Synthesis and characterization of chitosan/hemicellulose eco-friendly film

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Abstract

In this study, films were obtained from bio-based polymers using a simple and green method. The films have been prepared by hemicellulose (HC) and chitosan (CN) with glycerol as plasticizer. Films were obtained via the solvent casting and characterized in terms of structural and thermal properties by FT-IR and TGA, and DSC.

Introduction

Packaging is essential for extending food's shelf life, managing gas exchange and slowing down oxidative reactions. The majority of materials used in packaging today are non-renewable resources, like petroleum-based polymers, which not only results in resource waste but also poses substantial environmental issues [1].

In 2019, the world produced 360 million tons of plastic, with disposable goods accounting for half of that total. Due to their physicochemical characteristics and commercial viability, synthetic polymers have been used in a number of industries. However, if petroleum-derived polymers are disposed of improperly, their low biodegradability is one of the major causes contributing to the degradation of ecological conditions. To replace or supplement synthetic packaging, there is currently growing interest in using renewable and biodegradable (polysaccharides, lipids, or protein) packaging materials [2].

As a main component of plants, hemicellulose is a renewable, biodegradable, and environmental-friendly biomass resource. It is a polysaccharide consisting of five- and six-

carbon monosaccharides units, such as xylose, arabinose, glucose, mannose galactose, and so on [3].

Biobased materials such as hemicellulose, a water-soluble polysaccharide with lower molecular weight from plants and byproducts of pulping industry have attracted much attention for fruits and vegetables preservation purposes. Hemicellulose based films exhibit better gas barrier property, especially for oxygen. Meanwhile, hemicellulose could easily combine with other materials due to small molecular weight hemicellulose's [4]. Additionally, it has also been reported that hemicellulose film is said to have strong oxygen barrier qualities that can extend the shelf life of produce and food. However, water absorption originating from the hydroxyl groups of hemicellulose could cause the gas barrier and mechanical properties of hemicellulose materials to drastically deteriorate in a high humidity environment. Many studies are focused on enhancing the hydrophobicity and mechanical properties of hemicellulose film, including chemical modification, in order to overcome these disadvantages and expand the application of hemicellulose in a high humidity environment. [3]. Chitin, one of the most abundant natural polymers, can be obtained from exoskeletons of crustaceans and the cell wall of fugi. Its derivate chitosan (CN) offers intrinsic antimicrobial property, non-toxic, biodegradable and outstanding designability properties to be a suitable candidate for the active packaging films [5]. Biobased polymers are ideal materials for replacing petroleum-based polymers due to its renewability, biodegradability, and environmental friendliness. Furthermore, hemicelluloses-based films exhibited excellent oxygen barrier property due to their ability to form a dense macromolecular network via the hydrogen bonds, which contributes to the application of hemicelluloses in food-packaging [6]. Scheme 2 shows the obtaining and some applications of hemicellulose and chitosan films.

In this paper the edible film was prepared with hemicelluloses and chitosan. The film was characterized by FT-IR spectroscopy an TGA-DSC.

