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## The effect of hydrochloric acid-doped polyaniline to enhance the conductivity

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**Abstract.** The studies of polyaniline (PANI) and other conducting polymers have shown that they possess semiconducting-properties. PANI is one of the conductive polymers used as a battery electrode, corrosion inhibitor, and sensor. The study aims to investigate the effect of hydrochloric acid dope to PANI. Polyaniline was synthesised by the oxidation of aniline with ammonium peroxodisulphate (APS) as an oxidant by the interfacial method in an immiscible organic/aqueous biphasic system, with hydrochloric acid as a dopant. The result showed that, PANI has conductivities in the range of  $3.00 \cdot 10^{-2}$  -  $7.00 \cdot 10^{-2}$  S.cm<sup>-1</sup>. The morphology and molecular structure of PANI were characterised by scanning electron microscopy (SEM), and FTIR respectively.

**Keywords:** dopant, hydrochloric acid, polyaniline, conductivity

### 1. Introduction

The electrical conductivity of conductive polymers is affected by the metal conductivity. One of the common characteristics of a conductive polymer is the presence of conjugated backbone, which is related to the oxidation or reduction of the electron donor-acceptor properties [1-3]. Polyaniline (PANI) is one of the most widely studied conducting polymers due to its physico-chemical properties with broad application. PANI is highly stable in the environment, easily synthesised, and can undergo reversible electrical properties changes through protons [2, 3]. PANI can be synthesised in several forms based on its oxidation rates, such as leucoemeraldine (fully reduced), emeraldine (half oxidised), and pernigraniline (fully oxidised). The conductive form of emeraldine is called emeraldine salt (ES). The degree of emeraldine conductivity depends on the level of doping addition, such as the number of protons doped into the emeraldine structure [3-6]. Various methods have been developed for the synthesis of PANI, including electrospinning, bulk polymerisation, and interfacial polymerisation methods [1, 6]. The electrospinning method is rarely applied because it requires high potential sources and other complicated equipment. The interfacial polymerisation method is chemically performed on the non-mixed solvent boundary plane. This method has several advantages, such as the easy of synthesis and purification processes (without templates), the nanoscale diameter of product, and the uniform size of nanofiber samples (> 95%) [1, 7]. The purposes of this research is to study the effect of hydrochloric acid dope to PANI.



## 2. Material and Method

First aniline was purified using distillation by introducing a 100 mL of aniline into a round bottom flask. The flask was heated in a heating mantle. The distillation process was carried out until the temperature reached 184°C. Furthermore, two solutions were prepared separately: (1) A 100 mL of toluene solution added by 2 mL of 1.0 M aniline monomer as an organic phase and (2) A 100 mL of 1.0 M hydrochloric acid added by 5.708 g of ammonium peroxodisulphate (oxidation agent) as an aqueous phase. Both solutions were mixed into one container and allowed to stand for 24 hours. The product of a polyaniline precipitate was collected and purified by filtration, then rinsed with distilled water and methanol until the filtrate became colourless. The precipitate was then dried in an oven at 80°C for three hours to obtain an acid-polyaniline powder (PANI ES). The PANI ES powder was then added to a 250 mL of the 0.1 M ammonium hydroxide solution in beaker glass, then stirred for one hour. Afterwards the brownish brown sediment formed (PANI EB) was filtered using Buchner funnel, then rinsed using the distilled water and methanol. The product was then dried in an oven at 80°C for two hours. A total of 0.143 g of PANI EB was added to 10 mL of NMP solvent while stirred for 16 hours. A homogeneous EB-NMP PANI solution was printed on a 2x2 cm film and dried in an oven for six hours at 80°C. The film was then immersed in solutions of hydrochloric acid with variation concentration: 0.25, 0.5, 0.75, 1.0; 1.25, and 1.5 M for one hour, then dried in an oven at 80°C for two hours. The dried films were each measured for its thickness and conductivity by the four-point probe method.

The characterisation of morphology and functional group were determined using scanning electron microscope (SEM), FTIR, and four-point probe methods.

