Acidity's Impact on Yield, Morphological Structure, and Surface Functionalities of Polyaniline Synthesised via Oxidative Polymerisation

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ABSTRACT: *This research aimed to examine how varying the acidity levels during the chemical oxidative polymerisation (COP) of aniline affects the colour, yield, morphology, and surface functionalities of polyaniline (PANI). In the COP method, aniline monomer was first dissolved in hydrochloric acid (HCl) medium; the solution was then drop added with ammonium persulfate to initiate the polymerisation process. To answer the research objective, the medium acidity was manipulated using different concentrations of HCl (i.e., 0 M, 0.01 M, 0.1 M, 1 M and 10 M). The as-synthesised PANIs were then purified and characterised for their physicochemical properties. The findings revealed that reducing the medium pH from 2.35 (in distilled water) to 0.80 (in 10 M HCl) resulted in a colour change from light brownish to dark green, indicating the formation of emeraldine PANI. Furthermore, it was observed that the amount of PANI yield is inversely related to the medium pH. A decrease in medium pH from 2.35 to 0.80 remarkably increased the PANI yield by 3.2 times. Regarding morphological structure, higher medium acidity produced PANI with well-defined globule shapes, while lower HCl concentrations resulted in a mixed morphology including globules, tubes, and plate-like structures. In addition, it was found that the diameter of globule-like PANI has increased from ~266.67 nm to ~508.33 nm, when the HCl concentration was changed from 0 M to 10 M. Apparently, increasing the acidity of the COP medium promotes enlargement of the PANI size.*

Despite that, there is not much change in the surface functional groups of the formed PANI. Overall, this study offers insights into manipulating PANI properties by adjusting the medium acidity during the COP process. While the impacts of medium acidity on yield, morphology, and functionalities of PANI were revealed, further investigation is required to evaluate the effect on electrical properties.

Keywords: conductive polymer, conductivity, oxidative polymerisation, polyaniline, polymer chemistry

1.   INTRODUCTION

The remarkable potential of conducting polymers (CPs) to boost the speed, stability, and sensitivity of electrical devices has captivated the attention of researchers.[1] CPs are polymeric materials, also known as synthetic metals, that display good electrochemical activity, good thermal stability, high conductivities, and are biocompatible.[2,3] Unlike conventional metal or semiconducting matters, CPs are more biocompatible in addition to their flexibility to be shaped into different structures.[4] With these unique characteristics, CPs have been incorporated into electronics and used for advanced applications, such as electromagnetic interference shielding, supercapacitors, rechargeable batteries, biomedical, gas sensors and more applications.[5–11] Some of the common types of CPs which have been developed for broad use in technological enhancements are polyaniline (PANI), polypyrrole (PPy), polythiophene (PT) and poly(3,4-ethylenedioxythiophene) (PEDOT).[12,13] Among the commonly studied conducting polymers, PANI has been one of the most extensive studied materials that have several desired properties such as low cost, ease of synthesis, chemical and thermal stability and electrical conductivity.[14–16] More importantly, PANI exhibits excellent environmental stability.[17] Depending on the protonation medium, PANI may exhibit conductivity ranging from 10^{-10} S/cm–1.22 S/cm, density ranging from 1.2 g/cm^3–2.06 g/cm^3, and contact angle ranging from 32°–102°.[18,19] PANI can be synthesised from chemical oxidative polymerisation (COP) or electrochemical polymerisation (EP) process.[20,21] In COP, the aniline monomer is oxidised to cation radical; these cation radicals couple to form dications in a run cycle. Repetition of the radical formation and coupling eventually leads to polymer formation.[22] On the other hand, in EP, the formation of cation radical and the subsequent growth into polymer chain occur on the surface of an electrode material.[23,24] The EP method suffers from low yield, hard to be scaled-up and weak solubility of the produced products.[25,26] In contrast, the COP produce large quantity of PANI and the process is straightforward.[20,27]