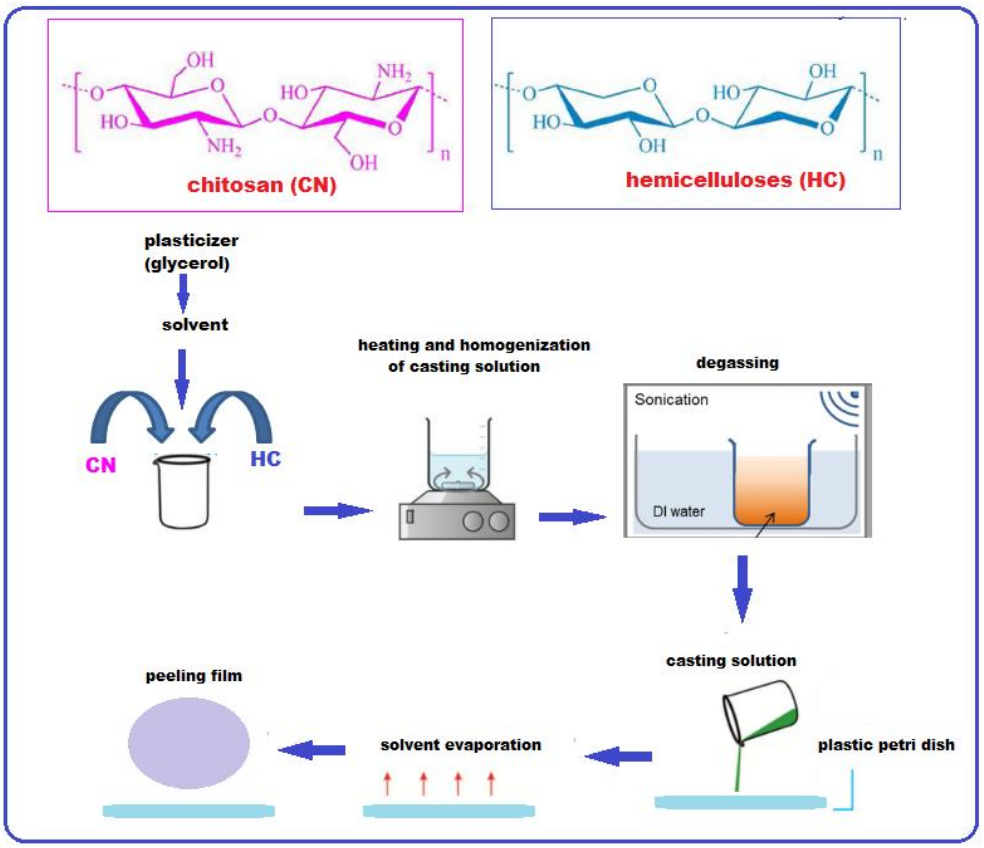
Materials and Methods

Chemicals

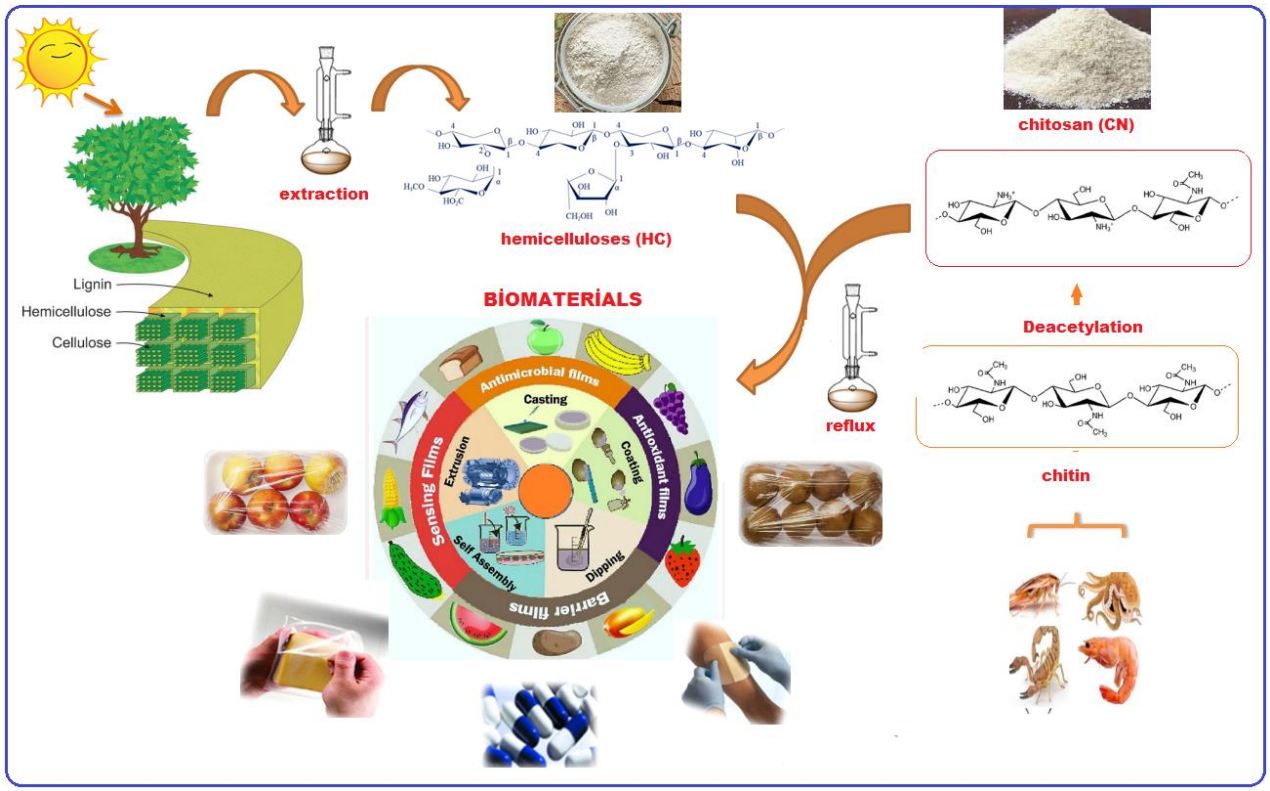
Low molecular weight chitosan was used from Sigma–Aldrich. Hemicellulose was obtained from a local company in Turkey. Acetic acid, glycerol and purified water were used.

