Dielectric properties and bioactivity of PVA/PEG/TiO$_2$ fibers for capacitive based body sensor

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Abstract. TiO$_2$ nanoparticles are known as a material which widely used in optoelectronic, industrial, and health sectors application. This material has a controllable dielectric constant making it possible to be utilized as a capacitive based body sensor. Many efforts had been studied by means of synthesizing TiO$_2$ nanoparticles in the form of conventional film depositions. It is also obtained that rare information of comprehensive study related to dielectric properties of the materials. In this report, we propose to synthesize PVA/PEG/TiO$_2$ fibers using electrospinning method at various TiO$_2$ concentration. Dielectric properties and bioactivity of samples are a focus of study. Electro spinning process has been performed with a voltage of 20 kV, and flow rate of 100 for 3 minutes. We used ITO glass as substrates. The FTIR spectra showed a successful synthesis of PVA/PEG/TiO$_2$ fibers. This is indicated by the appearance of the corresponding characteristics of PVA, PEG, and TiO$_2$ bonds. The XRD patterns showed the main peaks of TiO$_2$ as well as the diffraction peaks of PVA. We obtain that the average size of PVA/PEG/TiO$_2$ fiber is 268.27 nm. The dielectricity of PVA/PEG/TiO$_2$ fibers increased with the addition of TiO$_2$ nanoparticles. In addition, the increase of frequency effect to the decreased of dielectric constant. The toxicity test of PVA/PEG/TiO$_2$ fibers showed that the samples were non-toxic. On the other hand, the result of the anti-bacterial analysis showed that the samples had no anti-bacterial properties against S. aureus bacteria.

1. Introduction
Titanium dioxide (TiO$_2$) has been widely developed in both industrial and medical fields. The characteristic of TiO$_2$ which has been extensively studied and utilized is the optoelectric properties, which is transmittance and semiconductive. The dielectric constant of nanoparticles of TiO$_2$ was previously reported at 85 [1]. It was reported that the dielectricity of TiO$_2$ could be affected by several factors, including the mass of nanoparticles and particle size. Higher percentages of TiO$_2$ nanoparticle particles result in higher dielectric constant values [2]. Small particle size affects the number of particles per unit volume increased, resulting a high dipole moment per unit volume and dielectric constant. In addition to optical properties, bioactivity of TiO$_2$ nanoparticles also widely studied in some applications.

Bioactivity of TiO$_2$ nanoparticles is also investigated regarding its applications in the health field. The bioactivity properties of TiO$_2$ nanoparticles that have been studied are the toxicity and antibacterial properties. TiO$_2$ nanoparticles have antibacterial activity against e-Coli bacteria. It is reported that the higher of TiO$_2$ nanoparticles induce, the higher bacterial mortality rate in agar medium [3]. The pristine TiO$_2$ anatase nanoparticles (without coating) shows a toxic level. This nanoparticles demonstrate great appeal to proteins, which can damage cell mitochondrial function and...
make the decrease of cell survival [4-9]. Surface modification of TiO2 nanoparticles with polyethylene glycol (PEG) can affect its toxicity properties. PEG coatings can reduce the toxicity of TiO2 nanoparticles [10]. On the other hand, a non-toxic combination material with PEG is required to increase the water solubility level and to increase mechanical flexibility. PEG may act as a surfactant on the dissolution of TiO2 particles as well as to decrease the particle agglomeration rate.

So far there are many reports on the dielectricity of TiO2 thin film. But, it has not been comprehensively studied about TiO2 thin films with PEG combinations and their bioactivity properties. So it is essential to investigate PVA/PEG/TiO2 fiber synthesis by analyzing the dielectricity and bioactivity properties. In this report, we synthesized fiber by electrospinning method using polyvinyl alcohol (PVA) as fiber matrix and TiO2 nanoparticles as filler. A complete analysis of fiber structure was performed using XRD, SEM and FTIR characterization. Dielectricity of fiber were analyzed as a function of the mass of TiO2 nanoparticles and light intensity, while fiber bioactivity was expressed by analysis of toxicity as well as antibacterial properties.

