

Preparation and Study of Some Physical and Mechanical Properties of Plasticized Chitosan Films

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ABSTRACT

Keywords

Chitosan, Plasticizers, Films, Strength, Solubility.

Biodegradable polymer-based packaging materials are a practical replacement for traditional plastic packaging made of fossil fuels. 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 to enhance the physical and mechanical properties of chitosan cast films. A chitosan extract with a molecular weight of 2.702×10^5 g/mole with an 80% degree of deacetylation level was produced from the shells of local shrimp. Chitosan films plasticized with varied w/w ratios of diethylene glycol and poly(ethylene glycol) with molecular weights of 400 and 1500 g/mole were produced by casting from 2% acetic acid solutions. By using FTIR to analyze them, it was found that their spectra were compared to those of native chitosan, showing that the main backbone of the chitosan structure was unaffected. An examination of the mechanical properties of the films revealed that the results of the tensile strength measurement showed that the combination of diethylene glycol and poly(ethylene glycol) improved the mechanical properties of chitosan as films were obtained with more elasticity than unplasticized chitosan with better solubility.

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1. Introduction

Polymers are a broad category of materials that are widely used in daily life. They are generally changed with chemicals to induce desirable features, such as thermal stability, softness, electrical insulation, flame retardancy, and so on, to boost their utility [1]. Chitosan is a special cationic polysaccharide with a great affinity for various surfaces and outstanding cosmetic properties, even when left unaltered. Recent interest in natural polymers has increased because of the energy crisis and environmental concerns. Chitosan is a naturally occurring cationic copolymer that holds a lot of promise for a variety of uses. The development of chitosan-based materials has attracted a lot of attention due to their great qualities, such as nontoxicity, biodegradability, biocompatibility, antibacterial, and biofunctional characteristics, not only in the biomedical sector but also in the field of food contact materials. Plasticizers have long been a widely used ingredient in the plastics industry [2]. Automobiles, packaging, consumer products, medications, structures, and construction are just a few of its many uses [3]. However, because of environmental and health concerns, the industry is shifting away from phthalate-based plasticizers and toward bio-based plasticizers [4,5]. Good miscibility, i.e., strong intermolecular interactions between the plasticizer and the polymer resin, low cost per volume, low volatility and diffusivity, and low specific gravity are all desirable plasticizer qualities. At low temperatures, a well-plasticized product should be flexible, with high tensile elongation but low tensile strength, a low glass transition temperature, and a low elastic modulus [6,7]. Physical blending is a useful and significant technique for modifying chitosan to suit different purposes. The physical and structural properties of chitosan-based films for food packing, biomedical, and other applications have been studied frequently [8,9]. Plasticizers occupy the intermolecular gaps between polymer chains when they move away from each other, reducing chain retraction and increasing free volume, allowing polymer chains to move more freely [10]. The hydrogen bonding interaction between chitosan and plasticizer [11-13] controls the physical and mechanical properties of the films. The plasticization of extracted chitosan with three different plasticizers, namely diethylene glycol (DEG) and two poly(ethylene glycol) with different molecular weights, was physically blended with chitosan 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 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/mole as determined by the viscosity technique and a deacetylation degree of 80%. Plasticizers included diethylene glycol (DEG) and two poly(ethylene glycol), PEG, with molecular weights of 400 and 1500 g/mole, respectively, and acetic acid as a solvent. They were purchased from Sigma-Aldrich Company and utilized without further treatment.

