Microstructure and Electroconductivity using Silver Nano Particles of *Pterocarpus Indicus* W. Leaf Extracts Films

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**Abstract:** Indonesian is one of the enormous biodiversity countries in the world. Various types of tropical plants exist in Indonesia, one of which is *Pterocarpus Indicus* W (PIW). PIW is one of the ornamental plants and has a wide range of compound content including flavonoids. Flavonoids are natural polymer compounds with a chemical formula of C₆-C₃-C₆. There are many kinds of flavonoids which could exist in various plants, one of which is quercetin. Quercetin is a unique bioflavonoid that has antioxidant activity. We have performed an extraction of flavonoid using the maceration method which subsequently doped with several amounts of silver nanoparticles (Ag-NPs). It is suggested that transforming PIW -AgNPs in the form of the film will increase the crystallinity compared to its pristine form. The growth of this crystallinity will enhance the expected properties of the material. The films were prepared based on the content of Ag NPs, i.e., for 0.01, 0.02, 0.03, 0.04, and 0.05 g. It was found that the microstructure of PIW extract showed that flavonoids belonged to flavonoid with quercetin type. The XRD data analyses showed an increase in the crystallinity of the flavonoid PIW-Ag film indicated by the peak at 2θ = 38.51° of (111) Bragg’s plane influenced by increase of Ag NPs. From the SEM image, we found that AgNPs exist in the sample and also further revealed by TEM analysis. The conductivity of the flavonoid PIW-Ag film shows a linear increase along with the addition of Ag doping.

**Keywords:** Silver nanoparticles, PIW, flavonoid leaves, microstructure, electrical conductivity.

1. Introduction

Indonesia possesses a significant number of biodiversity. Various kinds of tropical plants grow in Indonesia, one of them is Angsana or *Pterocarpus indicus* Willd (PIW) plant. PIW is one of the ornamental plants and has a wide range of compound content including flavonoids. Flavonoids are natural polymer compounds with chemical structure C₆-C₃-C₆. Flavonoids are a class of phenolic compounds with chemical structure C₆-C₃-C₆ [1-4]. Flavonoids have a conjugate bond, there are carbon atoms that are single-bonded (C=C) and double (C = C) alternately [5].

There are more than 100 kinds of flavonoids that exist in various plants, one of which is quercetin. Quercetin is a unique bioflavonoid that has antioxidant activity. Hydrolytic and oxidative enzymes as well as anti-inflammatory measures [6]. Many researchers have studied the content of flavonoids in various plants, such as the flavonoid content of the nerifolia leaf Euphorbia [7-8], from tomatoes [9-12].
Flavonoid extraction was performed by using the maceration method. In our previous report, we used latex liquid as a source of flavonoid with a simple treatment [3]. We propose to use the leaf of PIW as a raw material using the maceration method. To modify electronics properties of the films we used silver nanoparticles (AgNPs). The inducing AgNPs together with transforming into a film expected to increase the crystallinity as well as their electrical conductivity of flavonoid PIW-AgNPs.

2. Materials and Methods
The initial stages of extracting PIW were started by preparing 800 g of Pterocarpus indicus Willd leaf powder which was mixed with 3 L methanol in a large bottle and shaken and kept for a week. Subsequently, it was filtered using a Buckner funnel under pressure with Whatman's nozzle paper 01. The filtered yield then put in a rotary evaporator to obtain a rough methanol extract. 25 grams of methanol extract was introduced into the separating funnel in which the mixture was manually shaken with 50 mL of n-hexane solvent for 30 minutes. Once separated, the two layers of this process were repeated with 50 mL of n-hexane. The hexane phase in the treatment was separated and the sum of the second procedure is combined and evaporated to obtain a crude hexane extract. The general procedure was applied to obtain extracts of chloroform (100 mL), ethyl acetate (100 mL) and butanol (100 mL), respectively.