## 3. Result and Discussion

In its free state, aniline tends to form dimers, aniline dimer is a reddish-brown and odourless solution. Without the purification process, aniline would not be polymerised into polyaniline. Instead, it will be converted into phenazines. The purification process was done by vacuum distillation method, in order to prevent the reactive oxygen diminishing the aniline. The distillate of aniline is colourless and has faulty odour, with a high boiling point of 184°C. The polymerisation of aniline can be carried out using various types of oxidising agent. Initially, the propagation of the polymer chain in the acidic pH requires high energy, in correspond to the oxidation potential of aniline (+1,05 V). When propagation takes place, the oxidation potential of the reaction will decrease. APS (ammonium peroxodisulphate) was used because it has higher oxidation potential (+1,94 V) than aniline.

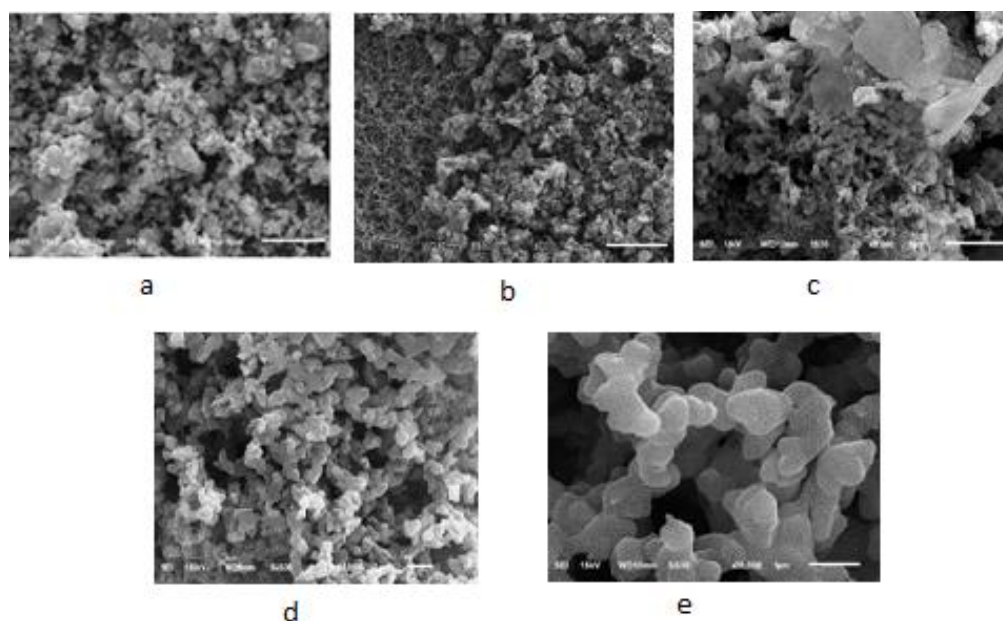
An obvious colour changes of the solution during the polymerisation was observed; indicating, the growth of macromolecules and polyaniline protonation levels. The colour was transformed from colourless into brownish red<sup>5-8</sup>, and gradually changed to navy blue (emeraldine base), dark purple (pernigraniline base), indigo blue (pernigraniline salt), and finally green Old (emeraldine salt) colours.

The product of the reaction was a shaded green emeraldine (ES) form. It was then separated from filtrate using filtration and rinsed with distilled water until the colour of the filtrate became clear. Furthermore, methanol was used to remove the low molecular weight intermediate of organic compounds and oligomers.

The subsequent polymerisation PANI was then dedoped into an emeraldine base form (EB). This step was done because the emeraldine salt (ES) is not soluble in polar solvent such as NMP which will be used in the plasticisation process. Moreover, the optimum concentration was determined by doping it with hydrochloric acid. The formation of PANI was reduced by the addition of ammonium hydroxide (NH<sub>4</sub>OH). When emeraldine salt was dissolved in NH<sub>4</sub>OH, it was deprotonated by releasing a proton (H<sup>+</sup>) followed by the binding of OH<sup>-</sup> from the NH<sub>4</sub>OH solution. Consequently, the emeraldine salt turned into a brown base emeraldine (EB).

