



Development of Single Layer Edible Film Composite from Chitosan Nanoparticles-based as Fruit Packaging Materials

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ARTICLE INFO

Received 29/09/2021
 revision 21/10/2021
 accepted 29/11/2021
 Available online 30/11/2021

ABSTRACT

Nowadays, food packaging materials are dominated by synthetic plastic materials that are based on crude oil, e.g. polyethylene (PE), polypropylene (PP), and polyvinylchloride (PVC). These plastics are categorized as non-degradable materials, and when plastic waste is mishandled, it will harm the environment. Furthermore, Bisphenol A (BPA), commonly used for strengthening plastic properties, might contaminate the foods wrapped in those mentioned plastic materials and adversely affect human health. One of the alternative solutions to reduce crude oil-based plastics as food packaging is edible film packaging. Edible film packaging on a biopolymer basis can be applied as food packaging to replace synthetic plastics and maintain fruit quality at the same time. This research aims to conduct modification and characterization of edible film chitosan-based for food packaging applications. In this research, the composite film was produced from chitosan nanoparticles and cellulose nanocrystal composite and mixed with a variation of plasticizer (glycerol) of 10% w/w in concentration and a variation of KMnO_4 concentration. Mixing of composite material was done at 50 °C with an interpretation of ultrasonic irradiation processes. Then, the composite was characterized by UTM, FTIR. The result showed that the optimum condition was CNC variation by 5% and glycerol by 10%. It gave a tensile strength result of 464.1 MPa. and 266.3 MPa on a nano chitosan-based film. Adding active agent KMnO_4 by as much as 8% can reduce the tensile strength value by 46.3%.

Keywords: Chitosan nanoparticles, Edible films, Composite films

1. INTRODUCTION

Plastic packaging used for food (fruit and vegetables) is currently dominated by petroleum-based materials such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC). With advanced processes such as blowing, injection, extrusion, plastic pellets can be shaped as desired [1]. The characteristics of plastics that are light, flexible, easy to form, resistant to water, have strong mechanical properties, and are economical are the main reasons this product is widely used for packaging.

Besides having many advantages and benefits, plastic packaging is a non-degradable material, so

that plastic waste that is not handled correctly will harm the environment. Based on data from the Ministry of Environment and Forestry in 2019, the amount of plastic waste or waste in Indonesia was 63 million tons per year or 175,000 tons per day. One alternative to reduce petroleum-based plastic packaging, especially food product packaging, is biodegradable and even edible packaging.

Edible packaging is a food packaging technique using edible polymers. Its nature is environmentally friendly, easy to decompose, so it does not produce waste compared to conventional plastic. Edible packaging is a material that is safe for health and is non-toxic, so it is safe for

consumption with the product it is packaged in. The primary function of edible packaging is in addition to protecting the packaged product. It also functions to add value to food as an anti-bacterial, anti-oxidant, and coloring agent [2]. Edible packaging can be grouped into two parts based on the packaging process: edible coating (coating directly) and edible film (sheet). The edible coating uses natural ingredients that are safe and healthy to extend the shelf life of food products. Several applications of edible coatings on food products are brushed, sprayed, immersion, or melting [3]. The edible film is a thin layer produced from the polymerization process of natural materials that can be eaten. It has a function to reduce mass transfer (such as moisture, oxygen, and fat) or as a carrier for food ingredients and additives and improve the ease of handling food [3]. One of the ingredients that can be used as edible film is chitosan.

Chitosan is a derivative of chitin through the deacetylation process or removing the acetyl group (CH_3CHO). Chitin is a natural polymer type of polysaccharide with the second most availability on earth after cellulose (Figure 1). Chitosan has the advantage of being a film-forming ability and abundant availability of chitosan because it comes from food processing waste of the crustacean group (shrimp, crab, mushroom). Chitosan is a renewable material or material, so its availability will continue to exist. Chitosan has hydrophilic and low mechanical properties; this limits its application to commercial food packaging materials. One way to improve the performance of chitosan as a food packaging material is to modify the size of the chitosan particles to be smaller, namely in the form of nanoparticles, and combine them with other materials into nanocomposites.

