Preparation of Nanocellulose Bioplastic with a Gradation Color of Red and Yellow

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Abstract. A bioplastic derived from nanocellulose isolated from the pine flower (Pinus Merkusii) waste has been made. The red and yellow colors of bioplastic were afforded from the extract of dragon fruit and turmeric. Meanwhile, nanocellulose was hydrolyzed by citric acid using concentrations of 10%, 30%, and 60%, and obtained crystallinity index of 61.00%, 57.24%, and 52.82% respectively. Each nanocellulose applied has a crystallite size of 15.09 nm (calculated using XRD data with Scherrer’s equation). The result indicated that the increase in both dragon fruit and turmeric extracts concentration increase the red and yellow color intensity of the bioplastic. This study paves the way for further application of nanocellulose in bioplastic.

1. Introduction

The increasing of plastic used in recent time brings a negative impact on human life. The main raw material for plastic comes from petroleum which is increasingly scarce and not sustainable. The European Council has demonstrated the need to reduce dependence on the use of fuel and gas to create sustainable energy. In addition, the use of plastic as food packaging such as plastic teabags can transfer various microparticles and nanoparticles to food, causing adverse effects on human health [1]. Therefore, an alternative raw material is needed to create environmentally, friendly, and biodegradable plastic with the same strength as petroleum-derived plastics. In addition, biodegradability is one of important properties needed in various bioplastic applications such as food packaging to reduce polymer-based waste from oil [2].

Bioplastics have emerged as substitutes for polymeric materials. It can be made using natural ingredients such as starch. Based on previous research, bioplastics can be made using starch, nanocellulose, and plasticizers [3]. Nanocellulose is the most effective material as a biopolymer matrix to improve the performance of bio-based materials [4]. Nanocellulose has the same backbone as cellulose in hydrolysis process [5]. Previously, Rambabu et al. [6] reported pine flower contains 44 wt% cellulose and 22 wt% lignin. Phenolic compounds in pine flower have been widely developed as starting material for industrial chemicals [7-8]. However, cellulose contained in pine flower is still rarely used. Dragon fruit and turmeric are natural dyes used as coloring additives in bioplastics [9]. The addition of dyes to bioplastics makes it more interesting for food packaging. The purpose of this study is determine the color results obtained in bioplastics from pine flower nanocellulose using natural dyes from dragon fruit and turmeric extracts also their further application in bioplastics.
2. Material and Methods

2.1. Materials
The sample used in this study was Merkusii Pine flower waste obtained from Coban Rais area, Batu, East Java, Indonesia. Chemicals used were sodium hydroxide (Merck), sodium hypochlorite 12% w/v (technical grade), citric acid 99-102% (SMART-LAB), polyvinyl alcohol (Merck), cassava, glycerol, turmeric, dragon fruit, and aquades. Equipment used in this study included: glassware, oven (MEMMERT), ultrasonicator (DELTA D150H), magnetic stirrer, hot plate, grinder, and analytical balance (Ohuas Pioneer PA214).

2.2. Procedures

2.2.1. Sample Preparation of Pine Flower. Sample preparation was in accordance with reported procedure [6] with modifications. Pine flowers were soaked in hot water at 100° C for 2 h, washed and dried for 24 h at 50° C. The pine flowers were grounded and soaked in hot water for 4 h then roasted for 24 h at 60° C.

2.2.2. Sample Isolation from Pine Flower. At this stage, cellulose isolation from pine flower was in accordance with references [6,10] with modifications. A total of 50 g of grounded pine flower was taken into a 1000 ml beaker and 500 mL of 6% NaOH was added. The ratio of pine flower powder and NaOH solution was 1:10 (v/v). The mixture was then heated at 70 ᵒ C for 4 h. After extraction, the mixture of NaOH solution and pine flower powder was washed to neutral pH. A total of 50 g of pine solid resulted from the process of alkalization underwent bleaching process using 6% sodium hypochlorite solution as much as 500 mL. Then it was heated at 70 ᵒ C for 2 h. This process was repeated until white cellulose was produced. The solid formed was filtered and washed with distilled water to obtain neutral pH. The cellulose obtained was then dried in an oven at 30-50 °C until constant weight was obtained. The dried cellulose was blended and filtered.

