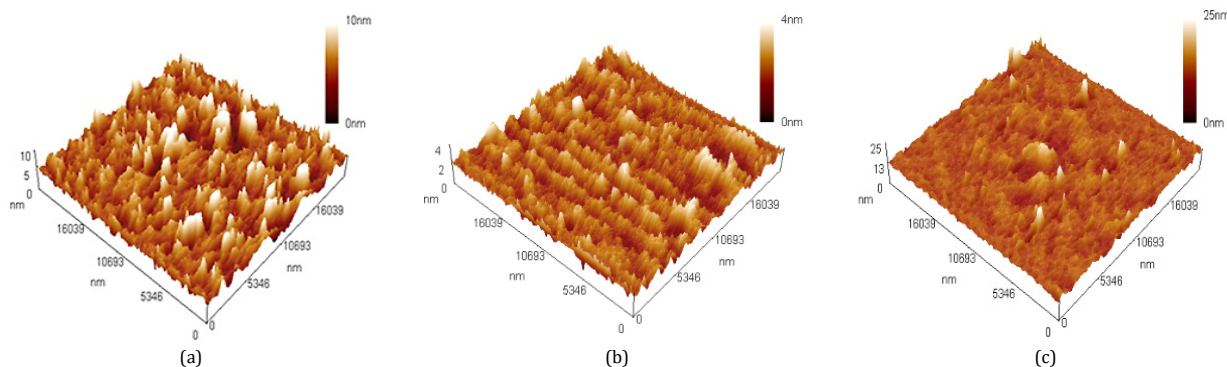


Figure 5. AFM topography images of (a) Unplasticized-unfractionated chitosan, Up-UnFCs, MW = 2.702×10^5 g/mole; (b) Plasticized-unfractionated chitosan: Maleic acid, P-UnFCs:MA (2:1), MW = 2.702×10^5 g/mole; (c) Plasticized-chitosan fraction-D:Maleic acid, P-FCs-D:MA (2:1), MW = 3.605×10^5 g/mole).

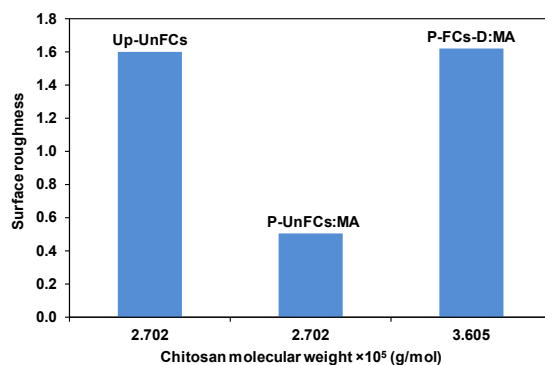


Figure 6. Effect of chitosan molecular weight on the surface roughness of plasticized film with 2:1 maleic acid. Up-UnFCs: Unplasticized-unfractionated chitosan; P-UnFCs:MA: Plasticized-unfractionated chitosan:Maleic acid; P-FCs-D:MA: Plasticized chitosan fraction-D:Maleic acid.