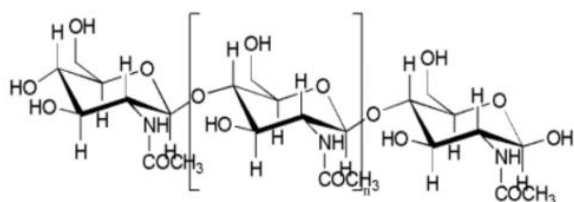


Figure 1. The structure of chitin [4].

The one method of creating nanoparticles is the ionic gelation of hydrophilic polymers [5]. Chitosan nanoparticles were created using this method. Chitosan nanoparticles were synthesized based on ionic cross-linking with sodium tripolyphosphate. Chitosan can be chemically and physically linked together to form nanoparticles because it contains

several ammoniac groups that use protonation to develop NH_3^+ in acidic solutions [6]. Crosslinking based on positively charged chitosan complexes with negatively charged multivalent ions. It is derived from sodium tripolyphosphate (TPP), citrate, and sulfate [7].

Nano chitosan is chitosan with nanoparticle size, having the advantage of a larger surface area and volume ratio compared to micro chitosan so that nanoparticles are more reactive [8]. The addition of nanoparticles into the film formula is one of the technologies that are developing to produce nanocomposites. Nanocomposites will increase the effectiveness of storage, absorption, and mixing [2]. Filler with nanoparticle size can maintain material transparency and form a strong matrix bond [9].

Research on edible packaging continues to be developed with many variations to get optimum results, one of which is edible films based on nanoparticle composites. Nanocomposites are multi-phase materials derived from two or more components, a matrix component as a continuous phase and a nano-dimensional phase as a discontinuous phase. The size of the nano dimension is 100 nm in diameter [10]. In this study, the composite matrix used was Cellulose Nano Particle (CNP) with glycerol as a plasticizer, KMnO_4 as an ethylene absorber, and Cellulose Nano Crystal (CNC) as a filler. In this research, an edible film will be made to obtain the resulting film's good mechanical characteristics and properties.

In 2010 [11], Fernandes developed a nanoparticle composite edible film with Chitosan-Cellulose nanofiber (CNF) as the base material. The results obtained are that the mechanical properties (flexibility and heat stability) of edible film reinforced with CNF are higher than chitosan that CNF did not strengthen, the particle size of the resulting CNF was less than 50 nm.

In another study [12], observed the optimization of CNF content (0 – 20% w/w) and glycerol concentration (0 – 30% w/w) as fillers. The research concluded that the most optimum dispersion of CNF in the film was obtained at the ratio of CNF to glycerol of 15% CNF and 18% glycerol, which is the most optimum mechanical properties value (tensile strength and stiffness). However, the flexibility and ability to hold water vapor produced were still poor; in other words, this film can only be applied to those that do not require high flexibility and water vapor permeability.

Chitosan nanoparticle composites with a mixture of chitosan – cellulose nanowhisker (CNW) have also been developed. Khan et al. (2012) [13] concluded that the composition of 5% w/w CNW of

dry chitosan could increase the film's tensile strength by 26% and reduce the water vapor permeability of the film by 27%. However, variations in the composition of CNW do not affect the heat stability of the film generated. In their research, Li, Zhou, and Zang (2009) concluded that by increasing the CNW concentration from 0 – 25% dry weight, the tensile strength of the film increased from 9.9 MPa to 17.3 MPa.

Another nanoparticle composite being developed is a mixture of chitosan–cellulose nanocrystals (CNCs). Wardhono (2019) [15] have formulated this film with a matrix of chitosan nanoparticles–sodium tripolyphosphate–cellulose nanocrystals (CNP–TPP–CNCs). The results obtained are that the mechanical strength of the nanoparticle composite film increases when compared with pure chitosan film. Tensile strength (Ts) increased from 56.5 MPa to 74.9 MPa, and film flexibility (elongation break) increased from 7.6% to 20%. The optimum composition was obtained from the CNCs ratio of 2.5% w/w dry chitosan basis. Stability, heat resistance, and water resistance are also good.

