Mechanical and barrier properties of Tapioca/PVA composite films reinforced with pineapple leaf nanocellulose

A Listyarini¹, V Fauzia¹, and C Imawan¹

¹Departemen Fisika, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Indonesia
Kampus Depok, Pondok Cina, Beji, Depok 16424 Indonesia

e-mail: cuk.imawan@sci.ui.ac.id

Abstract. Studies on mechanical and barrier properties of Tapioca/PVA composites reinforced with pineapple leaf nanocellulose have been done to obtain an alternative new biodegradable label for freshness label of smart packaging for food. The aim of this research is to investigate changes of mechanical and barrier properties of Tapioca/PVA/Nanocellulose compared with Tapioca/PVA composite. Composition of Tapioca/PVA was 50:50 with nanocellulose concentration vary from 1, 3, 6 and 10% in composites. Tensile strength and elongation were used to evaluate the mechanical properties of the films. While for water barrier properties was investigated by vapor transmission rate. The microstructure of the films was evaluated by using FT-IR, and SEM. The results showed that increasing the concentration of nanocellulose decreasing the tensile strength and elongation of composites. The concentration of 1% nanocellulose increased the WVTR and in greater amount will reduce the value of WVTR. Addition of nanocellulose decreased the transparency of the composite films. For further application, it can be used as a label for freshness label of smart packaging with the addition of functional material.

1. Introduction

The freshness indicator, as one of the smart packaging indicators, consists of functional material and a matrix. Functional materials can be synthetic dyes or natural dyes. The matrix for indicator labels can also be either synthetic or natural [1], [2]. Tapioca or cassava starch is one of the most inexpensive and renewable polysaccharide sources for biodegradable matrix label because it is abundant in nature. The film formation of pure starch has low mechanical properties and is relatively resistant to moisture compared to conventional synthetic polymers [3], [4]. Blending tapioca with other materials is one of the ways to produce material with good performance and increase the mechanical strength of starch. Polyvinyl alcohol (PVA) is a synthetic polymer that is non-toxic and soluble in water. PVA films have very good mechanical properties even though their resistance to water is very low. Blending starch and PVA has been reported to improve the physicochemical properties of materials [3]–[6].

However, the matrix label of the freshness label requires some modification of mechanical properties and barriers so that other compounds such as nanocellulose need to be added [7]–[9]. Nanocellulose has a high abundance in nature and can be found in various plants such as pineapple leaves[10]. Tapioca / PVA composite film with nanocellulose from pineapple leaf fiber is expected to be able to modify the mechanical properties and barrier of composite film. The aim of this research is to investigate changes of mechanical and barrier properties of Tapioca/PVA/Nanocellulose compared
with Tapioca/PVA composite in order to evaluate the possibilities of the film composites for use as a freshness label matrix.

2. Materials and Methods

2.1. Materials

The tapioca used in this study was produced by PT Budi Acid Jaya obtained from the local Indonesian market. PVA used is fully hydrolyzed with a molecular weight of about 60,000 g/mol from Merck, Germany. Nanocellulose from pineapple fiber is obtained from the Balai Besar Kimia dan Kemasan.

2.2. Methods

2.2.1. Preparation of Tapioca/PVA/nanocellulose Composites Films.

The tapioca solution (3 wt%) was obtained by dissolving 3 g tapioca powder in 97 g distillation water with continuous stirring at 90 °C for 2 hours. PVA solution (3 wt%) was prepared by dissolving 3 g PVA powder in 97 g distillation water with continuous stirring at 85 °C for 2 hours. Then, tapioca and PVA solutions with ratio 1:1 were mixed together with 300 rpm stirrer for 2 hours to form a homogeneous tapioca/PVA suspension. Nanocellulose with different weight percentages (1, 3, 6, and 10%) added to the tapioca/PVA solution. The solution was sonicated with an ultrasonic probe for 3 minutes to homogenize tapioca/PVA/ Nanocellulose composite solutions. Then they were poured into a flexy plate and then dried at 40 °C for about 18 hours. The Tapioca/PVA/nanocellulose films were marked as NC-x, where x is the content of percent nanocellulose in Tapioca/PVA/nanocellulose composites films.

