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Investigation of the potential use of halloysite nanotube doped chitosan films for food packaging

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Abstract − Polymer-based food packaging is widely used and causes serious environmental problems due to the chemical ingredients. Therefore, these packages should be replaced by biodegradable alternatives in order to prevent environmental pollution. Many biodegradable polymers are used in food packaging. Among them, chitosan is gaining attention since it is bio-sourced and biodegradable. In this study, the usability of chitosan films as physical and chemical tests investigated food packaging. In order to improve the packaging properties of the films, halloysite nanotube was used as filler with a concentration range of 1-4 wt.%. It was observed that the halloysite significantly increased the opacity, mechanical strength, water resistance, and antioxidant properties of the films.

Keywords: *Chitosan films, composite films, food packaging, halloysite nanotube*

Subject Classification (2020):

1. Introduction

The plastic-based environmental problems are increasing day by day in accordance with plastic consumption depending on the human population. Petrochemical-derived packaging materials, especially those that cannot be recycled after use, are known to remain in the soil and seas for a long time. It is also known that these are broken down into phthalates with sunlight and are harmful to the entire ecosystem. In addition, it has also been proven that chemicals in contact with food undergo plastic transfer to food under light and heat. Therefore, the use of bioplastics for food packaging will have a positive impact on both health and the environment [1-3]. However, it is known that the mechanical strength and water resistance of biopolymers are relatively low compared to the petrochemical-based packaging. For this reason, these deficiencies are tried to be overcome with strong fillers.

Chitin is one of the most abundant biopolymers in the world. It is found in the exoskeletons of insects, arthropods such as crabs, shrimp, and the cell walls of fungi [4]. Chitosan is also biocompatible, completely degradable, soluble in water, and forms a colloidal solution. It can be used in hydrogel or film form [5]. It is seen as a suitable polymer for many fields of study due to its antimicrobial properties, metal binding ability, high mechanical strength, non-toxicity, and biodegradability.

Halloysite nanotube (HNT) is a tubular natural clay with a large surface area. It is used as a nanofiller material in film formation and improves the mechanical properties of the film. Depending on the negatively charged surface of HNT, it enables the slow release of antimicrobial substances in its structure, allowing their effects

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to last for a long time [6] It has been revealed that it has a potential to replace traditional films in recent years due to its long-term durability and food spoilage retarding properties. In the literature, limited studies have performed on use of HNT in chitosan [7]. In studies where it was used other than chitosan, it was observed that it increased many properties of films simultaneously.

Salmos et al. [8] aimed to extend the shelf life of kiwi fruit by obtaining a biodegradable film by dispersing thymol-enriched halloysite nanotube structure in chitosan/polyvinyl alcohol gel. Mechanical properties, transparency, antimicrobial and antioxidant properties were investigated. It was reported that the HNT simultaneously increased both parameters. Risyon et al. [9] aimed to strengthen the low thermal resistance of biopolymers with nanostructure additives by producing polylactic acid/halloysite nanotube (HNT) films. When the mechanical, thermal, and barrier properties were examined, it was concluded that the optimum HNT doping was obtained as 3% by weight. The critical point in composite polymeric films is the homogeneous distribution of the filler through the films. Homogeneous distribution of filler improves the properties throughout the film. For this, it is necessary to determine the appropriate ratio.

In this study, HNT doped chitosan films were prepared, and their usability in food packaging was investigated. The HNT ratio was kept between 1-5% by weight. The effect of HNT doping on film opacity, moisture content, swelling, mechanical strength, and antioxidant properties was investigated.

2. Materials and Methods

Medium molecular weight Chitosan powder was purchased from Aldrich Chemicals. The HNT nanoparticles were kindly supplied from Esan Eczacıbası, Türkiye. Acetic acid (analytic grade) was purchased from Merck Chemical.

2.1. Film Preparation

Films were prepared by solution casting method. The aqueous solution containing 1 wt.% chitosan was stirred at room temperature for 24 hours. The solution contains 2% acetic acid. After the homogeneous mixture was obtained. HNT particles were added with the weight concentration of 1-5% and stirred for three hours. The solution was degassed under vacuum and casted on a polymethyl methacrylate plate. After casting, the films were allowed to dry at room temperature for 2 days and peeled off gently. The films were named according to the concentration of HNT (CS for the pristine chitosan, CS-HNT1, CS-HNT2, CS-HNT3, CS-HNT4 for the filled chitosan films)

2.2. Characterization

FTIR analysis of the membranes was performed with The Agilent Cary 630 FTIR spectrometer. This test was performed to determine the structural moisture retention properties of membranes and to examine their chemical bond structures. The test was performed in the wavelength ranges of 650-4000 cm^{-1}.