Based on the existing literature, the research that will be carried out refers to the method that has been carried out by Wardhono (2019) by adding the KMnO_4 variable as an ethylene absorber to the film.

2. METHODOLOGY

2.1. Method

In this research, the manufacture of edible films was carried out in several stages, including the preparation stage, the formation of chitosan colloids, the formation of nano chitosan composites, the manufacture of nano-composite matrices, film formation, and film characterization tests.

The flow chart for the preparation and characterization stages of the film is presented in Figure 2. The formation of the CNP-TPP-CNC matrix is carried out in three stages, namely:

- Preparation of 1% w/v chitosan solution, dissolved chitosan powder in 0.1 M acetic acid solution, stirred using a magnetic stirrer at 300 rpm for 24 hours, then filtered to remove impurities.
- Preparation of CNP-TPP colloid solution, heated chitosan solution at a temperature of 50 °C then added TPP solution with a concentration of 5% as much as 20% by weight of dry chitosan dropwise under constant stirring at 1000 rpm using a magnetic stirrer for five minutes.

- Preparation of CNP-TPP-CNC- KMnO_4 matrix, CNP-TPP colloid solution, added glycerol solution with variations of 5,10 and 15% w/w dry chitosan base and added CNC with variations 1-5% w/w dry chitosan base, stirred at 300 rpm for 30 minutes at room temperature. 8% w/w of dry chitosan base was added with KMnO_4 at a temperature of 50 °C under constant stirring at 1000 rpm for five minutes. The film solution was poured into a petri dish and then heated using an oven at 62 °C for 12 hours.

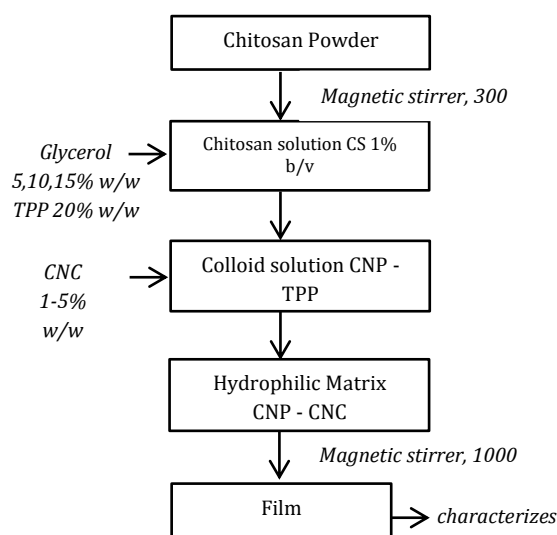


Figure 2. Flowchart of Film Preparation Stages and Characterization.

2.2. Tools and materials

Tool :

Magnetic Stirrer, Hot Plates, Vacuum Ovens, Petri dish, Chemical Glasses, Digital Balance

Material :

Chitosan powder, Acetic Acid 0.1 M, Sodium-tripolyphosphate (TPP), Cellulose Nanocrystal (CNC), Glycerol, KMnO_4 .

2.3. Characterization and testing

Mechanical characteristics were determined using the ASTM 638 technique and a Zwick Roell instrument. Each preconditioned sample was sliced into film strips of 11.5 cm x 1.9 cm (length overall x width overall) as in Figure 3 and put between the machine's grips. The grip separation and crosshead speed were initially set to 50 mm and 50 mm/min, respectively.

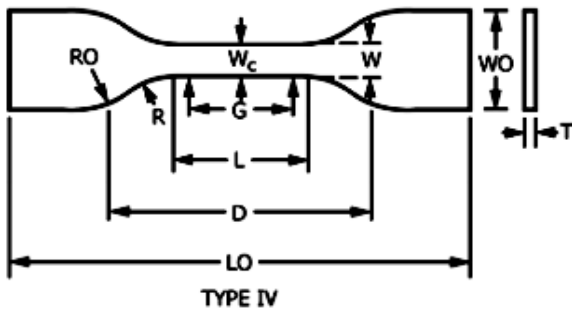


Figure 3. Test Specimen shape [16].

