Dielectric Properties of TiO₂ Nanoparticles Doped Flavonoid Extract of *Pterocarpus Indicus Willd* (PIW) Latex

M. Rynaldi Iqbal¹, Isnindar Tandya Asri¹, Harsipah¹, Sajida Rakhmah¹, Markus Diantoro¹,²,*, Yudyanto¹,²

¹ Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
² Central Laboratory of Minerals and Advanced Materials, Faculty of Mathematics and Natural Science, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia

*Corresponding author’s email: markus.diantoro.fmipa@um.ac.id

Abstract. Indonesia has many plants that contain flavonoids such as leaves or latex trunk from Angsana tree (*Pterocarpus indicus Willd*, PIW). To improve electrical properties, we can use several dopants such as protonation or introduce metal ions into the flavonoid of PIW extract. In our previous studies, we use silver nanoparticles in flavonoid films to increase the conductivity. It is rarely found the use of optical dielectric material such as TiO₂ induced in flavonoid. Flavonoid extraction from PIW latex was performed using the maceration method. Separately, we also prepared TiO₂ nanoparticle using the coprecipitation method. Meanwhile, the dissolving process of flavonoids and TiO₂ nanoparticle was carried out in an aquadest solvent with PEG 400. The FTIR spectrum shows the type of rutin. Analysis of XRD patterns showed an increase in the crystallinity of composite flavonoid-TiO₂ film along with the addition of TiO₂ nanoparticles. The SEM image shows that the TiO₂ nanoparticles are dispersed on the surface of the flavonoid-TiO₂ film. The dielectric constant of flavonoid film without TiO₂ nanoparticle dopant is 1.05×10⁴. The dielectric constant with 0.05 grams of TiO₂ nanoparticle decreased to 75.8.

Keywords: Dielectric, TiO₂, Nanoparticles, Flavonoid, PIW latex

1. Introduction

Indonesia possesses various kind of plants which contain flavonoids such as latex from Angsana tree (*Pterocarpus indicus Willd*, PIW). In PIW latex includes flavones which are polyphenols of natural polymeric builders [1]. Flavonoids produced from PIW are mostly biologically derived only as a bioactive preparation [2], used in traditional medicine [3], biodiesel plants [4], and anti-microbial metabolism [5], [6]. Flavonoids possess a conjugated single, double bond on the functional group so that it can be used as a semiconductor or conducting polymer.

Conducting polymer is widely studied due to exhibits sizeable electrical conductivity, corrosion resistance, and is easy to obtain [7]. In principle, conducting polymers could be used as transistors, organic light emitters (OLED), photovoltaic devices, sensors, bioimplants, corrosion protection and electrical energy storage. To obtain good conducting polymer properties, metal ions can be added into the polymer. Metal doping is usually done to produce materials with excellent electrical properties. Inducing metal ions such as iron and copper would be an increase in crystallinity and conductivity [8].
The growth of the crystallinity will enhance the desired properties of the material [9]. Among the metal materials, Ag metal shows high electrical conductivity [10], it can be used to modify the polymer's properties to form conducting polymers [11]. The study of flavonoids of PIW latex with silver nanoparticles dopant exhibits a significant increase in its electrical conductivity from 3.22 to 542.85 S/cm [12]. In the case of silver-doped flavonoid, the film was extracted from Jatropha multifida Lin. (JML) latex showed an increase from 2.71 S/cm (0.1 M) to 745.25 S/cm (0.5 M) [12]. Thus, it possesses an excellent potential for solar cell applications, primarily as the electrode of the DSSC device [13]. We may infer that flavonoids or other types of polymers can be modified of its electrical properties by employing Ag or other metal elements. So far according to our knowledge, it is still challenging to find a report using TiO$_2$ as a dopant for natural flavonoids films. In the lower dimension, the dielectric constant of TiO$_2$ can be controlled by changing the particle size to the nanometer. It is well-known that nanometer size shows many advantages over the micrometer scale [14].