The light transmittance of the prepared films is determined by opacity tests. For this test, the opacity of the films cut in certain sizes was examined by measuring the absorbance at 600 nm in UV/Vis spectrophotometer (Shimadzu-1280). The opacity was calculated as shown in (2.1)

$$Opacity = \frac{Absorbance}{Thickness\ of\ films} \tag{2.1}$$

The percentage of moisture trapping of the films in standard media was determined by moisture content tests. The films were dried at 105°C for 24 hours until to constant weight and measured gravimetrically (M_i). The films were kept on a water bath without contact at room temperature and the percentage of weight gain (W_g) was calculated as moisture content as shown in (2.2).

$$Moisture\ content = \frac{Wg}{Wi} * 100 \tag{2.2}$$

The swelling test is used to determine the water resistance of films. To test the swelling properties of the films, each sample was dried in an oven at 65 °C for 12 hours before the test. The films were soaked in 25 mL deionized water for 12 hours and the values before (Wi) and after (Wf) water retention were recorded as shown in (2.3).

$$Swelling\ Degree = \frac{Wf - Wi}{Wi} * 100 \tag{2.3}$$

The antioxidant properties of the added additives were determined by antioxidant activity test. According to this test, films weighing 0.1 gram were placed in 70% methanol and 2,2-diphenyl-1-picrylhydrazyl (DPPH) stable radical (10 ml 70% methanol, 0.2 mg DPPH) and kept in the dark for 90 minutes. When this radical reacts with the antioxidant, a change from violet to yellow is observed and the antioxidant activity is calculated by measuring the absorbance at 520 nm with UV-Vis Spectrophotometer [10].

The mechanical analysis of the films was analyzed in Ankarin brand mechanical analyzer according to ASTM D882 standard. The mechanical strengths were performed by measuring the mechanical strength (stress) and elongation (strain) from the force and elongation at break of the strips cut in 4*1 cm size. Experiments were performed at a tensile speed of 3 mm/min.

3. Results and Discussion

The FTIR spectrum of the films are shown in Figure 1. A prominent band within the range of 3000–3620 cm^{-1} is indicative of N–H and O–H stretching. It is clear that the intensity of the peak decreasing by increasing HNT depending on the reducing moisture content.