Fourier transform infrared (FTIR) spectroscopy of the chitosan and the composites was recorded using a Bruker Tensor 27 FTIR spectrometer with a testing range of 7500 cm^{-1} - 350 cm^{-1} . They were testing using ASTM standards E1252.

3. RESULTS AND DISCUSSION

This research was conducted to make edible films based on chitosan and chitosan nanoparticles. The experiment was carried out by making a film from a chitosan-based composite solution and chitosan nanoparticles which were poured into a petri dish and then dried in an oven at 62°C for 12 hours. The dried film was analyzed for mechanical properties and functional groups to observe the effect of the addition of CNC on chitosan-based films and chitosan nanoparticles. Some of the parameters observed in this study include:

3.1. Mechanical Properties of Edible Film

The edible film's mechanical characteristics or properties (chitosan and nano chitosan-base) were prepared according to ASTM standard number D638. The specimen shape of film and tools is shown in Figure 4 below.

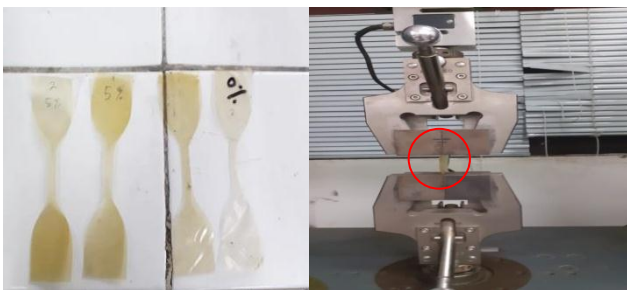


Figure 4. Film specimen shape, b. Zwick Roell for mechanical characteristics test.

3.1.1. Chitosan-based films

In Figure 5, it shows that with increasing CNC concentration, the tensile strength value also increases by 192.2 MPa for 1% CNC, 212.8 MPa for 2% CNC, 311.2 MPa for 3% CNC, 324.3 MPa for CNC

4%, and peaked at 464.1 MPa for 5% CNC. The addition of CNC variations increases the tensile strength of the chitosan film. According to Wardhono (2019) [15], CNC at the optimum concentration can improve the mechanical strength of the film. The increase in tensile strength due to the increase in the interaction of attractive forces between molecules that make up the thin layer forms inter- and intra-molecular hydrogen bonds to form a thin layer consisting of mutually reinforcing fibers. CNC supports the value of tensile strength because of the uniformity of the nano-sized material structure that can produce an adequate bond.

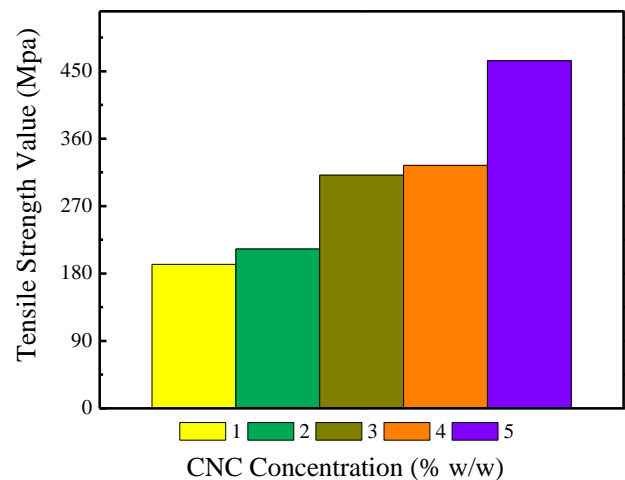


Figure 5. The Effect of the Addition of CNC Concentration on the Tensile Strength Value of Chitosan Film.

3.1.2. Nano chitosan-based film

Figure 6 shows that the addition of CNC concentration can increase the tensile strength of the nano chitosan film and generally decrease the flexural value of the film (Figure 7). The increase in the tensile strength value can be caused by a plasticizer, namely glycerol, which causes the molecules that make up the film to be dispersed better [17]. The elongation of the edible film is always inversely proportional to the tensile strength value. After all, the higher the force required to pull the edible film, the lower the elongation obtained.