2.2.3. Synthesis of Nanocellulose. Cellulose isolated from pine flower waste was synthesized to obtain nanocellulose referring to procedures [5,10] with modification. Five grams of cellulose from the isolated pine flower waste was added with 10%, 30%, and 60 % citric acid in 100 ml respectively. Ultrasonication was prepared at the temperature of 45 °C. After the temperature reached 45 °C, the sample was taken into the ultrasonication reactor for 60 mins. The reaction was stopped by the immersion of the reactor in a water bath containing cold distilled water followed by drying process using the oven at a temperature of 30-50 °C.

2.2.4. Preparation of Natural Dye. 200 g of fresh turmeric and dragon fruit respectively, was peeled and washed with clean water and followed by drying in an oven at 30 °C for 30 mins. The extract was obtained using juice extractor without additional water. The extract was then filtered and centrifuged at 2000 rpm for 15 mins. Each extract was carried out by varying concentrations of 5%, 15%, and 25% (v/v) [11].

2.2.5. Synthesis of Starch-based Bioplastic using Natural Dye. The starch-based bioplastic synthesis procedure was in accordance with reports by [12,13] with modification. Polyvinyl alcohol (PVA) solution was prepared by mixing 4% PVA, 25% glycerol, and 71% distilled water (w/w) in 500 rpm stirrer at 80 °C for 1 h. The starch solution was made by mixing 3% starch (cassava), 12% glycerol and 85% distilled water (w/w) in a stirrer of 500 rpm at 80 °C for 15 mins. Both solutions were mixed with PVA: starch ratio of 80:20 (w/w) and 500 rpm sterilizer at 80 °C for 10 mins. The resulting mix was then added with 1% nanocellulose, 10% turmeric extract and 10% natural dragon fruit extract with a concentration of 5%, 15%, and 25% (v/v).
2.3. Characterization

2.3.1. X-ray Diffractiometry (XRD) Analysis. The nanocellulose was analyzed by X-ray diffraction (XRD) Merk PanAnalytical type Expert Pro ranging from 10° to 90° with Cu K radiation (1.5406) at room temperature. The crystallinity index (CrI) of the nanocellulose was determined by Seghal’s method equation (1) and the crystallite size (Dhkl) was determined by Scherrer equation (2) [14,15].

\[ CrI = \frac{(I_{tot} - I_{amorph})}{I_{tot}} \times 100\% \]  

(1)

\[ Dhkl = \frac{0.9\lambda}{\beta\cos\theta} \]  

(2)

2.3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. The FTIR spectra of pine flower was recorded using Fourier Transform Infrared (FTIR) Spectrometer SHIMADZU 8400s. The samples were measured in the wavenumber range 4000-400 cm\(^{-1}\) using KBr pellet method.

3. Result and Discussion

3.1. Synthesis of Nanocellulose
Citric acid was used for chemical hydrolysis of cellulose from pine flowers as lignocellulosic waste. Nanocellulose hydrolysis produced in the form of yellowish white powder shown Figure 1. The yields obtained from nanocellulose hydrolysis using citric acid with concentrations of 10%, 30%, and 60% were 95.6%, 94.6%, and 93.4%, respectively.

![Figure 1. Nanocellulose products. (a) CA 10, (b) CA 30, (c) CA 60.](image)

3.2. Characterization of Nanocellulose using FTIR
The transmission of infrared spectrum on hydrolyzed nanocellulose using citric acid with varying concentrations (CA 10, CA 30, CA 60) is presented in Figure 2. The peaks were interpreted as following: presence of broad peak at 3433 cm\(^{-1}\) wave number for O-H stretching, the peak at 2962 cm\(^{-1}\) for C-H aliphatic stretching, and the peak at 1692 cm\(^{-1}\) of vibrations for C=C lignin [6,16]. The peak at 1160 cm\(^{-1}\) can be ascribed to C–O–C asymmetric stretching of lignin, hemicellulose, and cellulose [4].
3.3. Characterization of Nanocellulose using XRD

X-ray diffraction analysis for hydrolyzed nanocellulose using citric acid (CA 10, CA 30, CA 60) is shown in Figure 3. The XRD pattern results showed that in the case of nanocellulose from the pine flower, there were three intense peaks observed at the diffraction angle (2θ) = 15°, 22.5°, and 34°, in accordance to the crystalline cellulose [1].