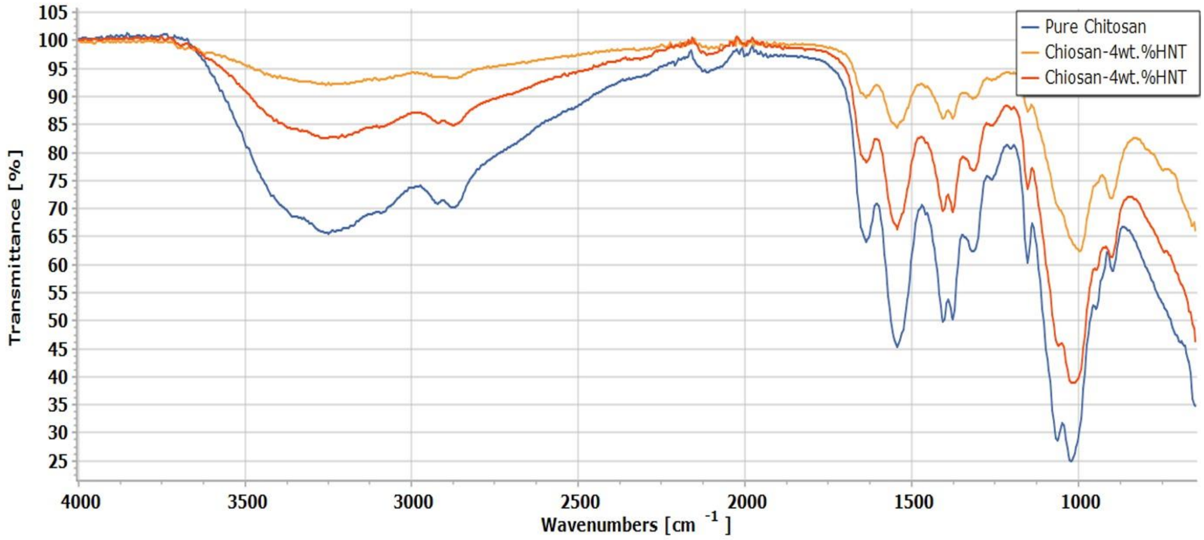

Figure 1. FTIR spectra of the pure and HNT loaded films

C-H symmetric and asymmetric stretching are responsible for the absorption bands at approximately 2920 and 2876 cm^{-1}, respectively. These bands are typical polysaccharide properties and are present in the spectra of various polysaccharides. The bands at about 1638 cm^{-1} (C=O stretching) and 1318 cm^{-1} (C-N stretching) respectively confirmed the presence of residual N-acetyl groups [11].

The light transmittance of the packaging films produced is a very important parameter [12]. While light can be degrading for some foods, an optimal degree of opacity is desired as a high degree of opacity reduces the visibility of the food [13,14]. Especially considering the freshness of the food, it is desired that it refracts and does not transmit too much light. Figure 2 shows the opacity of the films. Accordingly, all additive ratios increased the opacity values compared to pure chitosan film.

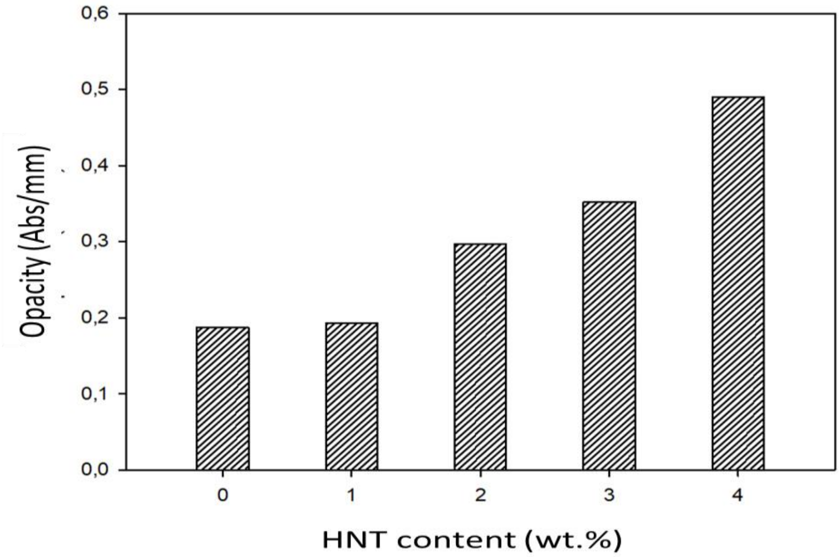

Figure 2. Opacity results of films with and without HNT loading

Figure 3a shows the results of the swelling tests of the additives in pure water for 30 minutes. Swelling tests are normally performed for very long hours, but in this study chitosan was not crosslinked. This is because the cross-linking process prevents understanding the antimicrobial activity or determining the actual character of the films. Therefore, the swelling tests were short because pure chitosan dissolves in water and disintegrates after 20-30 minutes. As can be seen in the figure, when the HNT content in the membrane increased from zero to 2 percentage, its resistance to water was significantly increased. However, there is a small increase of 3 percent and 4 percent. This shows that when the films are loaded with excess HNT, the HNT structure also interacts with water and fills its pores.

