Conductivity, Morphology and Thermal Studies of Polyaniline Fabrics

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ABSTRACT

In this work, conductive fabrics-based polyaniline (PANI) were fabricated using a facile method namely, immersion. Fabrics such as cotton and polyester (PES) were immersed in PANI solution followed by a drying process. In order to make the fabric conductive, the dopant was added into the polymer beforehand. The doping was completed by treating with HCl prepared in 0.3 v/v%, 0.6 v/v% and 0.9 v/v% concentrations. Consequently, the colour of PANI Emeraldine Base (EB)-blue transformed into green, characteristic of PANI Emeraldine Salt (ES). Field Emission Scanning Electron Microscope (FESEM) and Electro Impedance Spectroscopy (EIS) were used to analyse the morphology and conductivity of fabricated fabrics, respectively. FESEM analysis revealed the distribution of precipitates was homogenous in PES which provided better surface area and gave a strong bonding with the acid, compared to cotton. Electro Impedance Spectroscopy (EIS) results revealed that doping with 0.9 v/v% HCl gave excellent conductivity compared to 0.3

v/v% on PES fabric. The thermal properties of doped fabrics was analysed using Thermal Gravimetric Analysis (TGA). TGA analyses displayed three major stages of weight losses in the conductive fabrics, in which PANI in PES showed a major impact on the shift of degradation point, suggesting that a more stable fabric has been fabricated. Collectively, this study has presented a simple approach to produce a conductive fabric utilizing PANI as the conducting agent.

Introduction

Conducting polymers (CPs) such as polythiophene, polypyrrole and polyaniline are synthetic polymers that can exhibit special conductive properties. Among them, polyaniline (PANI) is popular and widely used in many applications including batteries [1], sensors [2], and electronic devices [3]-[5]. PANI can exist in three different forms which are leucoemeraldine base (LEB, fully reduced form), emeraldine base (EB, partially oxidized form) and base-pernigraniline (PNB, fully oxidized form). PANI is commonly reported as conductive material through a doping process. They can simply be treated with reducing or oxidizing agents such as hydrochloric acid (HCl), perchloric acid ($HClO_4$), *p*-toluuene sulfonic acid (*p*TSA) and camphorsulfonic acid (CSA). Mahat et al. (2015) reported that doping of PANI is a reversible process which depends on environmental conditions such as pH and temperature.

The use of PANI as bioelectronics device has been ventured since 2001 [6]. The requirement properties include wearable, flexible and environmentally stable. Since then, many studies have been conducted to fit these requirements [7]. Fabric is one of the best candidates to have flexibility and electronic properties. This can be achieved by incorporating CPs into a fabric [8].

Different types of fabric can portray different properties of conductivity, thermal degradation and physical. This is due to the nature of their physical structure. Gomes et al. (2012) [9] reported that polyester fabric can have high conductivity of 10 to 103 S/cm. In another study by Neelakandan and Madhusoothanan (2010) [10], PES fabric exhibited a high conductivity after incorporation of CPs that has more interlacement structure which shows higher resistivity. Thermal properties are important as they can determine the thermal stability of fabrics. The stability at high temperature is crucial since fabrics are easily burnt at low temperature [11]. The thermal properties can be measured using TGA. In the past, Jinsong et al. (2012) revealed the thermal properties of nylon fabric which are prepared using immersion method. They found that the

temperature of degradation can reach up to 408 °C. TGA analysis can show the degradation properties of fabrics, which can be indicated by measuring the amount of weight change of the fabrics [12].

In this study, we report the fabrication of a conductive fabric using a simple immersion technique. This is an approach to render the conductivity properties of fabrics utilizing PANI as the conductive agent. HCl was used as the dopant during the synthesis of PANI. Two types of fabrics, namely cotton and PES, were immersed in a PANI solution, followed by drying process. These fabrics were then characterized by Field Emission Scanning Electron Spectroscopy (FESEM), Electro Impedance Spectroscopy (EIS) and Thermal Gravimetric Analysis (TGA) for their morphological structure, conductivity and thermal stability, respectively.