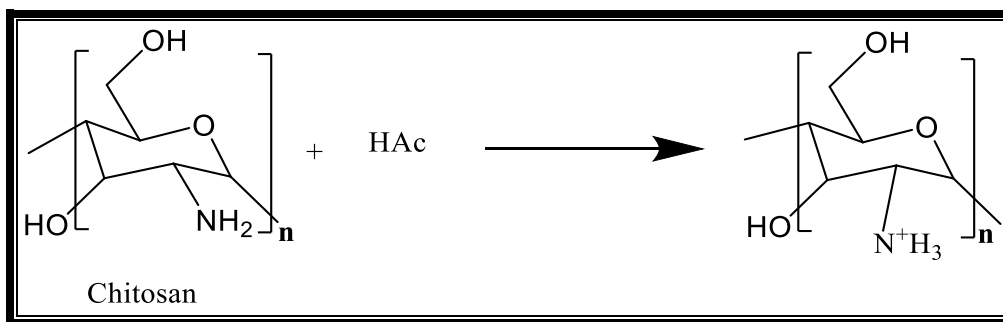
2.2 Instruments

To investigate the chemical structures of the unplasticized and plasticized chitosan films, an FTIR-8101M Shimadzu spectrometer in the $400\text{--}4000\text{ cm}^{-1}$ range was used. 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 ASTM D882-10 Standard Test Method 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 $20 \times 2\text{ mm}$. 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 cast films of unplasticized chitosan and its plasticized blends were prepared using the solvent evaporation method by dissolving 1 g of chitosan in 100 ml of 2% (v/v) acetic acid solution under stirring at ambient temperature. The reaction between chitosan and acetic acid is exhibited in scheme (1). 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].





Scheme (1): The Protonation of chitosan amin groups by acetic acid.

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 dried completely 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 constantly stirred at 25 °C for 24 hours while submerged in 50 ml of deionized water in a glass beaker. 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]:

$$\text{Water Solubility (\%)} = \frac{\text{Initial Dry Weight} - \text{Final Dry Weight}}{\text{Initial Dry Weight}} \times 100 \dots \dots (1)$$

3. Results and Discussion

3.1 Cast Film Formation and Appearance

The films were easy to peel from the cast Petra dish and also simple to handle and treat further. The majority of the cast films were transparent, uniform, thin, flexible, and manageable. Some cast films have a pale yellow color, depending on the kind of plasticizer and its concentration. Figure shows some of the prepared casted film.



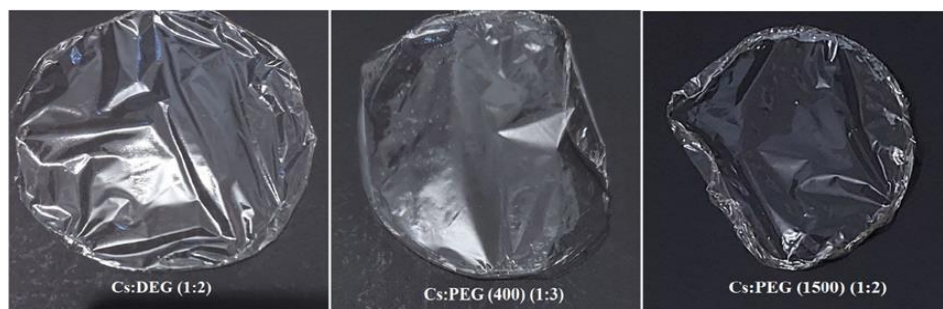


Figure 1: Some plasticized Chitosan caste films.

3.2 FTIR Characterization of Physically Plasticized Chitosan Films

FTIR spectra of the chitosan-based films were examined in light of the individual contributions made by various plasticizers to the plasticizing of chitosan physically as well as the modifications brought about at the structural and molecular levels. No matter the ratio, samples with and without plasticizers were investigated by concentrating on spectrum windows that show hydrogen bond interactions.

3.2.1 FTIR characterization of unplasticized Chitosan films

The spectrum of the unplasticized chitosan film cast from 2% acetic acid solution after being peeled off from the Petri dish and before storage is shown in Figure (2a). The chitosan spectrum's distinguishing characteristics in this investigation are comparable to those in earlier reports [19,20]. 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), and 1037 cm^{-1} due to vibration of C-O groups [21-24]. 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 [25]. The bands at 2912 and 2843 cm^{-1} indicate the vibrations of the aliphatic C-H [26].

3.2.2 FTIR examination of Cs-DEG blended films

As expected, the intensities of absorption bands of DEG characteristics in the range of 941 - 945 cm^{-1} increased as the plasticizer blend ratio increased, as shown in Figures (2b, c, d). This was also true for the free amino (1597 cm^{-1}) and chitosan bands (1000 - 1200 cm^{-1}) bands, which were shifted to lower and higher wave numbers, respectively. When the DEG blend ratio was raised, these bands were significantly displaced. Additionally, following Cs blending, the DEG



characteristic bands of blended films were likewise moved to a lower wave number. The results demonstrated that Cs and DEG interacted with one another at the molecular level [27,28].