2. Materials and Methods

Flavonoid extraction was prepared using a raw material of PIW latex which was obtained from PIW trees around the campus of the Universitas Negeri Malang. We first put the latex into a petri dish then heat it over hotplate until dry (turned into powder) at a temperature of 100 °C. It was followed by weighing 5 grams of PIW latex powder subsequently, put it in a measuring cup and then mixed them with 10 mL of methanol (1: 2). It proceeded with the blending and homogenization using a magnetic stirrer for 30 minutes. The obtained solution was subjected to sonication for one hour followed by filtering the solution using filter paper and kept it for 24 hours.

2.1. Synthesis of TiO$_2$ Nanoparticles

The initial steps of TiO$_2$ nanoparticles synthesis were dissolved 10 mL of TiCl$_4$, 0.3 mL HCl, and 4.7 mL of aquadest then stirred at 360 rpm for 5 min. Furthermore, 30 mL of HCl 32% was added. During the stirring process, 180 mL of NH$_3$ was subjected to the purpose of precipitation until a purple solution was achieved and then turn to white. The results were kept for 24 hours. The precipitate has been formed for 24 hours, filtered using filter paper and washed using aquadest up to five times. After washing steps, the soft white sediments were obtained. The finished residue was filtered and subsequently annealing at 400 °C for 6 hours.

2.2. Synthesis of Flavonoid-TiO$_2$ NPs Solution

This synthesis was carried out by mixing the latex extraction and TiO$_2$ NPs into the aquadest solvent and PEG 400. Flavonoids were diluted with aquadest of 0.25 mL and then stirred for 15 minutes and subsequently added TiO$_2$ powder with PEG 400 of 0.02 mL. It was continued by a homogenizing the solution for 30 minutes at 500 rpm.

2.3. Fabrication of Flavonoid- TiO$_2$ NPs Film on ITO Substrate

The film of Flavonoid- TiO$_2$ NPs on ITO substrate was conducted by using a spin coating method. Firstly, we used the TiO$_2$ NPs-flavonoid solution which was dripped onto the ITO substrate. Initially, the ITO substrate was cleaned using acetone under sonication and washed using aquadest. The spin coating was performed at a rate of 1000 rpm for 30 seconds. The resulting film was dried in an oven at 230 °C for 15 minutes.
3. Results and Discussion
FTIR test results after PIW latex extraction are shown in Figure 1.

![Figure 1. FTIR results from Angsana Latex Extraction](image)

We found that from the FTIR spectra some aromatic of C-H functional groups existed, C-O aromatic, C-O alcohol, C-H, C = C aromatics, C-H aliphatic and –OH. It can be said that this flavonoid compound is included in the Rutin type. The aromatic C-H functional group at the wave number of 765.74, 794.67, 821.68, and 856.39 cm\(^{-1}\). The peaks at wave numbers of 975.98, 1008.77, and 1060.85 cm\(^{-1}\) belong to the aromatic C-O functional group. The C-O alcohol functional groups occur at the wave numbers of 1109.07, 1157.29, 1203.58, 1249.87, and 1284.59 cm\(^{-1}\). At a wave number of 1371.39 cm\(^{-1}\) is an indication of a functional group of C-H. For the functional group of C = C aromatics occurs at the wave numbers of 1435.04 and 1606.70 cm\(^{-1}\) whereas the functional group of CH aliphatic occurs at the wave number of 2719.63 cm\(^{-1}\), 2839.22 cm\(^{-1}\). The wave number 3130.47 cm\(^{-1}\) is a functional group - OH because these wave numbers appear in the range 3000-3500 cm\(^{-1}\) [15].

3.1. XRD of Flavonoid-TiO\(_2\)
The diffraction pattern flavonoid-TiO\(_2\) films with a variation of TiO\(_2\) NPs is shown in Figure 2.

