Effect of TiO\textsubscript{2} Nanoparticles on Conductivity and Thermal Stability of PANI-TiO\textsubscript{2}/Glass Composite Film

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Abstract. Polyaniline (PANI), one of the conductive polymers has been intensively studied. The PANI has practically used in electronic device, and gas sensor. However, the PANI based on the electronic device has weaknesses such as fragile, and unstable of conductivity at high temperature and in an acidic environment. This obstacle can be solved by inducing other better thermal properties materials. One kind of the materials that meet the criteria is TiO\textsubscript{2}. However, TiO\textsubscript{2} has limitation due to the low conductivity compared to the conductivity of PANI. Theoretically, this problem can be solved by reducing the particles size of TiO\textsubscript{2} down to nanometric size. In this study, we prepared a composite film with a various amount of nano TiO\textsubscript{2} to obtain information related the microstructure, electrical conductivity, and their thermal stability. The results of FTIR spectra analysis showed that the PANI-TiO\textsubscript{2} composites films were successfully synthesized which is indicated by the appearance of PANI and TiO\textsubscript{2} characteristic bonds associated with the references. XRD spectra showed the increased crystallinity of PANI-TiO\textsubscript{2} composite films along the addition of TiO\textsubscript{2}. The SEM images presented the decreasing porosity of the samples by increasing the TiO\textsubscript{2} contents. Further, the conductivity of PANI-TiO\textsubscript{2} composite films decreased by increasing the TiO\textsubscript{2} nanoparticles. On the other hands, the thermal stability of the PANI composite films increased by increasing the TiO\textsubscript{2} nanoparticles.

Keywords: PANI, TiO\textsubscript{2}, Nanoparticles, Film, Composites, Conductivity, Thermal Stability

1. Introduction

Polyaniline (PANI) is one of the conductive polymers that are intensively studied. The PANI has some advantages like easy synthesis and inexpensive compared to other conductive polymers such as polypyrrole, polythiophene and inorganic semiconductors [1]. Also, its conductivity can be easily controlled via doping processes. These advantages made PANI potentially applied in various fields especially gas sensor.

The change of conductivity in a PANI Emeraldine Salt (ES) can be easily measured associated with its sensitivity when being exposed to various gases. So that, it was suitable to use in gas sensor applications. The PANI based gas sensor shows high sensitivity when exposed to the gas at room temperature. However, The PANI-based gas sensor has disadvantages such as fragile, and unstable conductivity at high temperature and in an acidic environment [3]. This condition will decrease the level of its sensitivity. Thermal stability of the PANI ES become lower caused by chemical reaction of PANI conjugate system with oxygen or loss of dopant as chlorine [14] on a polymer chain that can
limit its application. It was reported that the conductivity of the PANI-HCl decreased about 0.4 ± 0.03% S/cm [15] or 0.08% [12] by heating at 145 or 150 °C respectively from 25 S/cm. The decrease in conductivity is presumably caused by the formation of a PANI Emeraldine Base (EB).

The thermal stability of the PANI can be enhanced by introducing other materials such as a Titanium Dioxide (TiO2) [4]. On the other hands, The TiO2 has limitation due to the low conductivity compared to the PANI. Introducing TiO2 reduced conductivity from 1.91 S/cm to 1.06 S/cm and from 4.65 S/cm to 0.054 S/cm [20]. The nano TiO2 films synthesized using sol-gel with a Tetrabutyl orthotitanate and Titanium Isopropoxide (TTIP) precursor have conductivity 7 x 10^{-2} S/cm [5] and 1x10^{-2} S/cm [6] respectively. In this work, we report the influence of TiO2 nanoparticles addition on microstructures, conductivity, and thermal stability related temperature change of the PANI- nano-TiO2 film using a PVA solvents.

2. Experimental Methods
2.1 Synthesis Pani-TiO2/PVA Composite Film
Anilin (C6H5NH2) Merck (99%, PA), Distilled Water, Ammonium Peroxidisulfat (NH4)2S2O8 Merck (99%, PA), (Hydrochloric Acid) HCl (32%), TiCl3 Merck (99%, PA), Glass Substrate, NH2 Merck (99%, PA), Polyvinyl Alcohol (PVA) Merck (99%, PA). Pani was synthesized by using chemical polymerization methods. Meanwhile, TiO2 was synthesized by using Co-Precipitation methods.