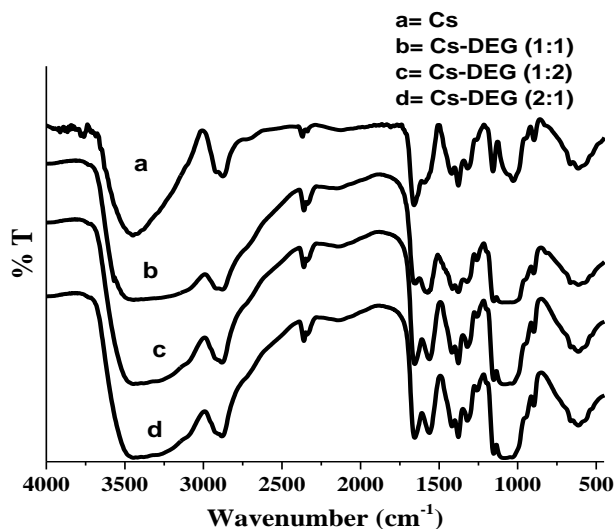


Figure 2: FTIR spectra of Cs-DEG films.

3.2.3 FTIR study of blended Cs-PEG films

The FTIR spectra of pure chitosan and chitosan/polyethylene glycol blend films having different molecular weights (400 and 1500 g/mole) are shown in Figures 3 and 4, respectively. In the absorption bands between 3610 and 3000 cm^{-1} in the spectra of pure chitosan, the stretching vibrations O-H and N-H are both observed [29,30]. Chitosan's amino groups are protonated, which results in a band that can be attributed to an N^+H vibration stretch between 3352 and 3063 cm^{-1} . The absorbance peak of the bending primary amine of chitosan that was previously at 1654 cm^{-1} has practically decreased, and the band at 1562 cm^{-1} , which was attributed to NH bending (amide II), has increased as the ratio of PEG has increased [31,32]. By comparing the FTIR spectra of the various blend films having PEG with those of pure Cs, it is possible to analyze how combining PEG and Cs affects the final product. Cs: PEG (400) film exhibits nearly an identical FTIR spectrum to pure chitosan in its 1:1 blend ratio. The majority of PEG's distinctive absorption bands become increasingly noticeable when the mass ratio of the PEG in the blended mixture of 1:2 and 1:3 increases, Figures (3 c and d). Although there is no evidence for the development of new bands or the disappearance of characteristic bands relevant to both neat Cs and PEG, in the spectra of blends, a slight change in intensity and a slight shift in the position of some characteristic bands of Cs and PEG have been noticed [33].

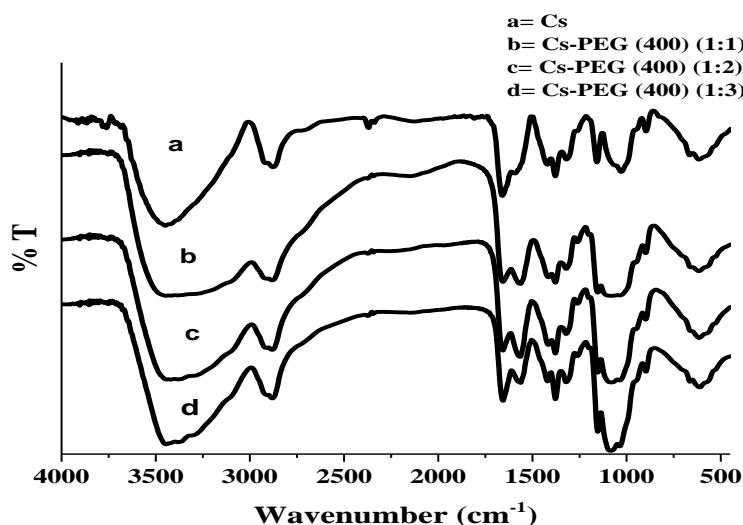


Figure 3: FTIR spectra of Cs-PEG (400) films.

This suggests that Cs and PEG may interact in a specific way, maybe as a result of freshly formed intermolecular hydrogen bonds between Cs and PEG [34–36]. This is also true for additional PEGs with a 1500 molecular weight that was combined with chitosan in a ratio of 1:2, Figure (4).

