Fabrication of PANI/Ag/AgCl/ITO-PET Flexible Film and Its Crystallinity and Electrical Properties

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**Abstrak.** PANI as one of the conductive polymers which have been widely used in electronics or storage devices such as a supercapacitor. PANI has recently become an option because of its potential for a broad area of application. Protonation or introduce a dopant can control the electrical properties of PANI. However, researcher facing a disadvantage since PANI also active in acidic conditions. To control the conductivity and the stability in an acidic environment, the researcher has introduced Ag/AgCl to PANI. We report the synthesis and analyses of silver nanoparticles (AgNPs), PANI, and PANI/Ag/AgCl/ITO-PET films. PANI was synthesized by chemical polymerization, while AgNPs were synthesized via a reductive chemical method using NaBH\textsubscript{4} as an AgNO\textsubscript{3} reductor. The resulting PANI was characterized using FTIR to determine the functional group, while to obtain the purity of the Ag phase was checked by using XRD. The preparation of PANI/Ag/AgCl solution was carried out by mixing method with the variation of the mass of AgNO\textsubscript{3}. The precipitate was carried out by using ITO-PET substrate. PANI/Ag/AgCl/ITO-PET films were characterized by using FTIR, XRD, SEM-EDX, and capacitance meters. It has was found that crystallinity increases with the addition of Ag films to PANI/Ag/AgCl/ITO-PET. The crystallinity reached 29.85 \%. It was also revealed that the dielectric constant decreased with increasing Ag in PANI/Ag/AgCl/ITO-PET films.

**Keywords.** Ag, AgCl, crystallinity, dielectric constant, ITO-PET, and polyaniline.

1. Introduction

Many kinds of polymers have been explored for various applications. The previous research of organic polymers worked on electronic applications such as silver doped flavonoid [1], and ZnO-cellulose acetate [2]. A specific interest of conducting polymers also being extensively studied due to their potential application in technology [3]. Among the various conductive polymers, PANI is attracting attention because of inexpensive, easy to synthesized, excellent conductivity and stability among polymers. Its electrical properties can be modified by oxidation or introducing other material such as iron and copper [4]. The use of acid in PANI provides a specific protonation state that can be used in broader applications [5]. We can use this polymer as microelectronic devices, diodes, sensors, supercapacitors, microwave absorption, and corrosion prevention [6]. Further, PANI also shows a good performance in optical devices since it has a high absorbance coefficient in visible light spectra.
as well as high load carrier [7]. The uniqueness of PANI compared to the other conductive polymers is its electrical properties which can be controlled by the transfer of doping charge and protonation [8]. However, the redox reaction of PANI is active only for acidic conditions, generally at pH < 4. It limits its application in bioelectrochemistry, which usually requires neutral pH in the environment [9]. To improve the shortcomings of PANI and to produce materials with desirable properties, various developments have been proposed. One of them through a combination of PANI with other specific materials [4, 10–11].

The previous work reported that a significant increase of electrical properties on PANI because of Ag-doped [8]. The electrical stability performance of PANI was achieved by inducing AgCl [9,12–13]. Here we report on the microstructure and dielectric properties of PANI-Ag-AgCl on ITO-PET substrate as a flexible film.

2. Materials and methods
The PANI ES was synthesized using polymerization while the AgNPs were prepared using the co-precipitation method. Both of those materials were blended as a precursor of solution for deposition on substrate flexible. The properties of a sample were characterized by FTIR, SEM-EDX, X-RD, and capacitance measurement using LCR-meter. The characterization focuses on microstructure and dielectric properties of PANI-Ag/AgCl/ITO-PET. A more detail procedure of this experiment distinctly showed below.

2.1. Synthesis of PANI
The first step by preparing two phases, namely organic and inorganic phases. The organic phase was a solution of aniline and HCl, while the inorganic phase was ammonium peroxdisulfate and distilled water. Both of the solutions were mixed for the polymerization process. This process lasts for 24 h. The result will create green sediment. The polyaniline sludge ES was cleaned using HCl to remove residual monomer, oxidant, and polymerized decomposition products and also further treatment using distilled water followed filtering and drying over a hotplate at 60 °C.