2. Method
This research was focused on the synthesis and characterization of dielectric response and bioactivity properties of PVA/PEG/TiO2 fiber at the various mass of TiO2 nanoparticles. The research was performed at Nanomaterial Laboratory of Universitas Negeri Malang, while the characterization and testing process was observed in Central Laboratory and Microbiology Laboratory of Universitas Negeri Malang also in Biomedical Laboratory of Muhammadiyah University of Malang. The synthesis of PVA/PEG/TiO2 fibers was performed in two stages. First, by preparing the fiber solution using stirring and sonication method and followed by electrospinning process. The fiber material consists of PVA polymer as a matrix and TiO2 nanoparticles as a filler [21].

The synthesis of PVA/PEG/TiO2 fiber solution begins by preparing a solution of TiO2 nanoparticles through mixing aquades (1.3 mL), TMAH (11 μL), and PEG-400 (99.6 μL) at 90 °C. Next, we add a 0.1125 grams of TiO2 nanoparticles into the previous mixture for further stirred at 90°C for 15 minutes. After that, the TiO2 nanoparticle solution was sonicated for one h to obtain a more homogeneous solution (A). The next step is dissolving PVA in aquades (3 mL) which was stirred at 120 °C with a 9% PVA concentration in the total solution. The solution was distilled for 1 hour at 120 °C to obtain a homogeneous PVA solution (B). The third step is to dissolve (solution A) and (solution B) with stirring 700 rpm at 120 °C for 1 hour, and then mixing the solution for 2 hours to obtained (solution C). The synthesis was carried out at different mass of TiO2 nanoparticles (0.225, 0.15, 0.1125, 0.09, and 0.075 g).

Furthermore, the electrospinning process begins with stirring (solution C) at 90 °C under 360 rpm for 15 minutes, followed by preparing the equipment such as putting ITO substrate on a plate and filling (solution C) on stirring. The controlled variable of electrospinning process is voltage (20 kV), flow rate (100), and runtime (3 minutes). The structure characterization of fibers is represented by its crystallinity using XRD, morphology investigated by SEM, and functional groups obtained from FTIR. The dielectricity test was performed by employing different frequency, and light intensity in each sample analyzed using LCR meter. The bioactivity properties of PVA/PEG/TiO2 fibers were observed by antibacterial test with agar diffusion method use S. aureus bacteria and toxicity test by isolated organ method.

3. Results and Discussion

3.1 FTIR Spectra of PVA/PEG/TiO2 Fiber
The FTIR spectra of the bonding groups of TiO2 powder, PVA, PEG-400, and PVA/PEG/TiO2 fibers, as well as the IR spectra of sample 1 to sample 5 are shown in Figure 1.
Figure 1a shows the IR spectra of TiO2 nanoparticles that appearing in the range 450 cm\(^{-1}\) to 600 cm\(^{-1}\) indicating the presence of Ti-O bond vibrations in the TiO\(_2\) [11-14]. Peak 1633.71 cm\(^{-1}\) and the peaks between 3100 cm\(^{-1}\) and 3600 cm\(^{-1}\) show the vibrations of the hydroxyl group (O-H) from the residual solvent water after synthesis. IR spectra of PVA/PEG/TiO\(_2\) fiber in Fig. 1a is more similar with the peaks of PEG-400 and PVA. The IR spectra of PEG-400 at 845-900 cm\(^{-1}\) indicates the presence of stretching O-O [16], whereas the presence of 1109 cm\(^{-1}\) peaks shows symmetry of C-O-C in the aliphatic ether. Spectral peak at 2882 cm\(^{-1}\) indicates the presence of C-H alkyl is stretching, whereas 1352 cm\(^{-1}\) indicates the presence of deforming of C-H alkyl.