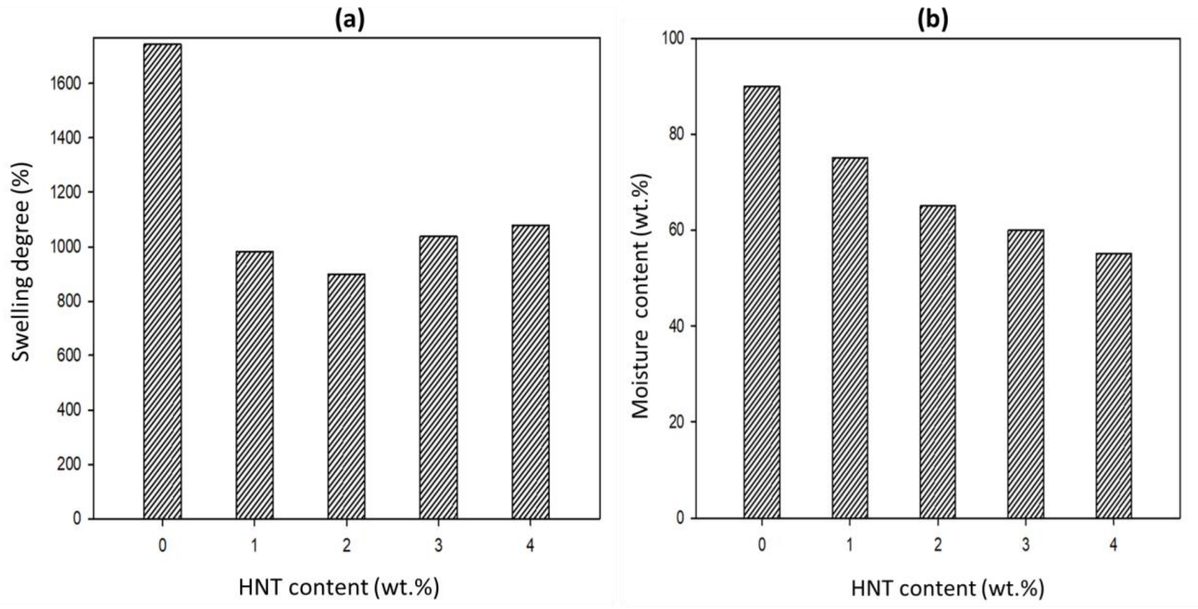

Figure 3. Swelling degree (a) and Moisture content (b) results of films with and without HNT loading

Similar to the swelling test, the moisture retention (content) test is a measure of the resistance of films to water vapor. Unlike swelling, in this test the films interact only with the vapor at room temperature. Moisture retention value is actually expected similar results to swelling. However, since there is no direct contact with water, the structure of the HNT particles is not expected to be filled with water. Therefore, as seen in Figure 3b, the vapor contents gradually decreased with the addition of HNT. While the pure film retains a lot of vapor, this value decreased significantly in HNT doped films. This shows that the resistance of the films to moisture retention increases under room conditions, and therefore the degree of degradation decreases.

Oxidative reactions change the basic properties of foods and cause them to deteriorate. Antioxidants are microcomponents that can scavenge free radicals by terminating oxidative chain reactions. Therefore, antioxidant activity is an important feature for food packaging [15-17]. In this study, DPPH free radical scavenging method is used to evaluate the antioxidant capacity of the chitosan films. Figure 4 shows the antioxidant values of the films depending on the DPPH reagent. This value is also an indicator of the resistance of the films against oxidation and is expected to be as high as possible. As seen in the figure, while the antioxidant value of the film was 20% in the pure film, this value increased to over 24% in the 4% added film. that is, more than 20% antioxidant properties were improved with 4% additive.