Films with nano chitosan matrix provide lower strength than chitosan matrix due to agglomeration of nano-particles due to poor dispersion, thereby reducing the potential for increasing mechanical properties[15].

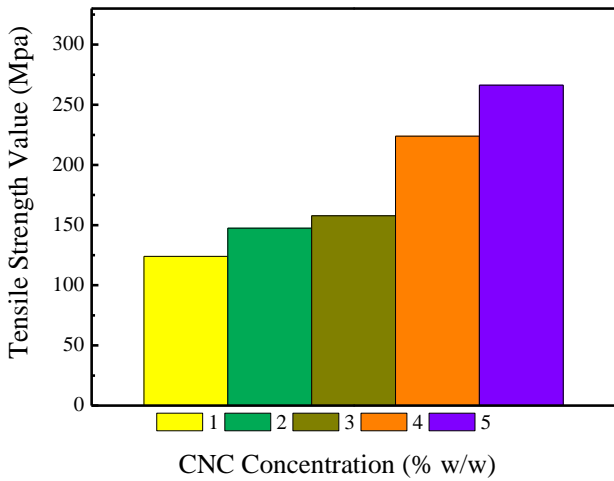


Figure 6. Effect of Addition of CNC Concentration on Tensile Strength Value of Nano Chitosan Film.

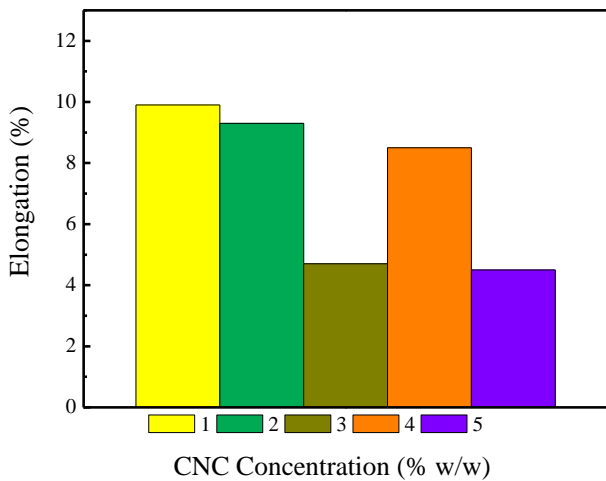


Figure 7. Effect of Addition of CNC Concentration on Flexibility of Nano Chitosan Film.

3.1.3. Composite Film with Active Content $KMnO_4$

The addition of active $KMnO_4$ content in chitosan film is functions as an ethylene absorber. That can be applied as a technique to inhibit the ripening rate of fruit. Therefore it is necessary to examine the effect of adding $KMnO_4$ to the strength of the chitosan composite film. In Figure 8, the addition of $KMnO_4$ into the film reduces the tensile strength of the film. In pure chitosan film, the addition of $KMnO_4$ decreased the strength from 195.2 Mpa to 167 MPa and decreased the composite strength of chitosan film from 464.1 Mpa to 263.5 MPa. In addition to lowering the film's tensile strength, the addition of $KMnO_4$ also affects the flexibility of the film.

From Figure 9, the film without $KMnO_4$ has the highest flexibility value. The addition of active $KMnO_4$ content in the chitosan film caused an

increase in the brittleness of the film. The bond formed between $KMnO_4$ and and chitosan may not be compatible, so that its strength is weakened. The more $KMnO_4$ added to the film; the more brittle the film will be [18].

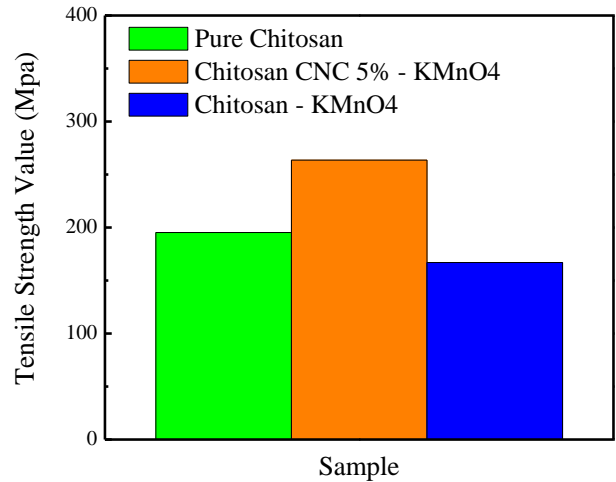


Figure 8. Tensile Strength Value of Composite Film with Active Content $KMnO_4$.