Materials

Polyester and cotton fabrics (50 cm × 60 cm) were purchased from fabrics company, Kamdar Sdn. Bhd. Aniline water base was purchased from Sigma-Aldrich. Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Ammonium persulfate $(NH_4)_2S_2O_8$, Sulfuric acid (H_2SO_4) and dimethylformamide (DMF) were purchased from ACROS, UK.

Experimental

Synthesis of PANI

A 10 mL of aniline was mixed in 100 mL of HCl and stirred at room temperature. Then, a 22 g of ammonium persulfate (APS) was dissolved in distilled water. APS solution was added drop by drop into aniline solution at room temperature and stirred for 4 hours until a green solution was obtained. Then, the green solution was filtered using filter paper, separating the solution and precipitate. The HCl, acetone and distilled water were used to wash the precipitation followed by a drying process for 24 hours. The precipitation was mixed with 1 M of NaOH and HCl, followed by stirring it for 4 hours. Next, they were dried in the furnace at 60 °C to obtain polyaniline emeraldine base (PANI-EB) powder (blue colour). This process was repeated 2 times

Preparation of Doped and Undoped PANI-EB with Hydrochloric Acid (HCl)

PANI-EB powder was dissolved in a 60 mL of dimethylformamide (DMF). A 0.18 mL of 1 M HCl was added into the solution. The solution turned its colour from blue to green, and labelled as doped solution which indicated its conductive state. The same step was repeated for different concentrations of

HCl (0.6 v/v%, 0.9 v/v%). PANI without the addition of acid served as a control solution (undoped PANI). The PANI solution was centrifuged for 30 minutes with 400 rpm of speed.

Immersion of Cotton and Polyester Fabric Doped and Undoped PANI

Both PES and cotton fabrics were cut into 5 cm × 5 cm. They were immersed in PANI solution for 15 minutes followed by a drying process. They were kept in the dark place until used for characterization using FESEM, EIS and TGA.

Materials Characterisation

Field Emission Scanning Electron Microscope (FESEM)

Field Emission Scanning Electron Microscope (FESEM) model TM3030 Plus was used for morphological analysis. The sample was firstly mounted on the sample stage by sticking it with carbon tape and placed in the chamber. Sample was viewed and magnified at 200× and 500×.

Electrochemical Impedance Spectroscopy (EIS)

HIOKI 3532-50LCR Hi Tester Electrochemical Impedance Spectroscopy was used and operated at 100 Hz to 1000 kHz frequency at room temperature. Two stainless steel disc electrodes with 2.0 cm diameter were used to sandwich PANI fabrics. The conductivity (σ) of the samples was calculated using the equation (1):

$$\sigma = \frac{L}{[RB \times A]} \tag{1}$$

where L is the thickness of the fabric, RB is bulk resistance and A is contact surface area of electrode with the fabric.

Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric analysis (TGA; SETARAM model) was conducted to measure the weight loss of sample. The temperature was set from 27 °C to 300 °C at the heating rate of 20 °C/min. The result of thermal reaction was compiled into a plot of percentage of weight loss versus temperature or time.

Results and Discussion

Visual Assessment

Polyaniline (PANI) was synthesized by oxidative polymerization process, in

which the aniline (monomer) was transformed into a long polymer chain, namely PANI. During the synthesis, HCl was used as the dopant, working to protonate the backbone in order to activate the conjugation of electrons along the backbone. This can result in the electrical properties of CPs. The HCl doped PANI was found to be in green colour, indicating a doped state after synthesis as seen in Figure 1 (a) [13,14].