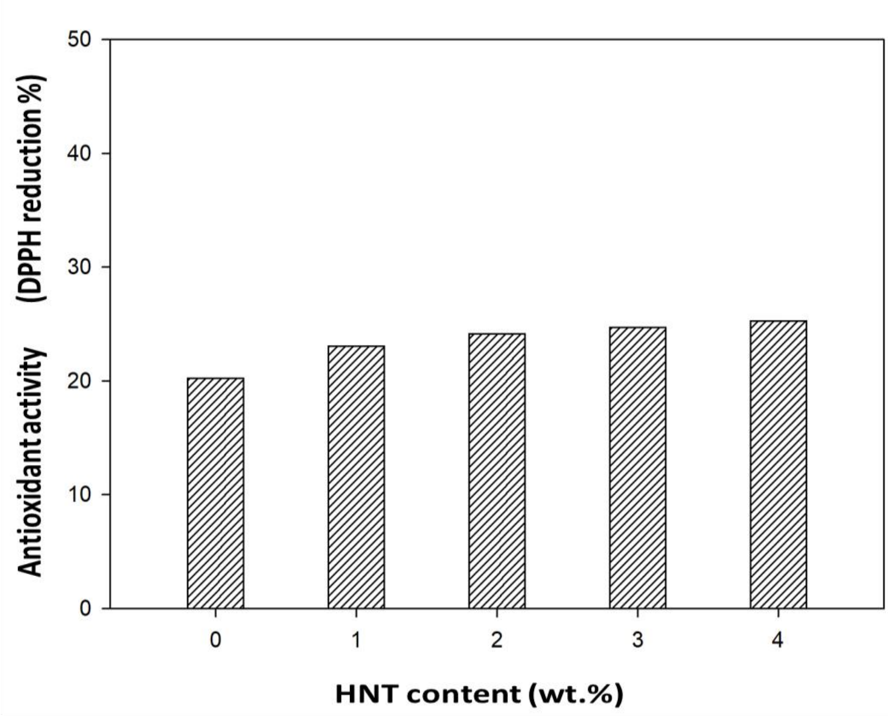

Figure 4. Antioxidant results of films with and without HNT loading

Figure 5 shows the mechanical analysis results of the additive ratios. Mechanical analysis is evaluated in two ways. The first is the stress, which is an indicator of the force applied at break, and the other is the strain value calculated based on the amount of elongation at break. The strength of the films is described by the stress value. Strain gives more information about elasticity. As seen in the figure, the stress value of pure chitosan is around 5.7 MPa. As seen in Figure 5, this value increased to 10.8 MPa with the addition of HNT. However, it decreased after this value. The reason for this is that the additive material added to the polymeric matrix increases the mechanical strength, contributes to load transfer in homogeneous distribution, but due to agglomeration caused by overloading, the load cannot be distributed properly and weak points are formed and cause rupture [18,19].

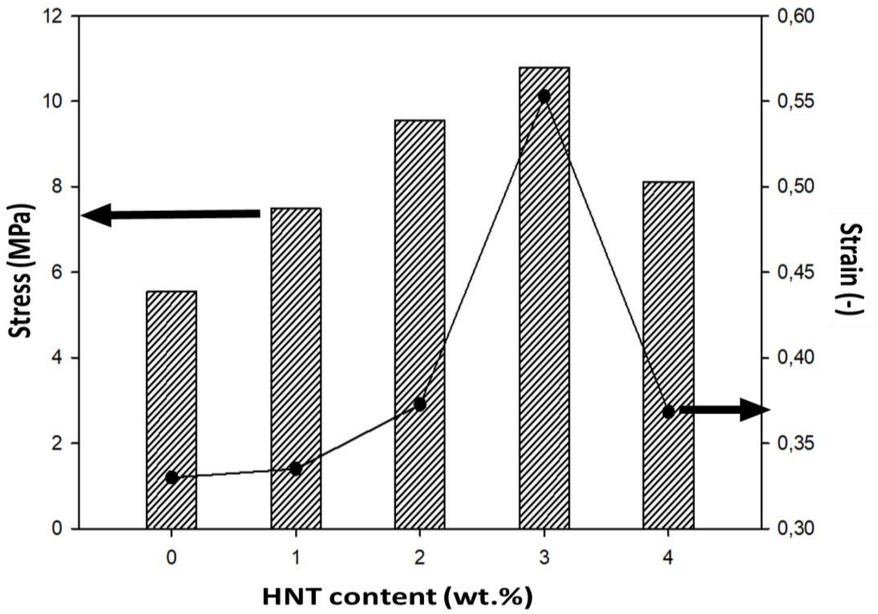

Figure 5. Stress-strain results of films with and without HNT loading

4. Conclusion

The environmental impact of reducing the use of plastic and replacing it with biodegradable packaging is increasing day by day. In this way, carcinogenic compounds resulting from plastic degradation are not formed, and naturally occurring films reduce the carbon footprint in nature. In this study, chitosan-based films were prepared for use in food packaging. In order to improve the mechanical properties, swelling and moisture retention properties, opacity, antioxidant and antimicrobial properties of the films, HNT additives were added between 1-4%. As a result of the study,

i. The HNT additives increased the opacity values depending on the increasing ratios and since this is an indicator that reduces the light transmittance of the films, it has an inhibitory effect on food degradation.

ii. The increasing ratio of HNT decreased the swelling and solubility of the films in water.

iii. Increasing ratios of HNT in films significantly decreased moisture retention. This is a factor preventing the degradation of the films and thus the food when exposed to moisture and steam.

iv. Increasing HNT content in films increased the mechanical strength and generally above 3% the mechanical strength decreased due to agglomeration.

v. Increasing HNT content improved the antioxidant properties.

In the next stage of the study, the degradation processes of the produced films in soil and atmospheric environments will be examined, and accordingly, their sustainability will be examined according to biodegradability criteria.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflict of Interest

All the authors declare no conflict of interest.

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