Thermoplastic starch-PVA-cellulose nanocomposite film for extending the shelf life of red chili

Farah Fahma12*, Opal Priya Wening1, Nurmalisa Lisdayana1, Purwoko1, Sugiar1

1Department of Agroindustrial Technology, IPB University, Indonesia
2Surfactant and Bioenergy Research Center, IPB University, Indonesia
*Corresponding author: farah_fahma@apps.ipb.ac.id

Abstract. The objective of this study was to evaluate the effectiveness of TPS-PVA-cellulose nanocomposite film for extending the shelf-life of fresh red chili. In this study, cellulose nanofibers were isolated from oil palm empty bunches by combination of ultrafine grinding and ultrasonification. Thermoplastic starch-PVA-cellulose nanocomposites were produced by solvent evaporation casting method. The resulting nanocomposite films were applied for packaging of red chili at chilled and ambient temperatures. The different storage temperature generated different physical and mechanical properties of the obtained nanocomposite films. The red chili packed in nanocomposite films and stored at ambient temperature was able to maintain its quality for 12 days, while at chilled temperature the red chili looked fresh up to 15 days.

Keywords: nanocomposite, cellulose nanofiber, thermoplastic starch, red chili, shelf life.

1. Introduction

Packaging plays an important role in maintaining the quality of a product by providing protection from the chemical and biological agents as well as physical disruptions in the environment. However, the use of petroleum-based polymer packaging negatively impacts for many years, such as the low degradation rate, the chemical migration, and non-renewable. It brings the spirit to explore the biopolymer production from the renewable, economical, and abundant materials, so that it potentially becomes the future packaging material.

Thermoplastic starch (TPS) has attracted much attention because it can flow when heated above a melting or vitrification temperature. Nevertheless, its structures are more complex than those of synthetic thermoplastics [1]. The characteristics of TPS are influenced by the chemical components of amylose and amylopectin. The high amylose content provides the more flexible of TPS properties [2]. The TPS film has many disadvantages, namely low physical-mechanical properties, not resistant to high temperature, brittle and hydrophilic [3]. Films produced from polysaccharide-based materials such as starch also tend to have a highly sensitive OTR (oxygen transmission rate) to moisture [4]. The TPS films were successfully prepared by casting method with cellulose nanofibers as reinforcement agent and glycerol as plasticizer. The addition of cellulose nanofibers up to 3 wt% was able to increase tensile strength and decrease the water vapor transmission rate (WVTR) of the TPS films [5]. Increased barrier properties are the most important applications in the food industry. Polymer composites are also stronger, more flame resistant, and have better thermal properties (such as melting
point, degradation and glass transition temperatures) than control polymers that do not contain nanosized fillers [4].

Cellulose is a natural polymer with abundant amounts in nature. Cellulose consists of β-D-glucopyranosyl repeating units joined by (1→4) glycosidic linkages [6]. We have already succeeded to isolate nanocellulose from oil palm empty fruit bunches (OPEFBs), coconut husk, sugar palm fiber (ijuk), and pineapple leaf [7,8,9,10].

Red chili (Capsicum annum) is one of the important horticultural commodities for the community of Indonesia, both to meet the daily needs as a complement to seasoning and the needs of the food or drugs industry. The red chili is one source of antioxidants and is rich in vitamins A and C, minerals and other photochemicals [11]. Important quality attribute of Capsicum is color and pungency. The pungency is one of five main tastes sensory, caused by capsaicinoids compounds. Two major capsaicinoids are capsaicin and dihydrocapsaicin [12,13]. During storage, the colorand pungency loses gradually. The color deterioration of red chili is because of the oxidative degradation of carotenoids [12].

The objective of this study was to evaluate the effectiveness of TPS-PVA-cellulose nanocomposite film on extending the shelf-life of fresh red chili. Some analysis such as shrinkage weight, firmness, color brightness were performed. The study on the application of TPS-PVA with the addition of cellulose nanofibers for food packaging has not been reported previously.