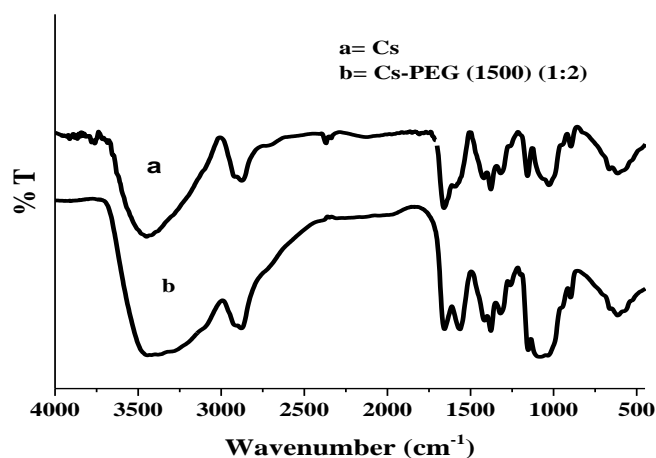


Figure 4: FTIR spectra of Cs-PEG (1500) films.

3.3 Tensile Properties of Chitosan Films

Flexibility is a crucial quality for plastics, particularly for single-use packaging when the material is stretched during use due to continual wear and tear. The spectrum of applications for synthetic bioplastics must be accurately determined by their mechanical characteristics. Mechanical testing indicates the strength and elasticity of polymer films [37].



The maximum tensile strength at break, elongation at break (%), and elastic or Young's modulus are the most common parameters that describe the mechanical properties of chitosan-plasticizer blend films, and they are all strongly related to the homogeneity and chemical composition of the blended material. The film strength is represented, the material's deformation capacity is represented by % elongation at break, and the film stiffness is measured by elastic modulus [38,39]. The mechanical characteristics, structural integrity, and flexibility of chitosan-based plasticized films are projected to increase [40]. Tensile strength measurements define the amount to which the film subjected to the applied draw force reacts. A plasticizer is a chemical that makes polymer materials more elastic when applied to them. This plasticizer is required to overcome the stiffness of chitosan-based films. The addition of a plasticizer to chitosan polymer chains can cause the inter-polymer connection to weaken and break. The plasticized and unplasticized chitosan films were tested in dry states according to ASTM D882 "Standard Test Methods for Tensile Properties of Thin Plastic Sheeting and Films," ASTM adopted in 2010.

3.3.1 Tensile strength of plasticized Cs: DEG films

Figures 5, 6, and 7, respectively, depict the impact of diethylene glycol (DEG) as a plasticizer for chitosan on the tensile strength, Young modulus, and percent elongation of plasticized chitosan films. They show how mixing with DEG alters the film's characteristics. The tensile strength tends to increase when DEG is blended with Cs in the first two ratios, Cs: DEG in 1:1 and 2:1, and they suffer more decreases with the ratio of 1:2 Cs: DEG, Figure (5). It may be due to a change in the film's level of internal stress, which He et al. [41] mentioned. A blend of these two materials with different compositions has a significant impact on mechanical properties. When DEG is present, hydrogen bonds occur between DEG and chitosan, causing the mixture to crosslink. The Cs-DEG mixture may be compatible due to the attractive intermolecular interactions [42]. The Young modulus also decreases when DEG is added to Cs, whatever the ratio is, Figure (6), implying that less stiff films were obtained. This is due to a decrease in the density of generating hydrogen bonds. Plasticizers are utilized because they can diminish internal hydrogen bonds between polymer chains while also increasing molecular space, and as the level of plasticizer increases, the film stiffness decreases [43]. Figure 7 shows the influence of chitosan variation and DEG plasticizer on elongation at break characteristics. With a higher diethylene glycol percentage, elongation at break increases. The percent elongation of the film increases when DEG is added, showing that the films are less stiff and more ductile than the chitosan-based material.