![Figure 2. X-ray Diffraction Patterns of (a) Flavonoid, (b)TiO\(_2\), and (c)-(g) Flavonoid doping TiO\(_2\) from 0.01 gram to 0.05 gram.](image)
Figure 2a shows the diffraction pattern of flavonoids. The diffraction pattern shows that flavonoids are included in the amorphous phase because there is no peak in the pattern [16]. Figure 2b shows the diffraction pattern of TiO$_2$. The phase shown is the anatase phase by matching the model data with TiO$_2$ data in this study. The grain size was calculated using Equation 1. The results of calculation using Equation 1 falls to 7.999 nm.

$$D = \frac{k\lambda}{\beta \cos \theta}$$  

(1)

From XRD patterns of the flavonoid-TiO$_2$ film with variations of TiO$_2$ NPs is shown in Figure 2c-e, where no visible TiO$_2$ nanoparticles peak observed. Figure 2f shows that there is a weak peak of TiO$_2$ nanoparticles at the $2\theta$ position of 25.356°. Figure 2(g) shows three small peaks of TiO$_2$ nanoparticles is observed at $2\theta$ of 25.356°, 38.617°, and 54.010°.

3.2. Crystallinity
Crystallinity can be measured using XRD patterns data and analyzed using a winPLOTR of Fullprof item to create an amorphous model. We used Origin to calculate the amorphous and total area.

![Crystallinity](image)

**Figure 3.** The crystallinity of TiO$_2$ Nanoparticles Mass Addition in Flavonoid-TiO$_2$ Films.

Figure 3 is a relationship between crystallinity and the addition of TiO$_2$ nanoparticles mass. The analysis results obtained crystallinity for TiO$_2$ mass of 0.01, 0.02, 0.03, 0.04, and 0.05 g respectively 0, 0, 0, 5.9%, and 7.5%. The 0% samples are associated with a no crystalline phase found in the patterns.

3.3. SEM EDAX of Flavonoid-TiO$_2$ Films
The morphology of flavonoid-TiO$_2$ films with a mass TiO$_2$ of 0.03 grams is shown in Figure 4. The SEM-EDX image shows that the white dots are scattered on the TiO$_2$ flavonoid film as in Fig. 4 a. with 20000x magnification is focused on white dots like Figure 4 b. The red box in Figure 4 b shows a selected area for EDAX test.
Figure 4. Morphology of the Flavonoid-TiO$_2$ Film (a) 500x of Magnification; and (b) 20,000x of Magnification.

Figure 5. Elemental composition of the Flavonoid-TiO$_2$ film.

The EDAX result is presented in Figure 5. The content of C, O, and Ti content falls to 30.5, 33.52, and 32. %. It can be concluded that the white dot on the flavonoid-TiO$_2$ film is TiO$_2$. Thus, according to Fig. 4, a TiO$_2$ is evenly distributed on the surface of the flavonoid-TiO$_2$ film.

3.4. Dielectric Constant of Flavonoid-TiO$_2$

The relationship between the addition of TiO$_2$ mass and the dielectricity of the TiO$_2$ flavonoid film is shown in Figure 6.

Figure 6. Dielectricity of Flavonoid-TiO$_2$ films with TiO$_2$ variation.
Based on Figure 6, it is found that the addition of TiO$_2$ affects the dielectric constant (dielectricity) of the flavonoid-TiO$_2$ film. The dielectricity of flavonoid film without doping of TiO$_2$ is $1.05 \times 10^4$. In flavonoid film with 0.01 gram of TiO$_2$ dielectricity obtained for $8.79 \times 10^3$. Dielectricity at 0.02 gram is TiO$_2$ of $4.3 \times 10^3$. The result of dielectricity obtained for the sample with 0.04 gram of TiO$_2$ is $1.04 \times 10^3$ whereas TiO$_2$ has a dielectricity of 53.1. Thus, the more nano mass of TiO$_2$ added, the dielectricity of the flavonoid- TiO$_2$ film decreases. This is consistent with previous research that TiO$_2$ nanoparticles decrease the dielectricity of PANI along with the mass of compounded TiO$_2$ nanoparticles sequentially dielectric constants is 3700, 3327, 1755, and 394 [17].

4. Conclusion

Based on the data analysis and discussion, it can be concluded that the extraction result from PIW latex (Pterocarpus indicus Willd) belongs to Rutin type flavonoid. The increase of TiO$_2$ gives rise to increase the crystallinity of the flavonoid-TiO$_2$ film. On the other hand, it decreases the dielectricity of the flavonoid-TiO$_2$ films. These results are supported by other similar reports.

Acknowledgments

Parts of this work were supported by the Ministry of Research and Higher Education of Indonesia through the DRPM of UM grant.

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