2.2. Synthesis of Ag nanoparticles
The silver nanoparticles (AgNPs) were synthesized using the chemical reduction method using Sodium Borohydride (NaBH₄) as the AgNO₃ reductor. During the reaction, we use mercaptosuccinic acid (MSA) as a stabilizer. We used distilled water and methanol as solvents. The next step, a 2.34 mL of MSA C₆H₅O₂S and 800 mL of methanol were mixed and blended by using magnetic stirrer at 700 rpm. The next step, we also prepared a solution of 0.68 g AgNO₃, and 13.548 mL of distilled water then mixed with the previous solution until the yellowish solution appears. Further, we added a 1.52 g of NaBH₄ in 200 mL of distilled water until the solution was blackish brown with the help of a burette. The temperature was kept at 5 °C to 10 °C. Furthermore, the solution was precipitated and filtered with 600 mL of ethanol for 3 times. The filtrate was dried using a hotplate over a temperature of 50 °C to obtain AgNPs.

2.3. Deposition film by spin coating method
We firstly prepared a 1.5 mL of distilled water maintained at a temperature of 80 °C, then mixed 0.05 g of PVA stirred at 750 rpm for 2 h. The next step was to introduce 0.2 g of PANI with different of Ag; 0.00 g, 0.02 g, 0.04 g, 0.06 g, and 0.08 g and stirred at 750 rpm for two hours without heating. Deposition of PANI/Ag/AgCl solution on ITO-PET substrate was performed by drop casting method then rotated at 500 rpm for 30 s.
3. Results and discussion

3.1. Functional groups of PANI/Ag/AgCl

Pani ES can be transformed from PANI EB by reacting HCl as indicated by Figure 1. The carbon-carbon of the chemical configuration of PANI EB and PANI ES is distinguishable. The functional group's structure of the resulted sample is depicted in Figure 2. It demonstrated that the C-Cl aromatic out of plane vibration occur at 601 cm$^{-1}$ as a specific characteristic of PANI ES. The absorption band of 821 cm$^{-1}$ and 881 cm$^{-1}$ is bending out of plane binding CH. The peak of wavenumber of 1010 cm$^{-1}$ indicates the presence of a C-H bond, while the band at 1155 cm$^{-1}$ showing the stretching vibration of -NH$.^+$. The Polaronic structure of C-N$^+$ occurs over an area of 1249 cm$^{-1}$, whereas for quinoid ring double bonds occur throughout the region of 1585 cm$^{-1}$ [15]. The vibration of stretching of N-H and O-H occurs within the area of 3142 cm$^{-1}$ and 3242 cm$^{-1}$ [16]. The modeling approach of IR spectra indicates that PANI has been successfully synthesized.

![Figure 1. The chemical structure of PANI EB and PANI ES [14].](image)

The effect of the addition of Ag on PANI is also observed from the FTIR spectra, as shown in Figure 3. A new peak shows Ag at 418 cm$^{-1}$ indicating an AgO bond (metal-oxide) based on Figure 3.b. In addition to these bands, a slight shift according to stretching C-N bond appear from 1315 cm$^{-1}$ to 1303 cm$^{-1}$. The latter indicates an interaction between PANI and Ag.
Figure 2. FTIR Spectra of PANI

Figure 3. Characteristic bending of FTIR Spectra on (a) PANi and (b) PANI/Ag/AgCl

3.2. Crystal structure of PANI/Ag/AgCl/ITO-PET

The silver diffraction pattern of the AgNPs is shown in Figure 4. The analysis results using Cellref indicates that a single pure phase obtained, under the cubic structure. The associated peaks position at 2θ of 38.10°, 44.32°, and 64.66° are indicating Bragg’s planes of (111), (200), and (220) respectively. The sample was randomly oriented. The predominant of the (111) Bragg’s plane intensity does not indicate merely the grains’ orientation but the crystal structure factor.
Figure 4 shows that sample 2 to sample 5 appear Ag peaks at 2θ of 38°, 44°, 77°, and 81°. Besides the peak of Ag, there were other peaks of AgCl. AgCl peaks are observed at 2θ of 27°, 32°, 46°, 54°, 57°, 67°, 74°, 76°, and 85°. The peak at 20 of 26° belongs to the substrate, ITO-PET. The Ag and AgCl phases belong to the cubic structure with a $Fm\overline{3}m$ space group. The appearance of AgCl peak occurs because of the Cl content in polyaniline. Also, AgCl may occur due to the mixing process that occurs in the liquid phase and opens for the reaction of $Ag^+$ and $Cl^-$. Based on Figure 5 it is seen that the more mass of Ag added, the higher the intensity of 2θ from Ag, and decreasing the intensity of AgCl. Lowering intensity may be originated from the more $Ag^+$ is reduced to AgO.
Figure 5. The diffraction patterns of PANI on ITO-PET substrate, and PANI/Ag/AgCl/ITO-PET.