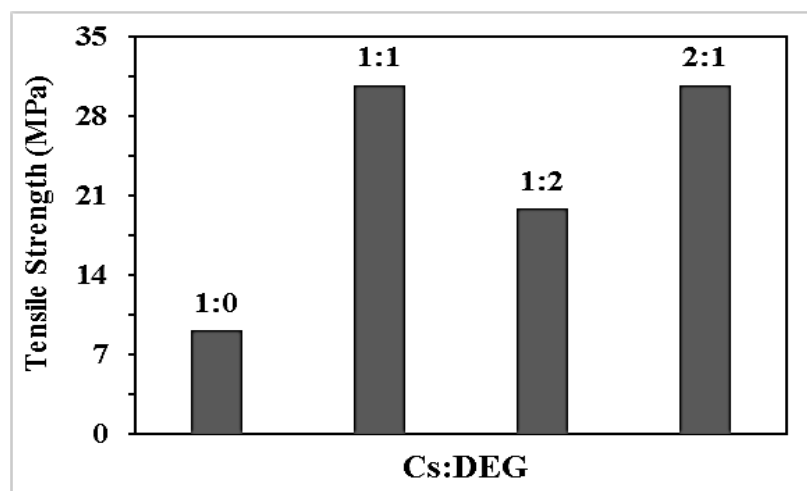


Figure 5: The effect of Cs: DEG ratios on the tensile strength of plasticized chitosan.

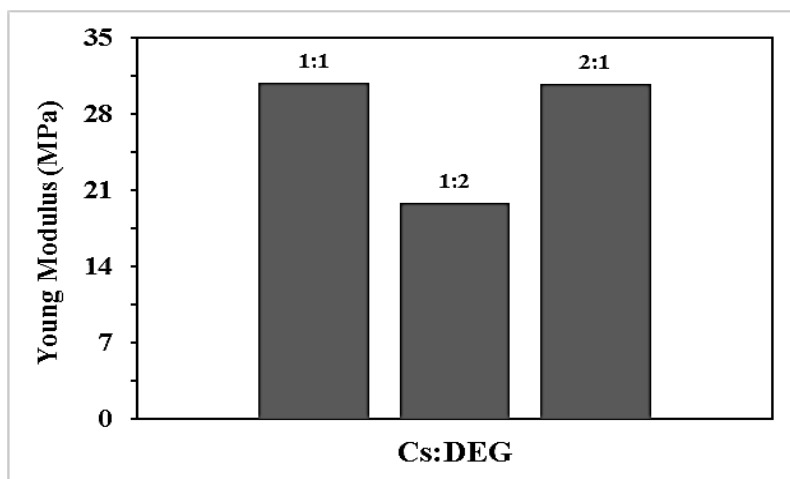


Figure 6: The effect of Cs: DEG ratios on the Young modulus of plasticized chitosan.

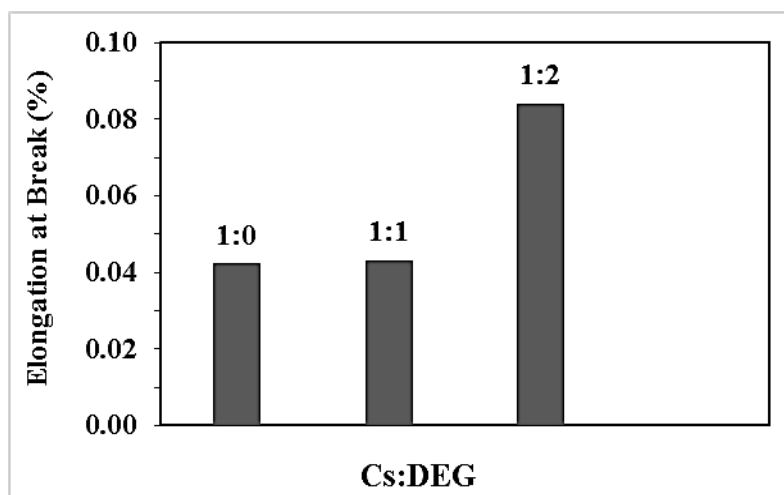


Figure 7: The effect of Cs: DEG ratios on the % elongation at break of plasticized chitosan.