IR spectra of PVA showed peak about 3434 cm\(^{-1}\) that indicating the presence of polymer blend of free hydroxyl groups and vibrations of bound O-H band [16];[11]. PVA spectrum at ~ 1650 cm\(^{-1}\) of wave number indicates the presence of vinyl alcohol deformation, and this peak is the specific peak of PVA [16]. The peak between 3450-3230 cm\(^{-1}\) shows the strain band of the hydroxyl group O-H, whereas the peak of 2940 cm\(^{-1}\) and 2916 cm\(^{-1}\) is strains of the group bands CH\(_2\) and CH\(_2\). Peak 2836 cm\(^{-1}\) indicate the C-H stretching vibration, peaks at 1732 cm\(^{-1}\) and 1569 cm\(^{-1}\) show the stretching form of the remaining C=O carbonyl group of the acetate group [11];[16]. The peak of 1430 cm\(^{-1}\) shows the symmetry bond of CH\(_2\), and the peak of 1375 cm\(^{-1}\) denotes a mixture of the C-H and O-H mode bonds and the combined alcohol. The 918 cm\(^{-1}\) peak shows the syndiotactic structure and exhibits strong vibration, while the 849 cm\(^{-1}\) & 608 cm\(^{-1}\) peaks indicate stretching of C-C vibration and OH [11].

The IR spectra of PVA/PEG/TiO\(_2\) fiber almost all show the PEG-400 and PVA spectra with different shifts and intensities. At 3452 cm\(^{-1}\) there is a Ti-OH bond [11], resulting from the hydrogen bonding between OH and PVA molecules with Ti\(^{+}\) titanium ions resulting in charge transfer. This complex charge transfer shows that with the increase of nano TiO\(_2\) mass will increase the amount of charge. Figure 3b shows the variation of the mass of nanoparticles TiO\(_2\) compared to pure PVA. A small shift is observed of OH, CH groups and Ti-O-Ti bonds. The OH group and CH group is observed at the broad peak of 3400 cm\(^{-1}\) and ~ 2800 cm\(^{-1}\) regions. The new peak formed at around 400-600 cm\(^{-1}\) represents the existing of Ti-O-Ti bond. These peaks indicate that the composite has created, and the peak at 514 cm\(^{-1}\) signifies the Ti-O-O bond [11]. The reduced mass of nanoparticles TiO\(_2\) produces a lower %transmittance at 400-500 cm\(^{-1}\) region.

3.2 Diffraction Pattern and Crystal Size of PVA/PEG/TiO\(_2\) Fiber

The crystal size of TiO\(_2\) nanoparticles was analyzed using Scherrer Equation showing that the crystal size is 16.77 nm. While the results of Rietica calculations obtained the average size of 19.45 nm nanoparticles with ($\chi^2$) is 1.175.

$$D = \frac{k\lambda}{\beta\cos\theta}$$ (1)
The result of XRD analysis using Rietica software is shown in Table 1.

**Table 1. The result of structure analysis of TiO2 nanoparticles**

| Parameter   | Result of analysis |
|-------------|--------------------|
| a (Å)       | 3.7913             |
| b (Å)       | 3.7913             |
| c (Å)       | 9.5203             |
| Crystal size (nm) | 19.45             |
| Rwp         | 25.44              |
| Rp          | 17.83              |
| $\chi^2$    | 1.175              |

Figure 2. shown the diffraction pattern of TiO2 powder, PVA fiber, and PVA/PEG/TiO2 fiber.

![X-ray Diffraction Patterns](image)

The diffraction peak of PVA appears at the 2θ from 15° to 30° that containing amorphous and crystalline phase [11]. The diffraction patterns of PVA/PEG/TiO2 fibers exhibit a more dominant peak with PVA intensities, i.e., a broad peak in the 2θ region between 15° and 30°. The diffraction peaks of TiO2 nanoparticles in PVA/PEG/TiO2 fibers showed at $2\theta = 25.307^\circ$ which is the specific peak of the anatase TiO2 nanoparticles. The diffraction peak of PVA/PEG/TiO2 fibers indicates that TiO2 nanoparticles have been successfully composed of fiber. The other peaks formed on PVA and PVA/PEG/TiO2 diffraction patterns at $2\theta = 20°, 30°, 35°, 50°,$ and $60°$ are the diffraction peaks of the ITO substrate that has been used [17].