2.2.2. Characterization

The UV–vis spectra of the Tapioca/PVA composites films were recorded using a UV-vis Genesys 10S spectrophotometer from Thermo Scientific.

Fourier transform infrared (FT-IR) analysis for Tapioca/PVA/NC composites films was conducted with a Thermo Nicolet spectrometer from 4000 to 500 cm⁻¹ at a spectral resolution of 4 cm⁻¹ using KBr method.

Water Vapor Transmission Rate (WVT) done according to ASTM E96 with some modifications.

Tensile tests were carried out according to ASTM D638 with a crosshead speed of 50 mm/min. The sample films were stored at 50% RH and 23 °C for 48 hours before testing.

3. Results and Discussions

![Image of composite films](image)

**Figure 1.** Picture of composite films of (a)Tapioca/PVA, (b)Tapioca/PVA with 1%, (c) 3%, (d) 6% and (e) 10% nanocellulose.

The presence of 1 to 6 % of nanocellulose in tapioca/PVA composites makes the film's transparency level decrease as shown in Figure 1. The transmission value of tapioca/PVA composite film was 86%. The transparency of the composite films with the addition of nanocellulose of 1% decreased to 75%. The concentration of nanocellulose of 1% in tapioca/PVA composites is not completely dispersed in the composite film, which causes the film to become opaque. But with the increasing concentration of nanocellulose above 2% in the composite film slowly increasing the
dispersion of the nanocellulose so that the transparency and transmission value of the composite film increases in the visible area. The transmission value of Tapioca/PVA composite film can be seen in Figure 2.

Figure 2. Transmission of Tapioca/PVA composite films with various concentrations of 0, 1, 3, 6 and 10% nanocellulose

Figure 3 shows the FTIR spectra of tapioca/PVA/nanocellulose composite films. The FTIR spectra of Tapioca/PVA film composites with nanocellulose, found the existence of a transmission peak located at 1427, 1333 and 1283 cm\(^{-1}\). These peaks were associated with vibration deformation of H-O-C and CH groups from nanocellulose. The existence of nanocellulose in Tapioca/PVA composites is proven by the existence of a transmission peak located at 1163 cm\(^{-1}\) and 1053 cm\(^{-1}\) which shows different types of C-O-C group vibrations from CNC. The transmission peaks at 1107 cm\(^{-1}\) from nanocellulose overlapping peaks at 1181 cm\(^{-1}\) and with peaks at 1085 cm\(^{-1}\) from Tapioca/PVA composites, forming wide peaks with maximum peaks at around 1090 cm\(^{-1}\) [9]. All these observations confirm the presence of nanocellulose in Tapioca/PVA composites.

Figure 4 show the value of Tapioca/PVA composite WVT with the addition of 0 – 10% concentration of nanocelluloses. Tapioca/PVA composite film without nanocellulose has a WVT value of around 27 g/(m2.day) and with the addition of nanocellulose by 1% in the composite film shows an increase in WVTR value to 49 g/(m2.day). Increasing the value of WVT is assumed because of its occurrence the nanocellulose agglomeration which can cause cracks or fractures. This crack or fracture is the way for water vapor to pass through the composite film [11]. The amount of nanocellulose of 3% in the composite film showed a decrease in WVT value to around 39 g/(m2.day). The WVT value then decreases with the increasing amount of nanocellulose in the composite to a WVT value of 22 g/(m2.day) on the 10% concentration of nanocellulose. The addition of nanocellulose to the film composite decreases the WVT value because the nanocellulose will provide a winding pathway for water molecules to pass through the composite film [12]. The decrease in WVTR value with addition of nanocellulose has been reported by Fahma et al., (2017) and Guimaraes, Botaro, Novack, Teixeira, & Tonoli (2015).
The effect of nanocellulose in Tapioca/PVA composite films on mechanical properties such as tensile strength and elongation is shown in Figure 5. Figure 5 show the value of tensile strength and elongation which decreases with the increasing concentration of nanocellulose in the composite. Tapioca/PVA composite film has a tensile strength value of 440 kgf/cm² which then decreased to 375 kgf/cm² at the 1% nanocellulose in the composite film. This tensile strength value continues to decrease up to 280 kgf/cm² when the concentration of nanocellulose is 10% in the composite film. Similarly, with the tensile strength, the elongation decreased by increasing the concentration of nanocellulose in the tapioca/PVA composite films. Tapioca/PVA composite has an elongation of 4% and with 10% concentration of nanocellulose in the composite films the elongation value reduced become 2.5%. The low performance of nanocellulose in the mechanical properties of this film composite may be due to the agglomeration of the nanocellulose which causes cracks and or fractures in the composite film microstructure [11].