3.3.2 Chitosan plasticized with PEG of different molecular weights

The tensile strength measurement results showed that blending with PEG changed the mechanical properties of chitosan. The results showed that the mechanical properties could be improved with low concentrations of PEG. As shown in Figure (8), for the chitosan-to-PEG (400) ratio of 1:2, the mechanical properties of the film deteriorated rather than improved, whereas using PEG (1500) with the same ratio improved the strength of the blended chitosan film. This may be attributed to the various intermolecular interactions of the different compositions. Several types of hydrogen bonds are formed in blends of PEG and chitosan. Some are intramolecular hydrogen bonds, and others are intermolecular hydrogen bonds that crosslink the blend [44]. The results obtained indicate that the chitosan: PEG polymer blend may be compatible and the intermolecular interactions are attractive, which is in good agreement with reported results in the literature [44,45]. This is also true for Young's modulus and %elongation at break, as shown in Figures (9) and (10), respectively.



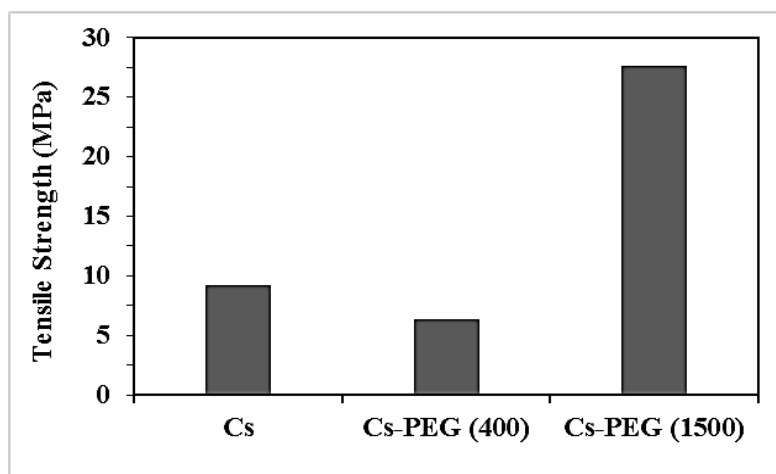


Figure 8: The effect of PEG molecular weight on the tensile strength of plasticized chitosan.

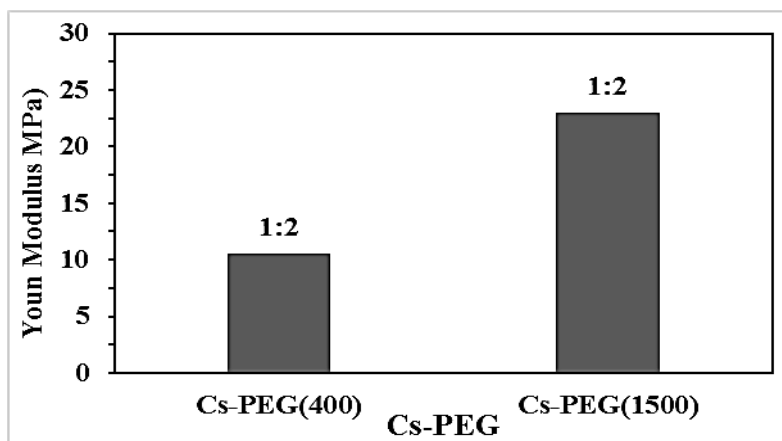


Figure 9: The effect of PEG molecular weight on the Young modulus of plasticized chitosan.

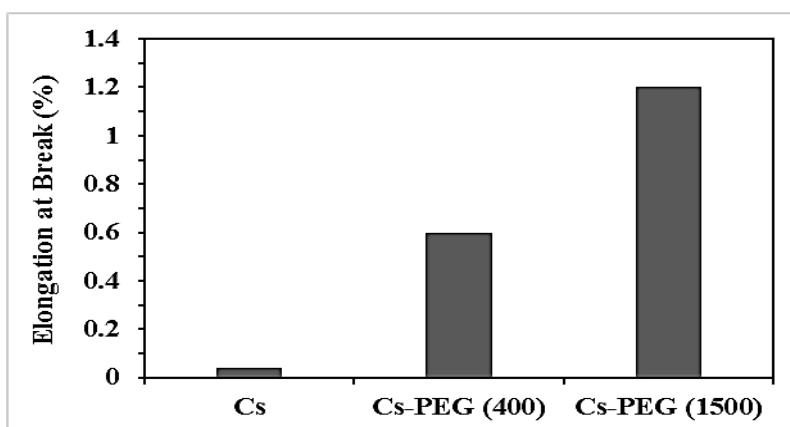


Figure 10: The effect of PEG molecular weight on the %elongation at break of plasticized chitosan.