2. Experimental Procedures

2.1. Materials
OPEFBs as the source of cellulose nanofibers were supplied by PTPN VIII, Kertajaya, Lebak, West Java, Indonesia. Corn starch and fresh red chili was purchased from traditional market. Polyvinyl alcohol (PVA) (produced by Celvol™ Sekisui Chemical Co.ltd), glycerol (commercial grade product), NaOH, H₂O₂, and other chemicals were used as received without any further purification.

2.2. Preparation of cellulose from OPEFBs
Cellulose from OPEFBs was prepared by delignification treatment using NaOH and bleaching treatment using H₂O₂. In the delignification treatment, OPEFBs were cut into small pieces, soaked in 10 wt% NaOH solution at 100 °C for 60 min and followed by the washing treatment until pH neutral. Then, in bleaching treatment, the alkali-treated fibers were soaked in 30 wt% H₂O₂ solution at 85 °C for 4 h and continued with the rinsing treatment until pH neutral.

2.3. Preparation of cellulose nanofiber
Cellulose nanofibers were prepared as described in detail in our previous study [5]. Cellulose nanofibers were isolated by mechanical treatment using the combination of ultrafine grinding and ultrasonication. The cellulose fibers were diluted to form a suspension with a solid concentration of 2 wt%. The suspension was then passed 65 times through ultrafine-grinder at 1500 rpm. Then, the obtained thick suspension was ultrasonicated at 80% amplitude for 50 min gradually. Finally, cellulose nanofibers were obtained.

2.4. Production of TPS-PVA-cellulose nanocomposite film
TPS-PVA-cellulose nanocomposite films were produced by evaporation solution casting method. Starch and PVA were mixed with a ratio of 4:1 (w/w). Then, glycerol was added into the mixture as much as 25%. Cellulose nanofibers 3 wt% was added to the whole mixture and homogenized at 90 ±5
°C at 500 rpm for 20 min. TPS-PVA-cellulose nanocomposite films were molded using mold with 0.2 cm thickness and dried at 50 °C for 12 h.

2.5. Application of TPS-PVA-cellulose nanocomposite film as red chili packaging
Fresh red chilies were sorted according to size, red colour, no overripe, free from microbial infection or insect infestation, and no mechanical damage, splitting or cracking. They were weighed and packaged in nanocomposite films as shown in Figure 1. Then, packaged-red chilies were stored at chilled and ambient temperatures for 3, 6, 9, 12, and 15 days. Unpackaged and polypropylene films packed red chilies were used as control samples.

![Image of red chili in nanocomposite film packaging](image.png)

**Figure 1.** Red chili in nanocomposite film packaging

2.6. Characterization
The morphology of cellulose nanofibers was observed with SEM (Scanning Electron Microscopy) (SEM Zeiss EVOMA 10) operated at 16 kV. Diameter of fifty nanofibers in SEM image were randomly selected and measured using ImageJ software. The crystallinity of obtained cellulose nanofibers was analyzed using X-ray diffraction (XRD) using XRD Bruker D8 with the radiation of KαCu (λ= 1.54060) operated at 40 kV and 35 mA. The mechanical properties of nanocomposite films were analyzed using universal testing machine (Instron) with a sample size of 45 mm × 20 mm × 40 μm. The measurement was performed at crosshead speed of 3 mm/min.

The percentage of weight loss was calculated from the weight decreasing during storage. The percentage of weight loss was calculated using the following equation.

\[
\text{percentage of weight loss (\%) = } \left( \frac{W_t - W_0}{W_0} \right) \times 100\%
\]

\[W_0\] = initial weight (g)
\[W_t\] = the weight after stored (g)

Water Vapor Transmission Rate (WVTR) of nanocomposite films was determined by gravimetric method. The nanocomposite film was cut to the size of 20 mm x 20 mm and conditioned in a desiccator for 24 h. Then, the nanocomposite film was laid on the top of small container and tied firmly. The ¾ of container volume was filled with silica gel. The sample was then stored in a water-
filled desiccator and the RH desiccator was maintained at 90-99% and 30 °C. The samples were weighed at room temperature periodically to determine the amount of water vapor that enters from outside into the container through a nanocomposite film (WVTR). The WVTR value was calculated by using the following equation.