Figure 6. SEM images of (a) Tapioca/PVA composite film and (b) Tapioca/PVA/nanocellulose composite.

Tapioca/PVA composite film with nanocellulose showed a roughness on the surface of the film due to the formation of aggregates/clusters of nanocellulose which in this case is nanofibrils [11], [14]. The morphology of this composite film as shown in the SEM image in figure 6. This aggregate has a wide
size distribution. However, the aggregate velocity and size are proportional to the amount of nanocellulose content in the composite film. Increasing the concentration of nanocellulose in Tapioca/PVA films will increase the formation of clusters so that there is a decrease in mechanical properties and barriers on film composites.

4. Conclusions

The addition of nanocellulose decreased the tensile strength and elongation of composites. The concentration of 1% nanocellulose increased the WVTR and in greater amount will reduce the value of WVTR. The experimental results showed the best percentage of nanocellulose in film composite for matrix of freshness label was 3%. For further application, it can be used as a label for freshness label of smart packaging with the addition of functional material.

Acknowledgement

This research was financially supported by the Kementerian Riset, Teknologi dan Pendidikan Tinggi Republik Indonesia through the Hibah Penelitian Disertasi Doktor Tahun Anggaran 2019 (No: NKB-1830/UN2.R3.1/HKP.05.00/2019). The authors acknowledge Balai Besar Kimia dan Kemasan for the nanocellulose materials.

5. References

[1] M. Vanderroost, P. Ragaert, F. Devlieghere, and B. De Meulenaer, 2014 Trends Food Sci. Technol. 39 1 47
[2] M. Ghaani, C. A. Cozzolino, G. Castelli, and S. Farris, 2016 Trends Food Sci. Technol. 51 1 20
[3] B. Ramaraj, 2007 J. App Polym Sci 103 909
[4] A. Cano, J.M. Kenny, A. Chiralt and C. Gonzales, Food Packag. Shelf Life 2016 10 16
[5] M. Teodorescu, M. Bercea, and S. Morariu, 2018 Polymer Reviews 58 2 247
[6] X. Tang and S. Alavi, 2011 Carbohydr. Polym. 85 1 7
[7] Y. Aitomäki and K. Oksman, 2014 React. Funct. Polym. 85 151
[8] K. Y. Lee, Y. Aitomäki, L. A. Berglund, K. Oksman, and A. Bismarck, 2014 Compos. Sci. Technol. 105 15
[9] M. Popescu, B. Dogaru, M. Goanta, and D. Timpu, 2018 International Journal of Biological Macromolecules 116 385
[10] Y. Habibi, L. A. Lucia, and O. J. Rojas, 2010 Chem. Rev. 110 6 3479
[11] M. Guimaraes, V. R. Botaro, K. M. Novack, F. G. Teixeira, and G. H. D. Tonoli, 2015 Ind. Crops Prod. 70 72
[12] X. Ma, P. R. Chang and J Yu, 2008 Carbohydr. Polym 72 369
[13] F. Fahma, Sugiarto, T. C. Sunarti, S. M. Indriyani, and N. Lisdayana, 2017 Int. J. Polym. Sci., 2017 1
[14] Z. Jahan, M. B. K. Niazi, and Ø. W. Gregersen, 2018 J. Ind. Eng. Chem. 57 113