Hydrolysis with acids not only able to remove the amorphous portion of cellulose but also damage the crystalline regions [17]. The increase of citric acid concentration in the hydrolysis process damage the crystalline area of the nanocellulose as shown in Table 1.
### Table 1. Result of XRD pattern of nanocellulose.

| Sample | Peak 2θ | CI (%) | Crystallite Size |
|--------|---------|--------|------------------|
| CA 10  | 22.40   | 61.00  | 15.09 nm         |
| CA 30  | 22.50   | 57.24  | 15.09 nm         |
| CA 60  | 22.55   | 52.82  | 15.09 nm         |

#### 3.4. Synthesis of Starch-based Bioplastics

Bioplastic color gradations were made using extracts of natural dyes which are turmeric and dragon fruit. According to the result in Figure 4, the increase in both dragon fruit and turmeric extracts concentration also increase the red and yellow color intensity of the bioplastic.

![Figure 4. Gradation color of bioplastic using turmeric extract in various concentration (a) 5% (b) 15% (c) 25%, and dragon fruit extract in various concentration (d) 5%, (e) 15%, (f) 25%.

#### 4. Conclusion

In conclusion, bioplastics were produced from pine flower waste and showed promising result. By using natural additive dyes, it is possible to ensure the utilization of pine flower waste for bioplastic as food packaging which is harmless to the environment.

#### 5. Acknowledgement

The research is supported by Penelitian Dasar Unggulan Perguruan Tinggi (2019) from DRPM of Ministry for Research, Technology and Higher Education of Indonesian. The authors gratefully acknowledge the contributions of Mr. Widji Sulistjo and Mr. Hadi Kurniawan.

#### References

[1] Henrique M A Neto F W P Silvério H A Martins D F Gurgel L V A Barud H and Pasquini D 2015 Industrial Crops and Products 76 128–140
[2] Muñoz-Bonilla A Echeverria C Sonseca A Arrieta M P and Fernández-García M 2019 Materials 12 641
[3] Agustin M B Ahmmad B Alonzo S M M and Patriana F M 2014 Journal of Reinforced Plastics and Composites 33 2205–13.
[4] Soykeabkaew N Tawichai N Thanomsilp C and Suwantong O 2016 Walailak Journal of Science and Technology 14 353-368
[5] Shaheen T I and Emam H E 2018 *International Journal of Biological Macromolecules* **107** 1599–1606
[6] Rambabu N Panthapulakkal S Sain M and Dalai A K 2015 *Industrial Crop and Product* **10** 1-9
[7] Masruri M and Pamungkas KK 2019 *IOP Conference Series: Materials Science and Engineering* **546** 042023
[8] Masruri M, Amini R W and Rahman M F 2016 *Indonesian Journal of Chemistry* **16** 59-64
[9] Putra E P D Thamrin E S and Saputra H 2019 *IOP Conference Series: Earth Environment Science* **258** 012047
[10] Liu C Li B Du H Lv D Zhang Y Yu G Mu X and Peng H 2016 *Carbohydrate Polymers* **151** 716–724
[11] Maizura M Aminah A and Wan Aida W M 2011 *International Food Research Journal* **18** 529-534
[12] Alashwal B Y Saad B M Gupta A Sharma S and Mishra P 2019 *Journal of King Saud University – Science* **31** 5
[13] Guimarães M Botaro V R Novack K M Teixeira F G and Tonoli G H D 2015 *Industrial Crops and Product* **70** 72–83
[14] Segal L Creely J J Martin J A E and Conrad C M 1959 *Textile Research Journal* **29** 786–794
[15] Jaboyedoff M, Kübler B and Thélín P 1999 *Clay Minerals* **34** 601–617
[16] Habibi Y Lucia L A and Rojas O J 2010 *Chemical Reviews* **110** 3479–3500
[17] Yu H Qin Z Liang B Liu N Zhou Z and Chen L 2013 *Journal of Materials Chemistry A* **1** 3938