### 3.3 Fiber Morphology Analysis using SEM-EDAX

The morphology of PVA/PEG/TiO2 fiber can be analyzed using the result of SEM analysis (Figure 3a). ImageJ software analysis was implemented to obtain the average diameter of the fiber. We obtained that nanofiber is 268.2695 nm in diameter. The percentage element of TiO2 nanoparticles in PVA/PEG/TiO2 fibers can be determined from EDAX analysis (Figure 3b). The result of EDAX shows the presence of the TiO2 peak and the conductive substrate used, i.e., ITO (Indium Tin Oxide). ITO peaks clearly appear because the arranged fiber in substrate still has large empty spaces, so the ITO substrate was also detected by electrons gun during characterization.
The EDAX analysis is shown in Table 2. The percentage of TiO$_2$ nanoparticles by EDAX characterization for the total area obtained 0.47% of weight is much smaller than the %weight of EDAX of a single point. These results confirm that nanoparticles that have been composed of fiber are still in small quantities. While EDAX results for one selected point show the %weight of TiO$_2$ nanoparticles is 14.37%. We can assure that TiO$_2$ nanoparticles are entering the fiber.

| Element | Total area | One point |
|---------|------------|-----------|
| C       | 15.04      | 19.50     | 35.18 | 36.98 |
| O       | 29.04      | 35.14     | 50.98 | 50.03 |
| In      | 55.44      | 30.99     | 13.56 | 16.15 |
| Ti      | 00.47      | 00.28     | 14.37 | 06.83 |

3.4 Toxicity of PVA/PEG/TiO$_2$ Fiber
The result of fiber toxicity testing of PVA/PEG/TiO$_2$ is shown in Figure 4. Toxicity testing was taken using the liquid sample. The observed data is the contraction curve of the marmot’s small intestine (ileum) which may indicate the response toxic or nontoxic of the injected sample. The ileum with no treatment is shown in Figure 4a, indicating a constant contraction that means the ileum is alive, as well as when injected sample 1 to 5 (represented by sample 1) (Figure 4b). After washing, the ileum contractions can return as well as the initial condition. The ability of the ileum to contract again indicates that the ileum still alive and the sample is not toxic.

As a comparison, controlled toxicity testing was conducted on ileum marmot with an injection of Atropin drugs. Atropin drugs exhibit high toxicity when used in 100% concentrations. After the injection of Atropine, it appears that the ileum contraction rises drastically and then the curve cannot return to the initial condition (Figure 4c), this indicates that the ileum was death. This result then confirms by washing; the ileum cannot contract as in the initial condition before being treated.

From the toxicity test, we may conclude that the sample is non-toxic. From several reviews, it is known that the fundamental properties of nanoparticles TiO$_2$ are toxic, whereas the PEG-400 polymer serves as a surfactant and PVA that acts as a fiber matrix is non-toxic. In the liquid solution of PVA/PEG/TiO$_2$ composite fiber, the percentage of the TiO$_2$ nanoparticle is low, starting from 1.5% - 4.5% of the total weight. We cannot observe the toxic part from TiO$_2$ due to encapsulating of TiO$_2$ by PVA-PEG. The encapsulation using PVA-PEG causes the toxic effects of the TiO$_2$ nanoparticles cancelled.
3.5 Antibacterial Testing of VA/PEG/TiO₂ Fiber

The antibacterial activity of materials occurs from the interaction of the electric field between the material and the cell wall of the bacteria. In this study, the analysis of antibacterial properties of PVA/PEG/TiO₂ fibers using *S. aureus* bacteria seen after 24 hours incubation. Selection of the type of bacteria is adjusted with the application of fiber PVA/PEG/TiO₂ that is applied to the skin, because that used the kind of bacteria that often breed in human skin. In previous studies, TiO₂ nanoparticles anatase are known to have antibacterial activity against *E. coli* bacteria.