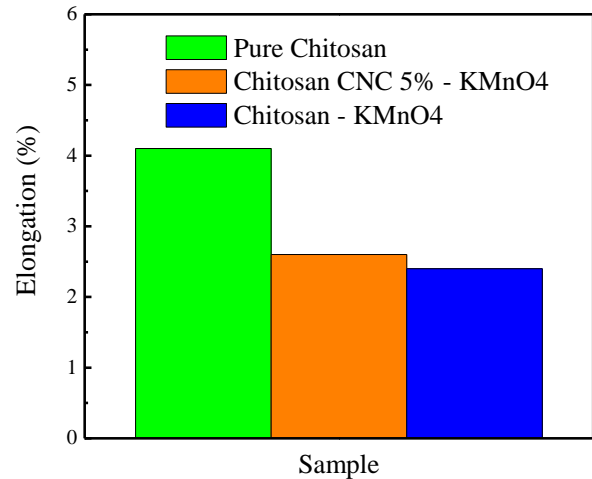


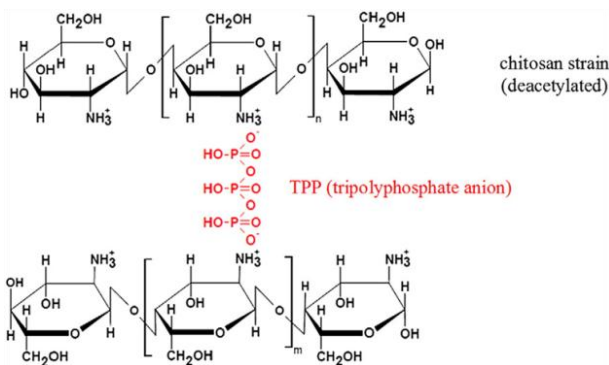
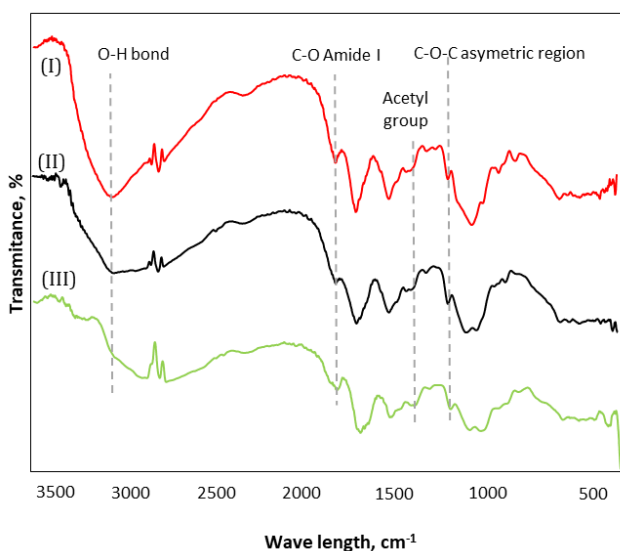
Figure 9. Flexibility Value of Composite Film with Active Content $KMnO_4$.

3.2. Inter-Molecular Interactions in Composites

FT-IR spectroscopy was performed to detect interactions between CNC nanofillers and chitosan nanoparticles in composite films (Figure 10) [4]. Each functional group obtained has an infrared absorption band characteristic at a specific wavenumber, thus obtaining a distinctive peak and identifying compound functional groups (Table 1).