Throughout post-doping, the PANI was de-doped using NaOH to the reduced state which transformed it into blue colour. The changes of colour in PANI powder indicated that the chemical composition and the backbone chains of the polymer were modified. The blue colour state (PANI EB) was in deprotonated state while the green colour (PANI ES) form in the doping process with acid (HCl) showed that the PANI was in the protonated state (Figure 1 (a)) [15]-[17].
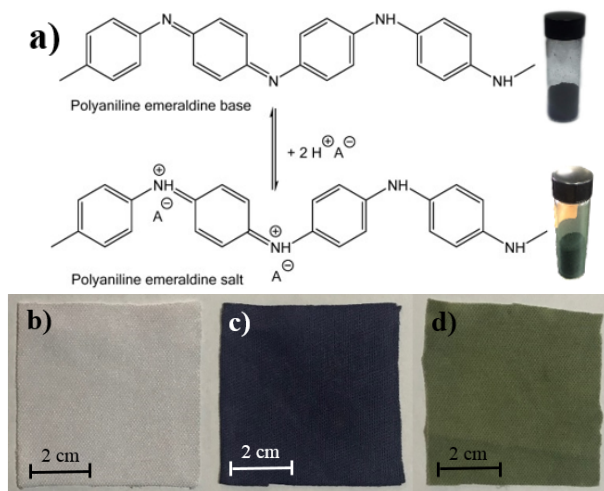

Figure 1: a) Chemical structure of PANI-EB and PANI-ES. b) Polyester (PES) fabric (bare) c) PANI EB and d) PANI-ES on PES fabrics

Following this, immersion was carried out to transfer the PANI into the fabrics [18]. Figure 1 (c and d) shows the images of PANI on fabrics in different PANI states. These visual assessments suggested that PANI fabrics can be fabricated using a facile immersion method, producing a conductive fabric.

EIS Measurements

EIS was used to measure the conductivity of all fabricated fabrics. Table 1 shows the conductivity of both PANI Cotton and polyester fabrics doped with

HCl.

Table 1. Conductivity of both PANI fabrics doped with HCl

Types of fabrics	Doping condition	Volume %	Conductivity (S/m)
Cotton	Bare	-	NIL
	Undoped	-	$1.06 \times 10^{-7} \pm 6.38 \times 10^{-8}$
	Doped PANI with HCl	0.3	$3.00 \times 10^{-4} \pm 3.14 \times 10^{-4}$
		0.6	$1.13 \times 10^{-3} \pm 5.44 \times 10^{-5}$
		0.9	$1.57 \times 10^{-2} \pm 1.11 \times 10^{-3}$
Polyester	Bare	-	NIL
	Undoped	-	$6.83 \times 10^{-7} \pm 4.24 \times 10^{-7}$
	Doped PANI with HCl	0.3	$2.70 \times 10^{-3} \pm 1.84 \times 10^{-3}$
		0.6	$4.30 \times 10^{-2} \pm 3.01 \times 10^{-2}$
		0.9	$4.24 \times 10^{-1} \pm 1.52 \times 10^{-1}$

We found that by incorporating PANI into fabrics, the reading of conductivity increased. For instance, cotton fabric reached the value of 1.57×10^{-2} S/m at 0.9 v/v%. Meanwhile, PANI fabric showed a major increment in conductivity, which was 4.24×10^{-1} S/m at similar concentration. It was observed that PES fabric reacted better in showing good conductivity as compared to cotton fabric. We hypothesized that PES fabric had better absorption of PANI onto the fabric which led to good conductivity properties.
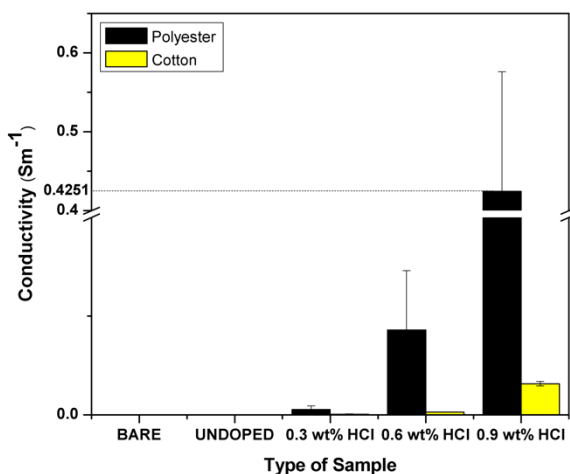