\[ \text{WVTR} = \frac{\Delta M / t}{A} \]  

\( \text{WVTR} \) = water vapour transmission rate (g/m².24 hours = g/m².day)  
\( \Delta M \) = mass difference of container (g)  
\( t \) = time (24 h = a day)  
\( A \) = area of nanocomposite film surface (m²)

Chili firmness was measured using a penetrometer. The measurement was performed at 3 different points (base, middle, and end). The probe was pushed into red chili for 5 sec.

Red chili surface colour was measured by chromameter (Minolta CR-310). The values of \( a^* \) and \( b^* \) were converted into the chromatic units of \( C^* \) and Hue angle (°hue). The value of \( C^* \) and \( \theta \text{hue} \) was calculated by using the following equation.

\[ C^* = \sqrt{a^{*2} + b^{*2}} \]  
\[ \theta \text{hue} = \tan^{-1} \frac{b^*}{a^*} \]

The \( a^* \) value indicates the level of redness or greenness, and the \( b^* \) value yellowness or blueness.

3. Results and Discussion

3.1. Morphology and crystallinity of cellulose nanofibers

The morphology of cellulose nanofibers is shown in Figure 2. The resulting cellulose nanofibers had a diameter of 26 ± 3.54 nm. Meanwhile, XRD profiles of cellulose and cellulose nanofiber of OPEFBs are shown in Fig. 3. The crystallinity of cellulose and cellulose nanofibers obtained was of 54.3 % and 60.2 %, respectively. The crystallinity of obtained cellulose was consistent with, while the crystallinity of obtained nanofibers was higher than those of reported by Fahma et al. [7] which was isolated from the same source (OPEFBs) and by sulfuric acid hydrolysis.
Figure 2. Cellulose nanofibers from OPEFBs

Figure 3. XRD profile of cellulose nanofibers from OPEFBs
3.2. TPS-PVA-cellulose nanocomposite films

3.2.1. Mechanical properties
Tensile strength and elongation at break of nanocomposite films stored at different time and temperature are shown in Figure 4. The tensile strength and elongation at break of unstored nanocomposite films were 22.50 ± 0.39 MPa and 16.44 ± 1.74 %, respectively. The tensile strength of nanocomposite films stored at chilled temperature was lower than those at ambient temperature. During 15 days of storage, the tensile strength and elongation at break of nanocomposite films did not change significantly since before films were stored, tended to be constant at both storage temperature. The elongation at break of nanocomposite film at chilled temperature was higher than those of at ambient temperature.

![Figure 4. Tensile strength and elongation at break of nanocomposite films stored at different time and temperature](image)

3.2.2. Water Vapor Transmission Rate (WVTR)
WVTR of nanocomposite films at different storage time and temperature is shown in Figure 5. The WVTR of un-stored nanocomposite film was 13.70 ± 3.54 gH₂O/m².day. Figure 5 shows that storage temperature gave a significant effect to WVTR of nanocomposite films.

![Figure 5. WVTR of nanocomposite films at different storage time and temperature](image)
WVTR of nanocomposite films in chilled temperature was lower than those of at ambient temperature. This showed that at chilled temperature water vapor penetrated into nanocomposite film less than those of at ambient temperature. The water vapor permeability of packaging might be affected by the crystalline structure of packaging. At chilled temperature, the structure of crystal bonding strengthened so that it was more resistant to water vapor permeability. The difficulty of water vapor penetration into obtained nanocomposite films was caused by the strong hydrogen bonding between cellulose nanofibers and TPS-PVA matrix. The cellulose nanofibers caused the changes in diffusion path of water vapor into the film from direct path into tortuous path, inhibiting the penetration of water vapor through the film [14].