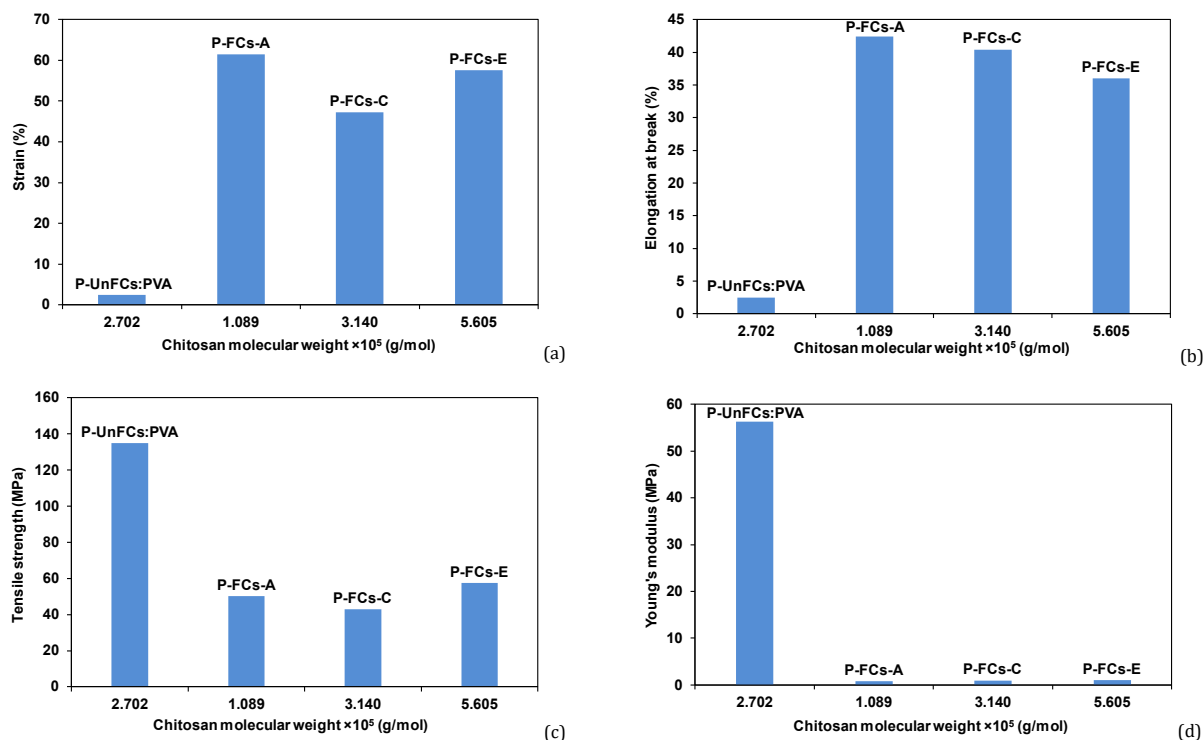


Figure 7. The effect of the molecular weight of the chitosan fraction on (a) the strain (%), (b) the Elongation at break (%), (c) the tensile strength (MPa), and (d) the Young's modulus (MPa) of the prepared films plasticized with 1:3 poly(vinyl alcohol). P-UnFCs:PVA: Plasticized-unfractionated chitosan:PVA; P-FCs-A: Plasticized-chitosan fraction-A; P-FCs-C: Plasticized-chitosan fraction-C; P-FCs-E: Plasticized-chitosan fraction-E with poly(vinyl alcohol).