Figure 2: Bar chart of conductivity for both PANI fabrics at different v/v% of HCl

Figure 2 shows the conductivity of polyester and cotton fabrics in undoped and doped states. The conductivity was found to be zero because no acid was incorporated into the fabrics. In another case, conductivity gradually increased for 0.3 wt% to 0.9 wt% in all fabrics. For instance, the value increased from 2.70×10^{-3} S/m to 4.24×10^{-1} S/m in PANI doped HCl PES fabric as the concentration was increased. In addition, PES fabric showed higher conductivity (4.2×10^{-1} S/m) as compared to 0.9 wt% HCl in cotton fabric (1.57×10^{-2} S/m). This indicated that there was an effect on different weight percentages of acid doped in the fabric. On the other hand, 0.9 v/v% of PANI-HCl in PES fabric showed that majority of the polymer chains were connected to PES fabric through hydrogen bonds. This situation also showed that higher fraction of PANI chains was chemically grafted onto the PES fabric surface.
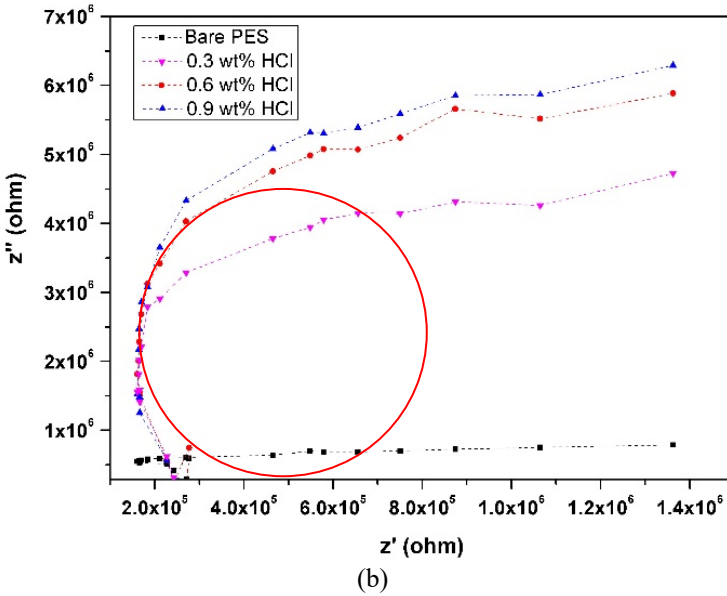

(a)

(b)
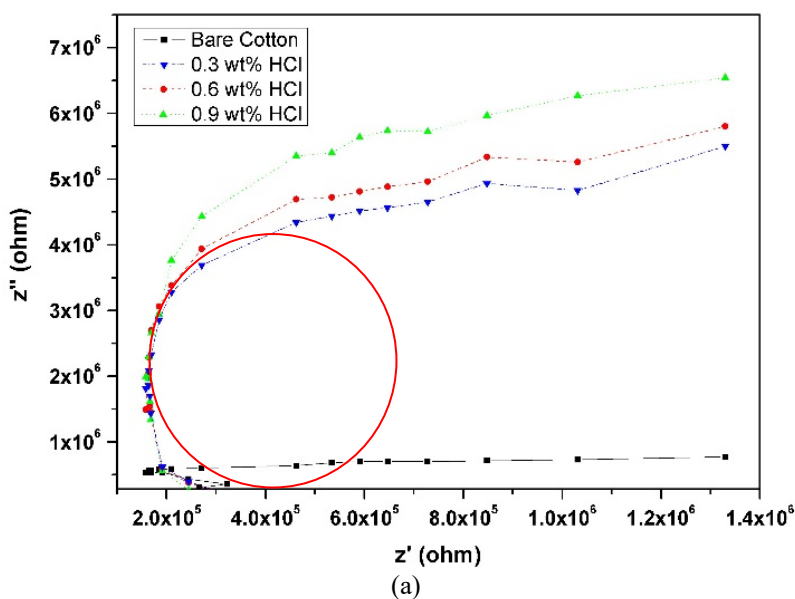
Figure 3: EIS spectra for PANI doped with different v/v% of HCl in (a) cotton fabric and (b) PES fabric

Figure 3 shows the electrochemical impedance spectra for PANI doped with 0.3 v/v%, 0.6 v/v% and 0.9 v/v% of HCl, displaying the electrochemical behavior of the fabrics. The impedance plot shows high frequency region in PES fabric as compared to cotton. This was observed at the high frequency intercept of the semicircle on the axis, which attributed to the resistance of the fabrics.