![Figure 4. Toxicity Testing of PVA/PEG/TiO₂ Fiber](image)

The test results in Figure 5 showed that an inhibited zone (transparent zone) is not formed around the sample. This result is caused by the type of bacteria used in this research is *S. aureus* bacteria which are gram-positive bacteria with one layer of the thick cell wall with thickness (15-80 μm). While the bacteria *E. coli* is a gram-negative bacteria, which has a thin 3-layer cell wall (10-15 nm). So the results of this test prove that the nanoparticle TiO₂ is not strong enough to produce an electric field interaction with the cell wall of *S. aureus* bacteria that resulted in nanoparticles cannot penetrate the thick cell wall of bacteria.

![Figure 5. Antibacterial Testing](image)
3.6 Dielectric Constant of PVA/PEG/TiO₂ Fiber

The influence of frequency varies to the dielectric constant of PVA/PEG/TiO₂ fiber showed in Figure 6a. The graph in Figure 6b shows the effect of light intensity on dielectric constant PVA/PEG/TiO₂ fiber. The value of the dielectric constant was obtained from the calculation of capacitance (C), with the sample area (A), and the sample thickness (d) using Equation 2.

\[ \varepsilon = \frac{Cd}{\varepsilon_0 A} \]  

(2)

Figure 6a describes the decreasing of dielectric constant with increasing frequency. The effect of frequency on the dielectric constant has been studied intensively. At low frequencies, the electrons can oscillate following the applied field, and the polarization mechanism can follow the applied field. However, at high frequencies, electron oscillations cannot follow application field fluctuations and cause the polarization mechanisms cannot follow the applied field [18].

Figure 6. a) Frequency influence and b) Light intensity influence of PVA/PEG/TiO₂ Fiber

After some data treatment, we found the effect of light intensity on the dielectric constant of PVA/PEG/TiO₂ fibers as in Figure 6b. The higher light intensity decreases the dielectric constant. The dielectric constant of the sample is close to a semiconducting material. This is due to the interaction between light and sample. The intensity of light that exists in the sample gives the energy that causes in the excitation of electrons in the atom. This situation produces an atomic swelling that occurs as the radius of the atom gets bigger. As the atomic radius increases, the electron binding energy becomes weaker, allowing for the electrons to escape from their core.

Figure 6a and 6b also explain the higher percentage of TiO₂ nanoparticle mass, have the higher the dielectric constant of PVA/PEG/TiO₂ fibers. The discussion in the previous section demonstrates that the dielectric constant of TiO₂ nanoparticles is 100 [19], 20 - 80 [20]. Because of the high dielectricity constant, the addition of a mass percentage of TiO₂ to PVA/PEG/TiO₂ fibers also increases the fiber dielectric constant.

4. Conclusion

We conclude that the addition of TiO₂ nanoparticles affects to PVA/PEG/TiO₂ fiber structure. The increase of TiO₂ nanoparticles induces the increase of IR spectra peak of Ti-O-Ti bond. We found that the sample shows a nontoxic material. It is obtained that the addition of TiO₂ nanoparticles did not improve the anti-bacterial properties of PVA/PEG/TiO₂ fibers for S. aureus bacteria. It is possible that the TiO₂ fraction is too small. In addition, this condition caused by a kind of bacteria is gram-positive which has a thick cell wall. We further obtain that the addition of TiO₂ nanoparticles increases the dielectric constant of PVA/PEG/TiO₂ fibers. The higher the intensity of light the lower the fiber’s dielectricity. The range and the possible control of dielectric constant open to this material to be applied to capacitive based body sensor.
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