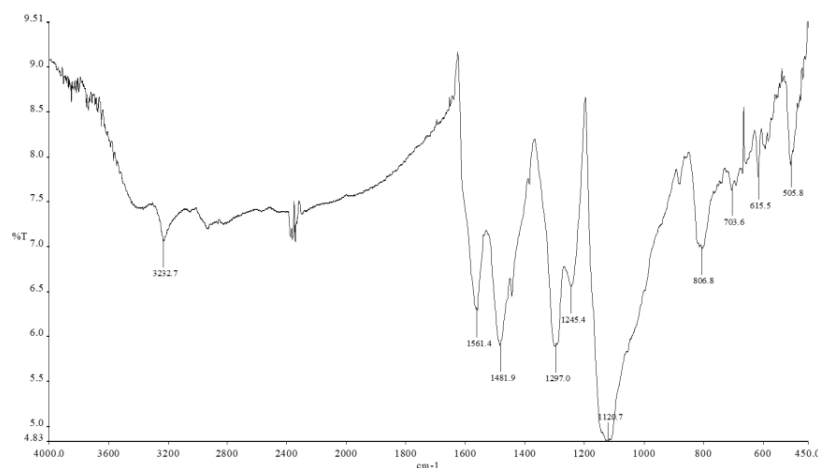
The acidic degradation was performed to determine the optimum doping level of PANI. Optimum doping has a higher conductivity value. Doping was done by soaking the thin film of PANI-NMP with HCl solution

in various concentrations 0.25, 0.5, 0.75, 1.0, 1.25; and 1.50 M. The morphology of PAN was characterised by the Scanning Electron Microscope (SEM) shown in Fig. 1.



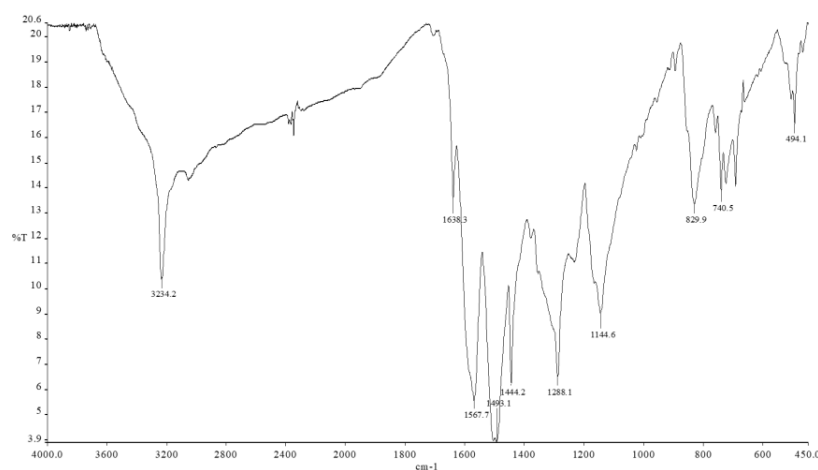
**Figure 1.** The SEM results of (a) pure PANI 5000x magnification; (B) PANI ES 500x magnification; (C) PANI ES magnification 5.000x; (D) PANI ES magnification 10.000x; (E) PANI ES (50:50) 20,000x magnification.