The diameter of the circle corresponds to the value of charge-transfer resistance of the fabrics. This is very much dependent on the ionic diffusion across the fabric [19]. The tilted straight line in the low frequency region (bare fabrics) indicated the limiting diffusion of electron migration in which no electron transfer was recorded. HCl electrolyte showed the characteristic feature of ideal capacitive behavior. In general, the semicircle diameter of PANI doped HCl in cotton fabric was smaller than PES fabric [20]. This indicated that C-N had incorporated well in PES fabric. In the process of electrochemical polymerization, N_2 ions were reduced to N^+ and the aniline was oxidized to PANI. In parallel, HCl had multiple doping positions which can bind to available nitrogen sites in PANI chains. Possibly, it formed inter-chain linkages among several adjacent PANI. Thus, this can enhance the strong bonding of the chain in PANI, which prevented the initial stage of PANI. In

addition, the H^+ ions may contribute to the delocalization of PANI; hence, it increased the electrical conductivity of PANI fabrics to cut-off ion diffusion path. It is deduced that strong acid like HCl with higher concentration gives extra conductive for the fabric.
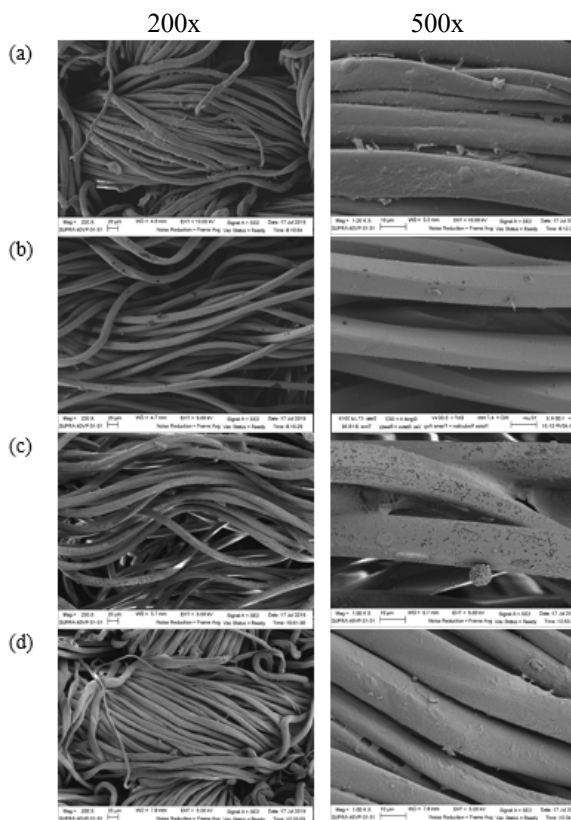

Figure 4: FESEM images of (a) bare cotton fabric (b) bare PES fabric (c) doped cotton fabric (d) doped PES fabric

FESEM

Field Emission Scanning Electron Microscope (FESEM) was used to reveal the morphology of fabrics before and after incorporating PANI in the textiles. We observed that bare PES fabric (Figure 4 (c)) had smoother morphology than cotton fabric (Figure 4 (a)). The fibrous surfaces of both bare cotton and PES were different cross-sectionally, in which the bare PES possessed a neater arrangement.