3.3. Weight loss and firmness of red chili
Weight loss in fresh fruits and vegetables is mainly due to the loss of water caused by transpiration and the respiration processes. This is the main cause of quality deterioration [15]. The weight loss of red chili stored at chilled and ambient temperatures are shown in Figure 6. At chilled temperature, all packaging type showed the same trend of weight loss of red chili, less than 20%. At ambient temperature, the weight of un-packed red chili dropped significantly until 12 days. Meanwhile, the obtained nanocomposite film was able to maintain the weight loss of red chili similar with that of polypropylene film until 12 days. After 15 days, the weight loss of red chili packed in nanocomposite film was higher than that of polypropylene film. This might be because cellulose nanofibers could not influence the physical and mechanical properties of obtained composite strongly so it did not compensate the ability of polypropylene films. In addition, the original properties of TPS-PVA matrix to maintain the weight loss of red chili were lower than that of polypropylene film. Our previous results showed that the addition of nanocellulose was effective in providing physical barrier to remove dehydration moisture. The presence of cellulose nanofibers was thought to increase tortuosity in TPS-PVA films so that the process of water vapor diffusion became slower [5].

![Figure 6. Weight loss of red chili stored at chilled (left) and ambient (right) temperatures](image)

3.4. Firmness of red chili
Another key factor in determining the deterioration of fruit and vegetable quality is the softening rate, which is usually represented by firmness [15]. The firmness of red chili stored at chilled and ambient temperatures are shown in Figure 7. During both storage temperatures, the firmness of red chili occurred in all treatments with different rate. The storage temperature gave a real effect on the firmness of red chili until 15 days. The nanocomposite films at both storage temperatures were able to keep firmness of red chili with the similar ability of polypropylene films. The structure of chili would be softened and wrinkled after 15 days of storage at temperature of 20-29 °C.
3.5. Lightness of Red Chili
The initial value of L* of red chili was 36.81 ± 0.23 N. The lightness of red chili packed at chilled and ambient temperature are shown in Figure 8. The lightness of red chili packaged in the polypropylene films and the nanocomposite films tend to be higher compared to those of un-packed red chili. The red chili packed in nanocomposite film for 15 days had the highest firmness. However, the polypropylene film had the ability to maintain the lightness of red chili more stable at chilled temperature than that of at ambient temperature. The storage at chilled temperature could suppress water evaporation, so that lightness of red chili could be maintained.

3.6. Color assessment
The value of C* of unstored fresh red chili was 18.97 ± 2.18. The chroma values of red chili stored at chilled and ambient temperatures are shown in Figure 9. The chroma value tended to decrease with increasing the storage time. Based on the figure, the chroma value was influenced by the storage temperature. Red chili stored at chilled temperature tended to have chroma higher than that of ambient temperature. The nanocomposite films were able to maintain the chroma value of red chili more than those of un-packed and polypropylene films. The change rate of chroma value (C*) and °hue at chilled temperature was slower than those of at ambient temperature.
Figure 9. Chroma of red chili stored at chilled (left) and ambient (right) temperatures

Hue angle (°h) is the colour combination of red, yellow and green indexes in the Cartesian diagram. The hue value of un-stored red chili was 22.75 ± 0.74°. The hue values of red chili packed at chilled and ambient temperatures are shown in Figure 10. Based on figure, the hue value of red chili was not influenced by the storage temperature. All hue value of red chili stored at both storage temperature and packed in different packaging decreased with the similar trend.

Figure 10. Hue angle of red chili stored at chilled (left) and ambient (right) temperatures

4. Conclusion
Red chili which was unpacked and packed in polypropylene and nanocomposite films showed different physical properties (weight loss, firmness and color). Red chili packed in nanocomposite film for 12 days at ambient temperature showed the similar physical properties with that of in polypropylene film. Meanwhile, the similar physical properties of red chili packed in nanocomposite and in polypropylene films could be maintained until 15 days. The quality of unpacked red chili was lower than that of packed in nanocomposite and polypropylene films.