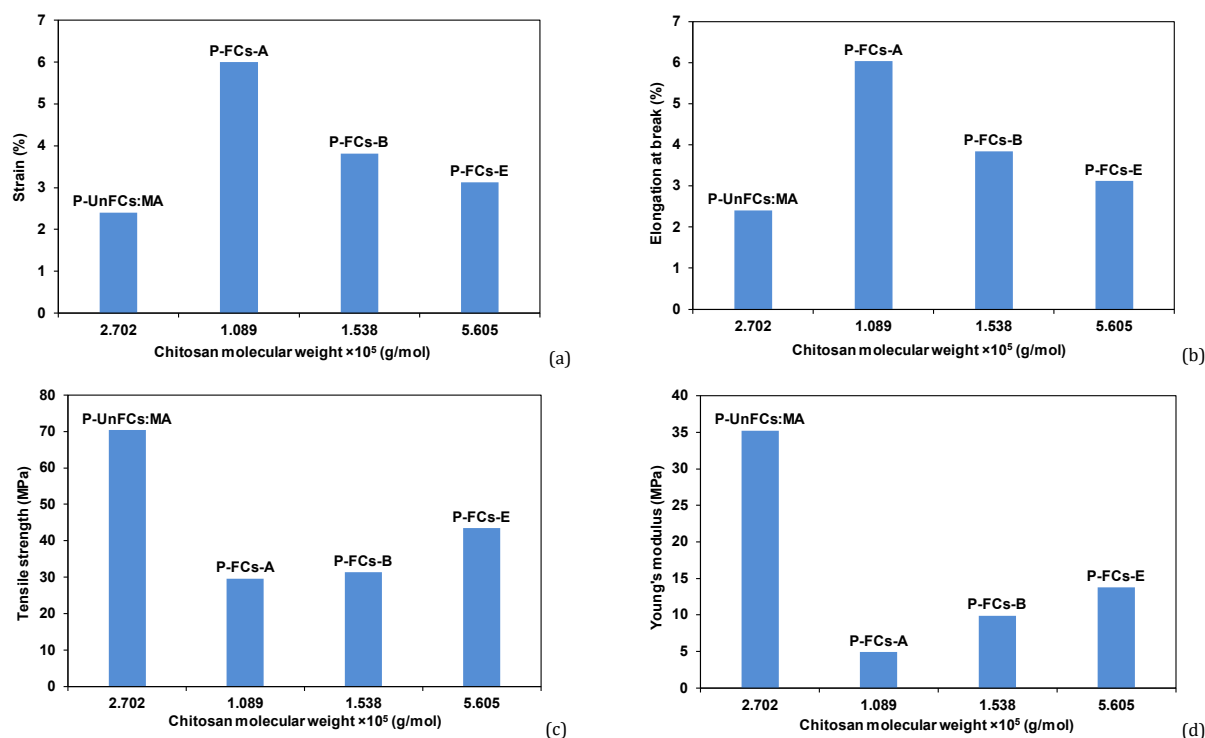


Figure 8. The effect of the molecular weight of the chitosan fraction on (a) the strain (%), (b) the elongation at break (%), (c) the tensile strength (MPa), and (d) the Young's modulus (MPa) of the prepared films plasticized with 2:1 maleic acid. P-UnFCs:MA: Plasticized-unfractionated chitosan:Maleic acid; P-FCs-A: Plasticized-chitosan fraction-A; P-FCs-B: Plasticized-chitosan fraction-B; P-FCs-E: Plasticized-chitosan fraction-E with maleic acid.

3.4. Mechanical properties

The plasticized different chitosan fractions were inspected for their modified mechanical characteristics, such as their tensile strength and elongation at break, so that they can tolerate the typical stress that comes with using and handling them. The test results showed that the molecular weight of different chitosan fractions affected the tensile properties of the cast films. For example, PVA was a plasticizer, almost showing an increase in strain and % elongation at break and a decrease in strength and elastic modulus as the molecular weight of the chitosan fraction increased compared to the plasticized unfractionated chitosan film with the same ratio of PVA, that is 1:3 (Figure 7). These results are in good agreement with the study by Velickova *et al.* [43,44].

The number of amine groups in chitosan polymer chains increased, the possibility of molecular contact was encouraged, and the self-entanglement of chitosan chains was strengthened, which resulted in a higher viscosity of the film-forming solution. When molecular weight rose, a more complete, self-aggregating, and crystalline film was created under the impact of charge transfer and molecular chain entanglement. These imply that the mechanical characteristics of chitosan films may be influenced by the degree of chain extension and the sequence of amino acid residues [45,46]. These results were true for the chitosan fraction plasticized maleic acid, as shown in Figure 8.

According to the results of AFM, the films became more complete at higher chitosan molecular weights, and subsequently, the mechanical strength was enhanced [47,48]. This might be explained by the fact that the molecular weight of chitosan affects the kinds and number of interactions between polymers, plasticizers, and solvents that shape the structure and properties of polymer matrixes. A high-molecular chitosan fraction has chains with a high degree of polymerization, which encourages polymer-polymer interactions and results in strong matrices that are typical of high-resistance films. Contrarily, the production of highly extensible polymers is encouraged when using a lower molecular weight chitosan fraction because

polymer-plasticizer and polymer-solvent interactions become significant. The mechanical characteristics of chitosan films have a wide range of reported data in the literature; variations may be ascribed to chitosan composition and suppliers as well as film preparation methods.

4. Conclusions

The purpose of this study was to investigate how the molecular weight of the chitosan fraction and the type of plasticizer affected the surface and mechanical and other characteristics of chitosan-cast films. To improve some of the physical and mechanical qualities of the resulting plasticized cast fractionated chitosan films, the properties of the original chitosan films were modified using the fractionation process and plasticizing method. The number of amine groups in a fractionated chitosan chain increased, the molecular contact was more likely, and the self-entanglement of the chitosan chain improved as the MW increased, which increased the preference for the film-forming solution. With increasing chitosan molecular weight, the mechanical performance of both plasticizers examined improved, and whatever the type and amount of plasticizers, they showed the conventional action of plasticizers in increasing elongation and decreasing tensile strength.

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Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

CRedit authorship contribution statement

Conceptualization: Hadi Salman Al-Lami; Methodology: Hadi Salman Al-Lami; Experiments: Sara Hikmet Mutasher; Validation: Hadi Salman Al-Lami; Formal Analysis: Sara Hikmet Mutasher; Data Curation: Hadi Salman Al-Lami; Sara Hikmet Mutasher; Writing-Original Draft: Sara Hikmet Mutasher; Writing-Review and Editing: Hadi Salman Al-Lami.

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