After incorporating PANI into the fabrics by immersion method, we found that PANI-PES fabrics showed an evenly-distributed surface (Figure 4 (d)), suggesting that PANI was greatly absorbed within the fabrics. In contrast, PANI-cotton had rough and non-uniform surface (Figure 4 (b)) [21]. The absorption of PANI into the fabrics depended on surface structure and wettability. It was observed that the distribution of PANI precipitation was much more deposited on cotton [22] as compared to PES surfaces. This is due to hydrophilicity properties in which PES fabrics have more ability to absorb more water content than cotton [23]. To conclude, the layer of PES fibers was intact and homogenous which had a certain interfacial adhesion with PANI substrate that can contribute to good binding and incorporation.

TGA

Thermal properties of fabrics were determined by Thermal Gravimetric Analysis (TGA). We observed that bare cotton fabric showed higher initial weight loss (100%) compared to bare PES fabric (90%) as seen in Figure 5 Interestingly, after incorporating PANI with the fabric, the thermal properties changed.
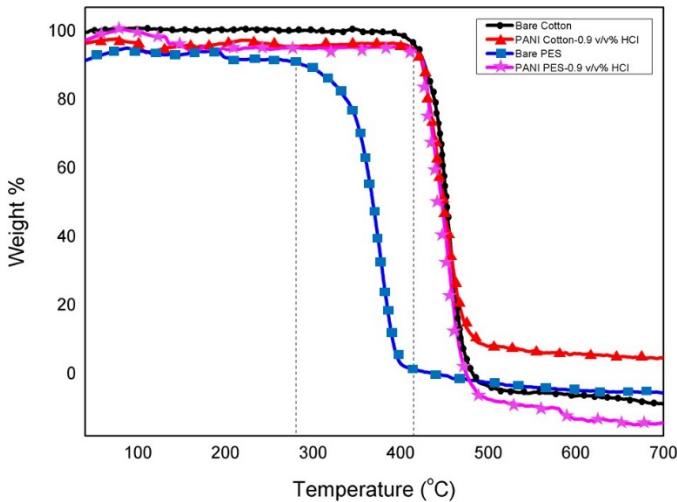

Figure 5: TGA curve for both bare fabrics and doped fabrics

For instance, both fabrics showed a small initial weight loss at the temperature of 100 - 200 °C and 80 - 200 °C for PANI-cotton and PANI-PES, respectively. These occurrences could be attributed by the water evaporation and depletion of dopant [24, 25]. In terms of thermal degradation, the major decomposition of bare cotton and bare PES was found to start at the temperature of 410 °C and 280 °C, respectively. This phase ended at the

temperature of 480 °C and 400 °C with 89% and 98% of weight losses. During this phase, the fibers were fully decomposed [12,26]. The introduction of PANI within the PES fabric had significantly improved the thermal stability. This was proven by the major shifting of degradation point from 400 °C to 477 °C. This is due to the structure modification by the strong acid like HCl [27]. In contrast, PANI-cotton did not show any shift (retained at ~480 °C) post-incorporation of PANI. The interaction of doped PANI onto the fabric was more apparent in PES than cotton due to the nature of their fibers. In the final phase, we found that the residue of thermal degradation of PANI-cotton fabric was 8% but PANI-PES fabric was fully decomposed which showed different degree of thermal degradation. PANI-cotton was found to have a higher thermal stability than PANI-PES as it can retain its composition after the temperature of 700 °C. According to Mentus et al. (2013) [28], the thermal stability of fibers could be due to the large surface that oxidation takes place.

Conclusions

PANI was synthesized using chemical oxidation method. The conductivity of PANI can be increased by adding a dopant, HCl at different concentrations. Both cotton and PES fabrics can simply be made conductive by incorporating a conducting polymer, PANI through a facile immersion technique. The conductivity of the fabrics can be achieved at 1.57×10^{-2} S/m and 4.24×10^{-1} S/m using 0.9 v/v % of HCl concentration. The morphological properties of the fabrics have shown different attributions. PANI-PES has a more uniform and homogenous structure than PANI-cotton. In terms of thermal stability, PANI PES has shown tremendous effect than PANI-cotton. Collectively, this study has presented a simple approach to produce a conductive fabric utilizing PANI as the conducting agent.

Acknowledgement

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