The PVA solvent was prepared by adding 0.05 g of PVA in 1.5 mL of distilled water, stirred at 400 rpm for two hours. A 0.2 g of PANI and 0, 0.02, 0.04, 0.06, 0.08 and 0.1 grams of TiO2 powders dissolved in a solvent stirred at 750 rpm for 2 hours. The composite films were prepared by using spin coating method in 1 x 1 cm² glass substrate and spun it for 30 seconds at the speed of 500 rpm. The produced film was then dried at room temperature for three days.

2.2 Characterization
The functional chemical bonds that were appeared in the sample was characterized using spectrophotometer ZHIMADU IR Prestige-21. The crystallinity, grain size, and phase that was formed in the samples Characterized using diffractometer x-ray PHILIPS XPERT-type PRO with CuKα radiation sources (λ1 = 1.54060). The morphological of the sample characterized using SEM FEI type INSPECT S50. Morphological that’s mean grain from and porosity of the samples. Electrical conductivity measurement was obtained from 4-probe methods, with the distance between probes is 0.2 cm and 50 at room temperature, 60, 80, 100, and 120 °C using a constant current of 0.05 A.

3 Results and Discussion
3.1 Microstructure Data Analysis
The PANI Emeraldine Salt (ES) has functional bonding characteristics on the range wavenumber 400-2000 cm⁻¹ as shown in Figure 1a. Bonding characteristic formed on the wavenumber in the range 1440-1600 cm⁻¹ indicated the presence of the C= C bond of benzenoid rings and quinoid ring. The peak at a wavenumber of 1307 cm⁻¹ indicates the presence of C-N bond or quinoid ring. This quinoid ring shows the existence π electron delocalization demonstrate through protonation process of polyaniline. The alternating bonding characteristic C = C and C-C in the PANI chain made the PANI potentially has conductive properties [7].

Figure 1b showed the bond nature that was formed on the PANI-ES film with PVA solvent. The form of films and powders and also the addition of the PVA solvent affected the strength properties of bonding force. The decrease of intensity occurred at C-Cl, C-H, C-N, and C = C bond [8], but the increase of intensity also happened on the C-O bond. It can be affected by remaining the PVA due to the temperature of the synthesis of the PVA solution just at 80 °C. The formation of hydrogen bonds occurred between hydroxyl PVA group with imine and the amino group of PANI chains that have a positive charge. IR spectrum of the PANI-TiO2 film in Figure 1c was not much different with the IR spectrum of the PANI ES film, but it appeared that the peak intensity became weaker than the beginning. The new peak showed the appearance bonding of Ti-O-Ti at a wavenumber of 418.55 cm⁻¹.
The appearance of this bonding characteristics without omitted PANI bonding characteristic was evidently explained the formation of the PANI-TiO$_2$/PVA composites film [11].

Figure 1. FTIR Spectrum of (a). PANI ES Powder, (b). PANI ES Film, and (c). PANI ES-Nano-TiO$_2$ Film with 0.08 g of TiO$_2$.

Figure 2. X-Ray Diffraction Patterns of Nano-TiO$_2$ Powder and PANI-Nano-TiO$_2$ Film with various TiO$_2$.

Figure 2 showed a powder diffraction pattern of the TiO$_2$ and the PANI ES-Nano TiO$_2$ film with a different mass of TiO$_2$. Figure 2a confirmed the formation of the TiO$_2$ anatase phase according to the match analyses the experimental data using High Score Plus software with reference of 00-021-1272. The data model used for the Cellref analysis was a tetragonal crystal structure with lattice parameters of $a = 3.780$ Å, $b = 3.780$ Å, $c = 9.510$ Å. The peaks analysis using Cellref indicates that the experimental data fit correctly with the reference of the TiO$_2$ anatase phase.

The grain size of the TiO$_2$ was 8.14 nm from the calculation using Scherrer equation. The diffraction patterns of PANI ES without TiO$_2$ (Fig. 3b) showing an amorphous phase with the bump positions around 20 of 22$^\circ$ and 25$^\circ$ [8]. The use of PVA solvent does not give impact on the peak position of the amorphous phase at 20 of 11, 20, and 23$^\circ$ [8]. The increase of TiO$_2$ nanoparticles in Figure 2 c-g. showed the increase of peaks intensity match with the reference [11], showing the increase of crystallinity from 0, 3.83, 8.25, 15.17, 15.47, 17.37% as function as the TiO$_2$ addition.