Table 1. Typical vibration band for the infrared spectrum of chitosan [19]

Wave number, cm ⁻¹	Bonding type
3342	O-H Bond Strain
2895	C-H symmetrical strain
1645	C=O amide I Strain
1550	N-H amide II bond
1383	Acetyl
960 - 1100	C-O-C asymmetric stretching

**Figure 10.** The structure of the chitosan-TPP complex, cross-linked [20]**Figure 11.** FT-IR Spectrum, Chitosan (I), Chitosan-CNC (II), Chitosan-CNC-KMnO₄ (III).

The molecular framework and functional groups contained in cellulose and amino polysaccharides from chitosan are the same. Vibrations at 3057 cm⁻¹, 2776 cm⁻¹, 1419 cm⁻¹, 1152 cm⁻¹, and 1017 cm⁻¹ correspond to O-H bonds, symmetrical C-H stretching, asymmetrical C-H angle deformation, C

glycosidic bonds -O-C is asymmetric, and the CH angle deformation is asymmetric. Several peaks were observed to shift down the wavenumber. Such as from 3334 to 3057 cm⁻¹ corresponds to the O-H strain band, and from 1653 cm⁻¹ to 1652 cm⁻¹ for the C=O stretching vibration. Meanwhile, the signal around 1553 cm⁻¹ identified the bending vibration of NH amide II as becoming wider. A shift in wavenumber, intensity of reduction, or band widening confirms the presence of non-covalent interactions in the composite film [21]. Implies strong hydrogen bond is formed between Chitosan and CNC molecules to increase the mechanical strength of the Chitosan - CNC matrix composite. Figure 11(III) showed the functional groups of O-H with a wavelength of 3278, C-H with a wavelength of 2833; 1415; 899; 654, C=C with a wavelength of 1653; 1560, C-N with a wavelength of 1338; 1251, C-O with a wavelength of 1153, C-O-C at a wavelength of 1073, 1027. On the addition of KMnO₄, the C-O functional group appears at waves 1153,48.

4. CONCLUSION

In this experiment, the manufacture of an edible film based on chitosan nanoparticle composite as a polymer matrix and CNC as a particle stabilizer and reinforcing agent, glycerol as a filler. The nanoparticles were prepared by a simple ion cross-linking methodology using a TPP solution and high-speed homogenization (1000 rpm). The tensile strength test and flexibility (elongation at break) obtained optimum results at 5% CNC variables and 10% glycerol. In chitosan-based composite films, the maximum tensile strength value is 464.1 MPa. In chitosan nano-based films, the maximum tensile strength value is 266.3 MPa with an elongation at a break value of 4.5%. The addition of active content KMnO₄ 8% in the chitosan-based composite film resulted in a 46.3% decrease in the film's tensile strength from 464.1 MPa to 263.5 MPa. The FTIR results support evidence that some of the non-covalent interactions in the composite film between CNC and chitosan are highly effective.

REFERENCES

- Cornelia M, Syarief R, Effendi H, Nurtama B. Pemanfaatan Pati Biji Durian (*Durio zibethinus* Murr.) dan Pati Sagu (*Metroxylon* sp.) Dalam Pembuatan Bioplastik. *J Kim Kemasan*. 2013;35(1):20-9.
- Winarti C, Miskiyah, Widaningrum. TEKNOLOGI PRODUKSI DAN APLIKASI PENGEMAS EDIBLE ANTIMIKROBA BERBASIS PATI. *J Litbang Pertan*. 2012;31(3):2012.
- Murni SW, Pawignyo H, Widyawati D, Sari N. Pembuatan Edible Film dari Tepung Jagung (*Zea Mays* L.) dan