Acknowledgments
This work was supported by Direktorat Riset dan Pengabdian Masyarakat, Ditjen Penguatan Riset dan Pengembangan, Ministry of Research and Technology of the Republic of Indonesia (HIKOM scheme, grant number: 5621/IT3.11/PN/2017).
References
[1] R. Shanks and I. Kong 2012 Thermoplastic Starch. in ‘Thermoplastic Elastomers’ (ed.: El-Sonbati A.) InTech.
[2] K. Krogars, J. Heinamaki, M. Karjalainen, J. Rantanen, P. Luukkonen, and J. Yliruusi 2003 Development and characterization of aqueous amylose-rich maize starch dispersion for film formation. *Eur. J. Pharmaceut. Biopharmaca*. 56, 215–221.
[3] J.A. Mbey, S. Hoppe, and F. Thomasa 2012 Cassava starch-kaolinite composite film. Effect of clay content and claymodification on film properties, *Carbohydr. Polym.* 88, 213-222.
[4] T.V. Duncan 2011 Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors, *J. Coll. Inter. Sci.* 363, 1–24.
[5] F. Fahma, Sugiaro, T. C. Sunarti, S. M. Indriyani, and N. Lisdayana 2017 Thermoplastic Cassava Starch-PVA Composite Films with Cellulose Nanofibers from Oil Palm Empty Bunches as Reinforcement Agent, *Int. J. Polym. Sci.* https://doi.org/10.1155/2017/2745721.
[6] M.M. De Souza Lima and R. Borsali 2004 Rodlike Cellulose Microcrystals: structure, properties, and applications, *Macromol. Rapid. Commun*. 25, 771–787.
[7] F. Fahma, S. Iwamoto, N. Hori, A. Iwata, and A. Takemura 2010 Isolation, Preparation, and Characterization of Nanofibers from Oil Palm Empty Fruit Bunch (OPEFB), *Cellulose*. 17, 977-985.
[8] F. Fahma, S. Iwamoto, N. Hori, A. Iwata, and A. Takemura 2011 Effect of pre-acid-hydrolysis treatment on morphology and properties of cellulose nanowhiskers from coconut husk, *Cellulose*.18, 443–450.
[9] F. Fahma, S. Iwamoto, N. Hori, A. Iwata, and A.Takemura 2016 Cellulose nanowhiskers from sugar palm fibers, *Emir. J. Food. Agric.* 28, 566–571.
[10] K. Wahyuningsih, E.S. Iriani, and F. Fahma 2016 Utilization of cellulose from pineapple leaf fibers as nanofiller in polyvinyl alcohol-based film, *Indonesian J. Chem.* 16, 181-189.
[11] A. Fudholi, M.Y. Othman, M.H. Ruslan, and K. Sopian 2013 Drying of Malaysian *Capsicum annuum* L. (Red Chili) Dried by Open and Solar Drying, *Int. J. Photoenergy*. https://doi.org/10.1155/2013/167895.
[12] A. Nawab, F. Alam, M.A. Haq, M.S. Haider, Z. Lutfi, S. Kamaluddin, and A. Hasnain 2018 Innovative edible packaging from mango kernel starch for the shelf life extension of red chili powder, *Int. J. Biol. Macromol*. 114, 626-631.
[13] M.M. Wall and P.W. Bosland 1998 Analytical methods for color and pungency of chiles (capsicums), In Instrumental Methods in Food and Beverage Analysis (ed(s).: D.L.B. Wetzel and G. Charalambous) Elsevier Science, vol 39, 347-373.
[14] N.S. Lani, N. Ngadi, A. Johari,and M. Jusoh 2014 Isolation, Characterization, and application of nanocellulose from oil palm empty fruit bunch fiber as nanocomposites. *J. Nanomater*. (2014). https://doi.org/10.1155/2014/702538.
[15] F. Dong, S. Li, C. Jin, Z. Liu, K. Zhu, H. Zou, and X. Wang 2015 Effect of nanocellulose/chitosan composite coatings on cucumber quality and shelf life. *Toxicol. Environ. Chem*. https://doi.org/10.1080/02772248.2015.1123488