We separately also prepared Ag nanoparticles which were synthesized using a chemical reduction method [15]. We used Sodium Borohydride (NaBH₄) as a reducing agent according to the following mechanisms.

\[
\text{AgNO}_3 + \text{NaBH}_4 + \text{H}_2\text{O} \rightarrow \text{Ag} + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{B}_2\text{H}_6 + \text{NaNO}_3
\]

Mercaptosuccinic acid (MSA) was used as a stabilizer, while aquades and methanol were used as solvents. The first step was mixing 2.34 mL of MSA C₄H₆O₇S with 800 mL of methanol at 5-10 °C with stirring speed of 700 rpm. The next step was to apply 0.68 gram of AgNO₃ into 13.548 mL of aquades to achieve a yellowish solution. Subsequently, we add 1.52 grams of NaBH₄ in 200 mL of aquades until the solution is blackish brown with the help of a burette. During this process, the temperature was maintained at 5-10 °C. Furthermore the solution was precipitated and filtered with 600 mL of methanol three times. The filtrated powder was annealed on a hot plate at 50 °C. To confirm whether the phase of AgNPs crystal is already formed or not, we performed an XRD examination.

The procedure to synthesize flavonoids-AgNPs is briefly described. The initial step was mixing of AgNPs and acetone. This mixture was mixed with flavonoid extract - CSA in beaker glass. The next steps were homogenizing using a magnetic stirrer at 80 °C as shown in Figure 1.

![Figure 1. Flavonoid synthesis with AgNPs.](image)

This stage aims to make a film from the synthesis of AgNPs nano flavonoid using a spin coating method. The initial step of sticking the nickel substrate on the spin coater holder. Then drop an AgNPs nano flavonoid solution on the glass substrate and set the spin coater at 1500 rpm for 10 seconds as depicted in Figure 2.
3. Results and Discussion
The results of FT-IR spectrophotometric characterization of PIW leaves extract are represented by a wave number and its transmittance shown in Figure 3.

![FTIR Spectra of PIW Leaf Extract](image)

**Figure 3.** FTIR spectra of PIW leaf extract.

Based on the above data the extract of PIW leaves shows a peak transmittance of 3358.48, 2946.66, 2834.98, 1656.87, 1449.42, 1111.89, 1024.54, 636.74, 535.07, and 474.01 cm⁻¹ wave numbers. These peaks are the primary indicators of quercetin kinds of flavonoids. So we inferred that the leaf extract of PIW in this work belongs to the quercetin [13].

3.1. Diffraction Pattern of Flavonoid PIW-Ag Films
The diffraction patterns of Flavon PIW-Ag/glass is shown in Figure 4. It is obtained that the main three prominent peaks indicate the existing of silver nanoparticles on the composite film. Briefly, we observed that the increase of AgNPs gives rise to the rise of the peaks’ intensity showing the relative increase of AgNPs phase in the films.
Figure 4. Diffraction pattern of XRD at different AgNPs in the flavon PIW-Ag film

Further detail analysis showed that there is a small shift of main peak of AgNPs. The film with AgNPs concentration of 0.01 g in the PIW-AgNPs flavonoid showed a peak at $2\theta = 38.03^\circ$. For Flavonoid PIW-Ag 0.02 g produces a peak at $2\theta = 38.18^\circ$. As for Flavonoid PIW-AgNPs of 0.03, 0.04, and 0.05 g produces a peak at $2\theta$ of 38.12°. We have also found on our previous work that there is a small shift of the XRD patterns due to the introduction of AgNPs on natural flavonoids [3,14].

The X-ray diffraction patterns were analyzed by using the Gaussian fitting model. The silver phase on the whole of the X-ray diffraction patterns was performed under AMCSD 9011608 as a reference. Based on this model the peaks observed at $2\theta = 38.51^\circ$, 44.51°, 64.69°, 77.78°, and 81.79°. It was found that the crystal volume falls to 66.8 Å³ with a lattice parameter of $a = b = c = 4.058$ Å under cubic spinel system. The data was used for refinement of Ag NPs for main Bragg’s plane of (111), (002), (022), (113), and (222). By using Scherrer’s formula, we found that the crystal size is 45.5, 54.5, 52.2, 45.0, and 59.7 nm respectively for 0.01, 0.02, 0.03, 0.04, and 0.05 g of AgNPs content in the films. The average calculated of crystal size falls to 38.45 nm. The crystallinity of AgNPs in the film is depicted in Figure 5.