- Kitosan. In: Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia. Yogyakarta: Program Studi Teknik Kimia, FTI, UPN "Veteran" Yogyakarta; 2013. p. 1-9.
4. Venkatesan J, Kim S. Chitosan Composites for Bone Tissue Engineering — An Overview. *Mar Drugs*. 2010;8:2252-66.
 5. Mohanraj VJ, Chen Y. Nanoparticles - A review. *Trop J Pharm Res*. 2007;5(1):561-73.
 6. HASANZADEH KAFSHGARI M, KHORRAM M, KHODADOOST M, KHAVARI S. REINFORCEMENT OF CHITOSAN NANOPARTICLES OBTAINED BY AN IONIC CROSS-LINKING PROCESS. *Iran Polym J [Internet]*. 2011;20(5 (131)):445-56. Available from: <https://www.sid.ir/en/journal/ViewPaper.aspx?id=196713>
 7. Shu XZ, Zhu KJ. Chitosan/gelatin microspheres prepared by modified emulsification and ionotropic gelation. *J Microencapsul*. 2001;18(2):237-45.
 8. Tiyaboonchai W. Chitosan Nanoparticles: A Promising System for Drug Delivery. *Naresuan Univ J Sci Technol*. 2003;11(3):51-66.
 9. Pasquini D, Teixeira E de M, Curvelo AA da S, Belgacem MN, Dufresne A. Extraction of cellulose whiskers from cassava bagasse and their applications as reinforcing agent in natural rubber. *Ind Crops Prod*. 2010;32(3):486-90.
 10. Sudibyo A, F.Hutajulu T. Potensi penerapan polimer nanokomposit dalam kemasan pangan. *J Kim Kemasan*. 2013;35:6-19.
 11. Fernandes SCM, Freire CSR, Silvestre AJD, Neto CP, Gandini A, Berglund LA, et al. Transparent chitosan films reinforced with a high content of nanofibrillated cellulose. *Carbohydr Polym*. 2010;81(2):394-401.
 12. Henriette M.C. de Azeredo. Review: Nanocomposites for Food Packaging Applications. *Food Res Int*. 2009;42(9):1240-53.
 13. Khan A, Khan RA, Salmieri S, Tien C Le, Riedl B, Bouchard J, et al. Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. *Carbohydr Polym*. 2012;90:1601-8.
 14. Zhao L, Shi L, Zhang Z, Chen J, Shi D, Yang J, et al. PREPARATION AND APPLICATION OF CHITOSAN NANOPARTICLES AND NANOFIBERS. *Brazilian J Chem Eng*. 2011;28(03):353-62.
 15. Wardhono EY, Pinem MP, Kustiningsih I, Agustina S. Cellulose Nanocrystals to Improve Stability and Functional Properties of Emulsified Film Based on Chitosan Nanoparticles and Beeswax. *Nanomater Artic*. 2019;9(1707):1-17.
 16. American Society for Testing and Materials. ASTM D638-14, Standard Practice for Preparation of Metallographic Specimens. *ASTM Int*. 2016;82(C):1-15.
 17. Nurfajrin ZD, Mahendrajaya GS, Sukadarti S, Sulistyowati E. Karakterisasi dan Sifat Biodegradasi Edible Film dari Pati Kulit Pisang Nangka (Musa Paradisiaca L .) dengan Penambahan Kitosan dan Plasticizer Gliserol. In: Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia [Internet]. Yogyakarta: Program Studi Teknik Kimia, FTI, UPN "Veteran" Yogyakarta; 2015. p. 1-7. Available from: <http://jurnal.upnyk.ac.id/index.php/keuangan/article/view/501>
 18. Warsiki E, Sianturi J, Sunarti TC. EVALUASI SIFAT FISIS-MEKANIS DAN PERMEABILITAS FILM BERBAHAN KITOSAN PHYSICAL-MECHANICAL. *J Teknol Ind Pertan [Internet]*. 2011;21(3):139-45. Available from: <https://journal.ipb.ac.id/index.php/jurnaltin/article/view/4775>
 19. M FQ, KR M, DA S, GL S, HA R. Does the use of chitosan contribute to oxalate kidney stone formation? *Mar Drugs*. 2015;13(1):141-58.
 20. Kašpar O, Jakubec M, Štěpánek F. Characterization of spray dried chitosan-TPP microparticles formed by two- and three-fluid nozzles. *Powder Technol*. 2013;240:31.
 21. Gokila S, Gomathi T, Sudha PN, Anil S. Removal of the heavy metal ion chromium (VI) using Chitosan and Alginate nanocomposites. *Int J Biol Macromol*. 2017;104:1459-68.