SEM image(doesnot included) analyses of the PANI film and PANI-TiO$_2$ Film showed that the PANI ES has a spherical grain-shaped morphology with an inhomogeneous distribution and some porosity or cavity. On the other hand, the PANI ES-TiO$_2$ film has granular shaped morphology with the homogenous distribution and little cavity or porosity. The spherical shape of TiO$_2$ particles prominent visible out around the surface of PANI ES. The spherical shape of TiO$_2$ seems fused with a surface of the PANI through adsorption mechanism when the process of synthesis. This process will lead agglomeration on the structure of the PANI ES-TiO$_2$[12]. The porosity of PANI-TiO$_2$ film with mass variations of 0 and 0.08 grams analyzed by ImageJ software analysis, indicates that the porosity of the film was 4.6% and 1.33% respectively. This porosity showed that the addition TiO$_2$ mass on the PANI ES enhanced the density of the PANI. The presence of the TiO$_2$ with 13.6 Wt % in the PANI ES film also confirmed by EDX data which was supported by XRD data. The addition of TiO$_2$ into the PANI ES film relatively caused reducing C, N, O elements. This occurred because these elements have been replaced by a Titanium (Ti) that from the TiO$_2$ compound.
3.2 Electrical Conductivity Measurement Against to Temperature

The room temperature electrical conductivity of PANI ES decreased proportionally with the increase of TiO$_2$ of 286.5, 226.3, 223.4, 205.5, 145.2 and 135.5 S/cm respectively for 0.0, 0.02, 0.04, 0.06, 0.08, and 1.0 fractions. The decrease of the film conductivity attributed to TiO$_2$ conductivity which is lower than the conductivity of PANI ES. Several factors may also contribute such as the approximate ratio of oxidant/aniline 1.25, protonation process involving the HCl and the drying process was done at 40 °C during the synthesis made its conductivity can be improved reached to 265.8 S/cm [13]. Another factor could also be induced by intrinsic defect or purity of nano TiO$_2$.

![Conductivity of PANI and PANI-TiO$_2$ Film against Temperature.](image1)

![Conductivity Degradation of PANI and PANI-TiO$_2$ Film against Temperature.](image2)

In general, the electrical conductivity of the composite film decreases drastically from room temperature to about 60 °C, then somewhat insignificant change as indicated by Figure 3. A detail observation, the conductivity above 60 °C is slightly increased as the increase in temperature. These features suggest that the conductivity becomes stable due to incorporating TiO$_2$ nanoparticles in the PANI ES. A relative decreasing of electrical conductivity from its room temperature is displayed in Figure 4. It is seen that the strongest reduce conductivity is showing by the pure PANI ES, followed by the increase of TiO$_2$ incorporation. This feature is also shown by PANI ES-TiO$_2$ with NMP solvent [14].

The PANI has covalent bond types, while TiO$_2$ has ionic bond types. These bonding types appropriated with the binding energy (E$_b$). The binding energy of PANI ES is 400 eV [15]. On the other hand, the binding energy of TiO$_2$ is 459.2 eV [16]. The presence of TiO$_2$ in PANI ES-TiO$_2$ composite film may increase its binding energy. This condition caused the higher thermal energy in degradation process of PANI ES-TiO$_2$ composite film. The presence of nano- TiO$_2$ in PANI ES-TiO$_2$ composite film may increase the crystallinity of the film PANI ES from 0; 3.83; 8.25; 15.17; 15.48 and 17.38%. In addition, the density of the PANI ES-TiO$_2$ films is higher compared to the PANI ES film. When PANI composed with 0.08 of TiO$_2$, demonstrated the reduced porosity surface PANI from 4.6 to 1.33%. The increased of crystallinity and density of PANI composite films caused the higher thermal energy for degradation process of the PANI ES-TiO$_2$ composite film. According to this theory, we can explain the thermal stability of the PANI-TiO$_2$ film increased as function as the TiO$_2$ addition.
4. Conclusion
Thermal stability of the PANI-TiO$_2$ film increased as function as the TiO$_2$ addition. This feature suggests that conductivity of the PANI becomes more stable at high temperature due to incorporating of the TiO$_2$ nanoparticles. There is many factors influence this condition, such as different the binding energy, phase, and density of PANI compare to PANI-TiO$_2$. Further study is required to examine thermal stability of the PANI-TiO$_2$ in more various range temperature.

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