Composite surface morphology composed of large aggregates caused by adjacent particles during the drying process. Fig. 2 shows FTIR spectra of PANI which are in protonation form. All of them show the characteristic tapes of PANI emeraldine salts at the wave numbers of  $1560\text{--}1570\text{ cm}^{-1}$ ,  $1480\text{--}1490\text{ cm}^{-1}$ ,  $1302\text{--}1304\text{ cm}^{-1}$ ,  $1243\text{--}1245\text{ cm}^{-1}$ ,  $1108\text{--}1119\text{ cm}^{-1}$ ,  $800\text{--}805$  and  $819\text{--}822\text{ cm}^{-1}$ . The tape occurred due to the vibrations in the  $\text{Cl}^-$  ion counter observed at the wave number of  $750\text{--}800\text{ cm}^{-1}$ . An important difference was observed in spaces where the bands at the wave numbers of  $780\text{ cm}^{-1}$  are stronger than other bands at  $750\text{--}800\text{ cm}^{-1}$  wave numbers. The differences may be correlated with a higher form of polaronic delocalisation of the PANI chain (polaronic lattice) in the PANI ES sample with a larger molar ratio, stabilised by  $\text{Cl}^-$  ion, rather than the PANI EB sample. The main peaks of the wave numbers of  $1570$  and  $1490\text{ cm}^{-1}$  can be associated with stretch vibrations of  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  of quinone rings and benzene rings, respectively. Peaks at the wave number of  $1300$  and  $1240\text{ cm}^{-1}$  are the  $\text{C}\text{--}\text{N}$  stretch mode. The peak at the  $1150\text{ cm}^{-1}$  wave number is a quinonoid unit in the PANI doped.



**Figure 2.** Infrared Spectra of PANI ES.

Characteristics of the new band of emeraldine base PANI appear at the wave numbers of  $\approx 1380\text{ cm}^{-1}$  as shown in Fig. 3. The N-Q-N/C-H in-plane deformation bands appear at the wave numbers of  $1165\text{--}1167\text{ cm}^{-1}$  for deprotonated samples. At the wave number of  $\approx 1415\text{ cm}^{-1}$ , a unit such as phenazine, which is quite difficult to be seen in the protonated PANI sample spectra, becomes more apparent after the deprotonation of the sample. The vibrational deformation of the C-H band away from the plane of the banded aniline unit observed by the doublet at the  $\approx 800/820\text{ cm}^{-1}$  wave number in the protonation sample spectrum appears with increasing intensity and blue shift in the wave number of  $\approx 832\text{ cm}^{-1}$  in basic-shape spectra. This might be the result of a change in the N-containing group, acting as a substituent in the benzene ring, due to deprotonation.



**Figure 3.** Infrared Spectra of PANI EB.

From the results of conductivity measurements as shown in Table 1, there was a change in the conductivity value in each variation to the added dopant concentration. In addition, the dopant concentration of  $0.25\text{ M HCl}$  resulted in a low conductivity value of  $4.3417 \times 10^{-2}\text{ S.cm}^{-1}$  due to the addition of a small dopant.

**Table 1.** PANI conductivity values of HCl with various concentration.

M (HCl)	S.cm <sup>-1</sup>
0.25	4.3417x10 <sup>-2</sup>
0.50	7.3277x10 <sup>-2</sup>
0.75	3.3085x10 <sup>-2</sup>
1.00	7.0787x10 <sup>-2</sup>
1.25	6.2702x10 <sup>-2</sup>
1.50	1.6554x10 <sup>-2</sup>

In addition to the dopant concentration of 0.50 M, the conductivity increased to 7.3277x10<sup>-2</sup> S.cm<sup>-1</sup> and at the addition of 0.75 M dopant, the conductivity value was 3.3085x10<sup>-2</sup> S.cm<sup>-1</sup>. This result shows that the conductivity value is still in the same order. In addition to the dopant concentration of 1.00 M, there was a significant increase in conductivity to 7.0787 x 10<sup>-2</sup> S.cm<sup>-1</sup>. Furthermore, the dopant concentration of 1.25 M showed a decrease in conductivity value to 6.2702x10<sup>-2</sup> S.cm<sup>-1</sup>. In addition, the concentration of 1.50 M dopant showed a reduction in conductivity value to 1.6554x10<sup>-2</sup> S.cm<sup>-1</sup>. This was caused by the destruction of the polymer chain structure when the concentration of acid given was too high resulting in a decrease in the conductivity of the PANI produced. Increased acid concentration was given up to certain number resulted in an increase in conductivity, but the addition of subsequent concentrations will decrease the conductivity value.

#### 4. Conclusion

PANI can be synthesised with APS and the addition of hydrochloric acid by interfacial polymerisation. The optimum hydrochloric doping concentration in polyaniline is 0.50 M with a conductivity value of 7.3277x10<sup>-2</sup> S.cm<sup>-1</sup>

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