Preparation of the films

2% (w/v) chitosan solution was prepared in 1% (v/v) acetic acid aqueous under magnetic stirring at 800 rpm at 40 °C for 2 h. 2% (w/v) hemicellulose solution was prepared in 1% (v/v) acetic acid aqueous under magnetic stirring at 60 °C for 2 h until the solids were almost completely dissolved. The solution obtained was degassed using an ultrasound bath (15 minutes, at room temperature). The specified amount of glycerol was added to the above solutions (30 % (w/w) plasticizer (glycerol) based on the mass of chitosan or hemicellulose). The chitosan and hemicellulose solutions were mixed with the quality ratio of 1:1. The prepared solutions were cast onto acrylic plates and dried at 40 °C for 24 h. The dried films were peeled from the casting plates and stored in desiccators [6, 7, 8, 9] (Scheme 1).



Scheme 1: Systematic representation of solution cast synthesis of CN/HC film.



Scheme 2: The obtaining and applications of hemicellulose and chitosan films.

Characterization studies

The CN/HC film was characterized by Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Infrared spectra of the CN/HC film was obtained from a Perkin Elmer FT-IR spectrometer equipped with ATR sampling in the range of 4000 to 400 cm^{-1}. Thermal data of CN/HC film was obtained by using Perkin Elmer Diamond Thermal Analysis. The TGA measurements were performed between 20 and 400 ^oC (in N_2, 10 ^oC/min). DSC analysis were carried out between 25 and 300 ^oC (in N_2, 10 ^oC/min) using a Perkin Elmer Pyris Sapphire DSC.

Result and Discussion

Figure 1 shows FT-IR spectra of the chitosan (CN), hemicellulose (HC) and CN/HC film. The chemical structure of CN/HC film was approved from FT-IR. The spectrum of CN exhibits a broad peak at 3363 cm^{-1} that related to O–H and N–H stretching, at 2871 cm^{-1} for aliphatic C–H stretching, 1644 cm^{-1} for C–O stretching of amide I band, 1581 cm^{-1} for N–H stretching of amide II band, 1257 cm^{-1} for amide III band, 1148 cm^{-1} for asymmetric stretching of C-O-C groups, 1060–1030 cm^{-1} for C–O stretching of the C-OH groups and 892 cm^{-1} for CH_2 bending of the saccharide structure, respectively which was coincided with the reported data of others [6,10]. As shown in the spectrum of QH, the peak at 1640 cm^{-1} is originated from -COO of hemicelluloses. The signals at 1075 and the broad peak at 3374 cm^{-1} are related to C–O–C stretching vibration and with the –OH stretching, respectively [6, 9]. The C–O–C stretching vibration of the film was broadened and shifted to 1088 cm^{-1}, which was owing to the overlap of the ether bond in both hemicelluloses and chitosan. This indicated that the hemicellulose and chitosan were miscible due to the strong hydrogen bonds and electrostatic interactions between the polymer chains [6]. The TGA–DTA and DSC curves of the CN/HCfilm is given in Figure 2 not given CN and HC. The initial degradation temperatures