3.4 Solubility of Chitosan films

Chitosan is a semi-crystalline biopolymer that is insoluble in the majority of solvents, including water, alkali or alkaline solutions ($\text{pH} \approx 7$), and typical organic solvents due to its hard crystalline structure. Chitosan is soluble in a small number of acids, including hydrochloric, lactic, propionic, phosphoric, tartaric, citric, succinic, acetic, and formic acids, at specific pH levels when stirred continuously [46,47]. Lower solubility values of chitosan may indicate insufficient protein removal [48]. The effect of different plasticizers on the water barrier properties represented by film water solubility of chitosan films with various chitosan: plasticizers (w/w) were determined. The method described in section (2.4) was used to measure the solubility of films in water in triplicate. The water solubility of the films increased depending on the type of plasticizer and its proportional ratio, as can be seen in Table (1). This may be attributed to the fact that the plasticizers are more hydrophilic than chitosan. The solubility of chitosan/plasticizer films and blends may be regulated by altering the kind and the ratio of each plasticizer used in the fabrication of those films, which is opening up a wide range of industrial uses. Although some of these applications could need these materials to be insoluble to guarantee the reliability and durability of the implemented product, in other situations, the film solubility may be something desired to happen before consumption. As a result, it will depend on how each plasticizer is applied during sample preparation [49,50].

Table (1): 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-DEG	1:2	6.54	9.5	11.9	16.07
Cs-PEG (400)	1:3	7.9	11.7	19.11	27.9
Cs-PEG (1500)	1:2	15.38	23.8	33.07	39.2

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.

4. Conclusions

This work aimed to investigate the molecular structure, solubility, and mechanical properties of chitosan cast films about the molecular weight of the kind of plasticizer. The attributes of the



original chitosan film were assessed in parallel with those of the other films to enhance some of the physical and mechanical properties of the resulting plasticized cast plasticized chitosan films. It was discovered that the mechanical performance of every plasticizer tested had improved, and regardless of the kind and quantity of plasticizers used, they all displayed the typical plasticizer action of boosting elongation and lowering film stiffness.

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تحضير ودراسة بعض الخواص الفيزيائية والميكانيكية لأفلام الكيتوسان الملدنة

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المستخلص

تعد مواد التعبئة والتغليف القائمة على البوليمر القابلة للتحلل بديلاً عملياً للتغليف البلاستيكي التقليدي المصنوع من الوقود الأحفوري. الوزن الجزيئي ونوع الملدنات الموجودة في هذه المواد هما المتغيران الأساسيان اللذان يؤثران على قابليتهما للاستخدام والأداء. شرعت هذه الدراسة في مزج الكيتوسان فيزيائياً من أجل تعزيز الخصائص الفيزيائية والميكانيكية لأفلام الكيتوسان المحضرة. تم الحصول مستخلص الكيتوسان بوزن جزيئي يبلغ 2.702×10^5 غم/مول مع درجة إزالة الأستلة 80%. من قشور الروبيان المحلي. تم إنتاج أفلام الكيتوسان الملدنة بنسب وزن/وزن متنوعة من ثنائي إيثيلين كليكول وبولي (إيثيلين كليكول) بأوزان جزيئية تبلغ 400 و 1500 غم/مول عن طريق الصب من محاليلها في 2% حامض الخليك. فحصت الأفلام المختلفة باستخدام FTIR لتحليلها، وجد أن أطيافها كانت قابلة للمقارنة مع أطياف الكيتوسان الأصلية، مما يدل على أن العمود الفقري الرئيسي لبنية الكيتوسان لم يتأثر. كشف فحص الخواص الميكانيكية للأفلام أن نتائج قياس قوة الشد أظهرت أن المزج مع ثنائي إيثيلين كليكول وبولي (إيثيلين كليكول) حسن الخواص الميكانيكية للكيتوسان حيث تم الحصول على أفلام ذات مرونة أكثر من الكيتوسان غير الملدن وبذوبانية أكبر.

الكلمات المفتاحية: الكيتوسان، ملدنات، أفلام، شدة، الذوبانية.