Although the crystallinity of AgNPs in the films does not linearly increase with the increase of AgNPs, we could see that the trend is increasing. It is also possible that in the higher amount of AgNPs mixed in the films could lower the crystallinity as shown by the 0.05 sample. This trend is generally in line with the Ag-doped PANI.
3.2. Electrical Conductivity of PIW-AgNPs film

The four probe method was implemented to measure the electrical conductivity of flavonoid PIW-AgNPs thin film. The electrical conductivity of AgNPs-Flavonoids film is displayed in Figure 6.

![Figure 5. The crystallinity of AgNPs in the flavonoids PIW films.](image)

![Figure 6. The electrical conductivity of PIW-AgNPs film](image)

AgNPs doped of PIW flavonoid will cause a significant increase in its conductivity. This dependency of electrical conductivity on AgNPs content looks linearly. This trend is also reported previously silver doped natural flavonoids [3], silver doped PANI [16], Fe and Co-doped PANI [18], AgNPs on various materials [20]. We may predict that by introducing a lower conductivity of metal oxide as SnO$_2$ will reduce the electrical conductivity [19]. We found interesting evidence found that the conductivity of the film depends on the content of AgNPs. Flavonoids are closely a kind of conducting polymer. The typical range of its conductivity lays around $10^{-3}$ to $10^{-1}$ S/cm as other conductive polymers. A pure silver shows about $10^7$ S/cm. A linear relation of AgNPs on its electrical conductivity could be used to control in what range of films desired. At lower range of AgNPs content, the electrical conductivity dependent of
AgNPs may also be affected by its crystallinity. The AgNPs content and crystallinity dependent of conductivity could be observed by comparing Figure 5 and Figure 6. This fact gives us a way to control the band gap using AgNPs concentration for solar cell application [21].

3.3. SEM analysis of PIW-AgNPs Film

The results of Flavonoid PIW-Ag film micrograph from SEM characterization and EDX elemental analysis is presented in Figure 7.

![SEM analysis of PIW-AgNPs Film](image)

**Figure 7.** The morphological structure (a), and elemental composition (b) of PIW-AgNPs Film.

A microscopic agglomeration of flavonoids PIW-Ag films is observed. In this image, we may infer that the polymeric flavonoids take a significant role in the agglomeration. From the SEM image, we could not observed where and how the nanosilver lays in the polymeric nets. According to the EDAX analyses, it could be obtained that silver nanoparticles are in the films. Other metallics, as well as organics elements, also observed in the films is come from the substrate and the flavonoids of PIW. Of course that the concentration and the distribution of the elements can be influenced by various factors including the concentration of precursors, reductants, temperatures, and preparation methods [14, 15, 17, 20]. To look for detail nanostructural of Ag-nanoparticles in the flavonoids PIW is better to be observed using TEM.

3.4. TEM Image of PIW-AgNPs

The results of the Flavonoid PIW-Ag image based on the result of TEM characterization is displayed in Figure 8.

![TEM Image of PIW-AgNPs](image)

Based on the image of TEM image can be presented that the size of Ag nano at TEM Figure 8a is in the range of 30 nm to 50 nm with an average size of 38.45 nm which corresponds to the initial discussion on XRD analysis. Figure 8b shows the result that flavonoids and Ag nanoparticles are inhomogeneously distribute. It is also obtained that the silver nanoparticles are compositred rather than in the form of the compound system. This composite system is expected to exist since the procedure which we used is mixing and blending without any further chemical routes of synthesis. It should also depend on several factors including solvents, concentrations, and preparation methods.
Figure 8. TEM image of (a) Ag NPs, and b) Flavonoid-Ag NPs

4. Conclusion
We conclude that the flavonoids extract from PIW leaf using maceration method belongs to quercetin type. The grain size of AgNPs obtained in this work is of 38.45 nm. The addition of AgNPs in the PIW extract films increases the crystallinity. The electrical conductivity of PIW-AgNPS is increase with the increase of AgNPs. The SEM results of flavonoid PIW-AgNPs showed that the size of the AgNPs exhibits in the range of 30 nm to 50 nm which is good agreement with XRD data. The TEM analysis of AgNPs showed that the grain size in AgNPS was around 50 nm. We further analyze that AgNPs are not homogeneously distributed in the PIW extract. What the flavonoids extract from PIW leaf is potentially be used as an electronic application by modifying using AgNPs.

Acknowledgments
We thank to the Ministry of Research and Higher Education of Indonesia through the funding grant of this research for MD.

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