Figure 6 shows the increase of crystallinity from initially amorphous, increasing the crystalline extent with increasing Ag on the composite. The maximum crystallinity degree of the film is 29.85%. The crystal size of a material can be reviewed using the Scherrer equation through FWHM from the peaks of XRD. The grain size of Ag ranged from 28.74 nm to 41.32 nm, whereas AgCl ranged from 27.19 nm to 36.23 nm.

Figure 6. The Crystallinity of PANI/Ag/AgCl/ITO-PET

The increase of crystallinity of PANI/ITO-PET is depended on the doping of Ag. The crystal size of Ag impacted to higher crystallinity. This fact implied that small dopant of Ag and AgCl insert to PANI structure. Therefore, the dopant has two issues, there is a change of PANI chain and enhanced
the regularity of crystallinity of PANI [17]. The kind of PANI has been determined its crystallinity, such as PANI ES have a high crystallinity than EB. On this research, PANI ES has been formed by adding HCl. The part of Cl- insert to the weakest chain of PANI and bound with Ag.

3.3. Morphology of PANI/Ag/AgCl/ITO-PET
The surface morphology of the sample and the elements contained in the sample has been observed using SEM-EDX. The SEM-EDAX of PANi and PANi/Ag/AgCl/ITO-PET film with the addition of 0.06 g Ag mass and mapping have been examined. From the mapping visible the distribution of elements in the composite. Figure 7 shows the morphology of PANI.

![Figure 7. Morphology of PANI](image1)

The result of SEM EDX and mapping with the addition of Ag 0.06 g in PANI/Ag/AgCl/ ITO-PET film and its thickness is shown in Figure 8. The distribution of element on the surface spread well. Its shape is granular.

![Figure 8. (a) Microstructure of PANI/Ag/AgCl/ITO-PET and (b) mapping of PANI/Ag/AgCl/ITO-PET](image2)

The microstructure of PANI/Ag/AgCl/ITO-PET is granular as indicated by Figure 8.a. The elemental analyses by EDX are shown in Table 1. The content of PANI film are C, N, O, and Cl indicated that PANI film has successfully formed.
Table 1. EDX result of PANI

| Element | Wt%  | At%  |
|---------|------|------|
| C       | 64.79| 72.54|
| N       | 11.45| 11.00|
| O       | 16.16| 13.58|
| Cl      | 07.59| 02.88|

Table 2 showed that the atomic percentage of element C approximately 80.33%. The addition of PVA to form a solution is a polymer with the dominant element C is the same as PANI. The results of the mapping also show a uniform, i.e., the C element that dominates and is evenly distributed on the sample surface, seen in Figure 8.b.

Table 2. EDX result of PANi/Ag/AgCl/ITO-PET

| Element | Wt%  | At%  |
|---------|------|------|
| C       | 70.05| 80.33|
| N       | 10.54| 10.37|
| O       | 07.98| 06.87|
| Cl      | 03.76| 01.46|
| Ag      | 07.67| 00.98|

3.4. Dielectric constant of PANi/Ag/AgCl/ITO-PET

The dielectric constant of the PANI/Ag/AgCl/ITO-PET is shown in Figure 9. Based on it, the dielectric constant decreases with the increasing of Ag mass in composite with maximum 17.897. The previous study showed that the addition of Ag in the composite increases the conductivity of the samples as in the PANI/Ag composite [18], although there is another phase of AgCl. The results of this measurement introduced that the decreased dielectric constant as function as the increasing of a conductive material.

![Figure 9. The Dielectric Constant of PANI/Ag/AgCl/ITO-PET and addition of Ag.](image-url)
4. Conclusions
It can be concluded that the composite of PANI/Ag/AgCl/ITO-PET was successfully synthesized. We also observed that the increase of Ag inducing on the film effect to the increase of crystallinity of silver in the film but a decrease of the film dielectric constant. The decreasing of dielectric constant on PANI/Ag/AgCl/ITO-PET film indicated that the conductivity is increased. In this research, the dielectric measurement indirectly showed electrical conductivity measurement. Based on this result, it is open that PANI/Ag/AgCl/ITO-PET film is possible to be used as an electrode material for pseudo capacitor supercapacitor.

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