($_{Ton)}$ of CN, HC (powder) and CN/HC have been found to be 270, 65 and 70°C, respectively. Furthermore, temperature values weight losses of 20 % (T_{20}) and 50 % (T_{50}) were determined 279, 200 and 220 ^{o}C and 335, 300 and 315 ^{o}C for glass transition temperature-softening temperature respectively. T_g (glass transition temperature-softening temperature) of the HC (powder) and CN/HC are calculated from their DSC curve and found as 73 and 81 ^{o}C. CN/HC film is thermally more stable than raw hemicellulose due to the strong hydrogen bonds and electrostatic interactions between the hemicelluloses and chitosan [6].

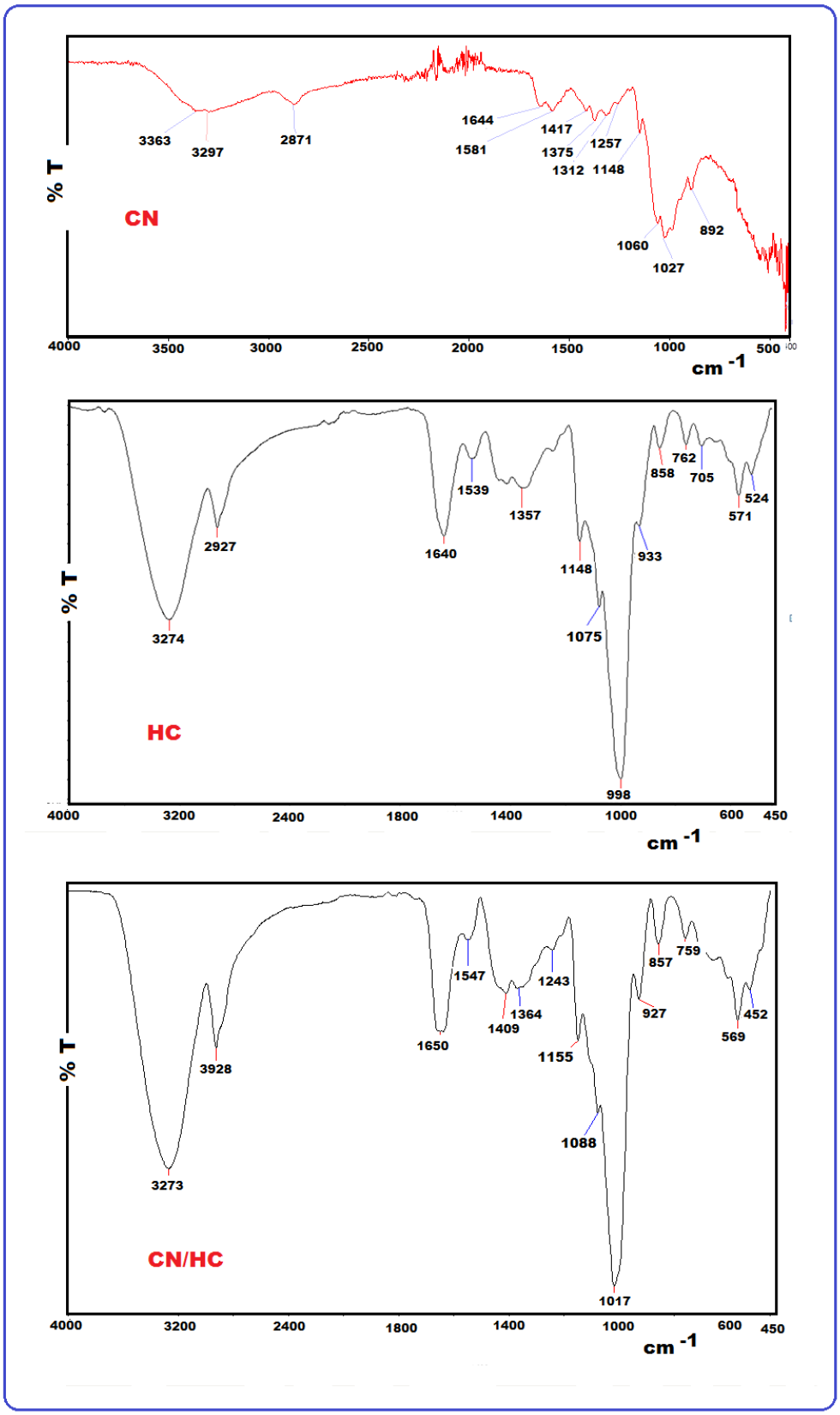


Figure 1: FT-IR spectra of chitosan, hemicellulose and CN/HC film

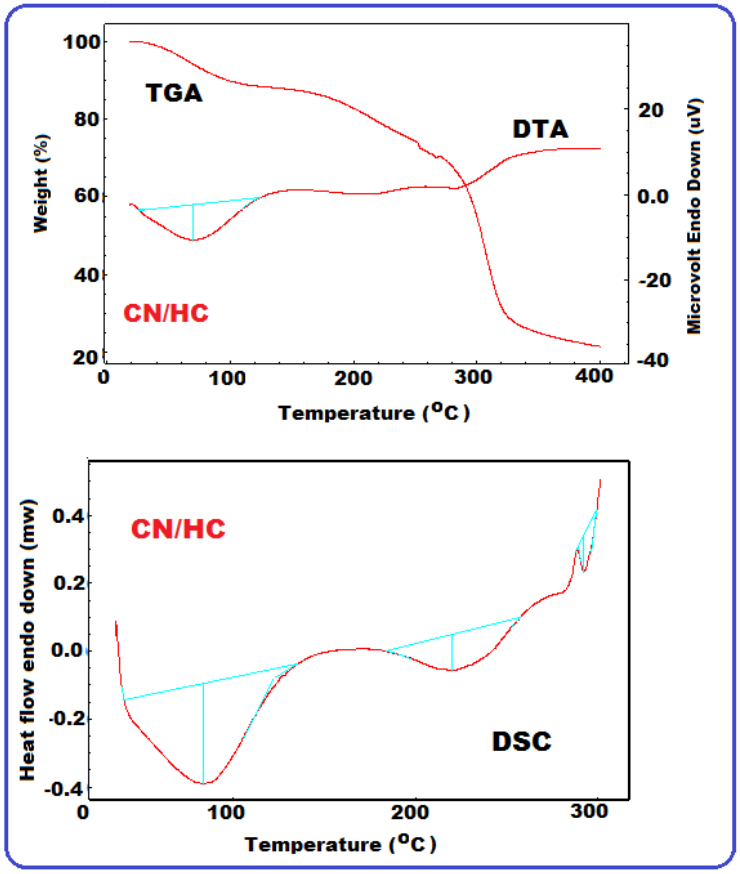


Figure 2: TGA-DTA and DSC curves of the CN/HC film.

Conclusion

The plasticized chitosan/ hemicelluloses edible films were successfully prepared in this work. The bio-based packaging films can be used as alternative eco-friendly materials to diminish the impact of synthetic or non-biodegradable plastics on the environment.

References

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