PANI exhibits electrical conductivity due to the presence of conjugated π-electrons systems that are easily delocalised, and thus, conduct electricity.[28] The chemical structure of PANI comes in various forms (namely emeraldine, leucoemeraldine

pernigraniline) of which each is characterised by a different current conductivities and oxidation states; emeraldine, leucoemeraldine and pernigraniline are half oxidised, fully reduced and fully oxidised forms of PANI, respectively. Out of all, emeraldine is regarded as the most conductive form because it contain alternating single and double bonds.[29] Study has shown that emeraldine PANI exhibits π-π* transition, polaron-π* transition and polaron-π transition characteristics; the polaron represent charge carrier and therefore, indicating good conductivity of this form of PANI.[23,30] The tendency of charge carriers to be generated along the PANI chains is also influenced by the structure of the chains and the synthesis procedure.[31] For instance, it was reported that the conductivity of PANI strongly depends on the degree of protonation and the type of dopant use.[32–35] In addition to the electrical property, other features such as the size, the structural morphology and the mechanical property of PANI can be fine-tuned by producing polymer chains with fewer defect sites and branching, which can be fulfilled through proper synthesis protocol.[36] It is important to have PANIs with different morphological characteristics, as all of them exhibit various electrical properties suitable for different applications[37] as well as various toxicity levels.[38] For instance, Koh et al. found that PANI-globules have higher conductivity than PANI-tubes, PANI-plates and PANI-microspheres.[39] Meanwhile, Zhang et al. reported that PANI nanofibers were more toxic than the nanosphere counterpart.[38]

The acidity of the COP medium could be one of the factors influencing the physicochemical properties of the formed PANI. In specific, it is known that the acidity of the initial synthesis medium will affect the oxidation process, and thus, the properties of the final product.[36,40] In fact, the polymerisation process of a monomer depends on various factors, including thermodynamic and kinetic considerations, with pH of the solution being one of them.[41] Despite the development in PANI research, there is a lack of systematic investigation to reveal the correlation between the acidity of the synthesising medium (during COP) on the yield, colour, morphology and surface functional groups of the formed product. The outcome from this study can serve as a guideline on designing of PANI with desired structure and properties for a specific application.

2.   EXPERIMENTAL

2.1   Synthesis of PANI

PANI was synthesised through a facile COP method following the procedure reported in the literature,[42] with slight modification. First, stock aniline monomer solution (Merck KGaA, Malaysia) was dropwise added to a 100 ml of 1 M HCl solution under constant stirring until the mixture was completely homogenised. Afterward,

the mixture was placed in an ice bath to keep the solution temperature within 0°C–5°C. On the other hand, 31.26 g of ammonium persulfate (APS) (Chemiz, Malaysia) was dissolved in 100 ml of distilled water. The APS solution was then dropwise added to the aniline solution, the mixture was constantly stirred for 2 h for the polymerisation process to complete. The produced PANI, which appears as a dark green precipitate, was filtered and thoroughly washed with distilled water before being dried into powder form. The mass of the dried PANI was repeatedly measured until a constant mass was achieved. The same experimental procedure was repeated by varying the molarity of HCl to 0 M (pure distilled water), 0.01 M, 0.1 M and 10 M to observe the effect of medium acidity on the formation of PANI.

2.2   Morphological Properties Study

Morphological properties of the PANI formed under different acidity mediums were evaluated through scanning electron microscopy (SEM) (Tescan VEGA3). The samples were completely dried in an oven, sprinkled on a metal holder using sticky carbon tape, and pre-coat with platinum to ensure a high-quality image can be obtained. Observation was done at 10 kV and 5,000× of accelerating voltage and magnification, respectively.

2.3   Compounds and Surface Functional Groups Analysis

To understand the influence of medium acidity on the compounds and surface functionalities of the formed PANI, all of the PANI powders (dried in an oven) were characterised through attenuated total reflectance-Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer). The samples were scanned from the wavenumber range 400 cm^{-1}–4,000 cm^{-1}. Before analysing the sample, a background spectrum was collected so that the spectrum of the instrument itself could be excluded from the spectrum of the sample of interest.

3.   RESULTS AND DISCUSSION

3.1   Effect of Medium Acidity on the Yield of PANI

Table 1 summarise the amount of PANI yield along with the pH of the final synthesising medium upon conducting the COP using HCl of different concentrations. In terms of pH of the final synthesising medium, all of the products appear to be highly acidic even for the mixture produced using a water medium (i.e. 0 M HCl). This observation was due to the acidic environment imposed by the initial reactants (aniline and ammonium persulfate), and the yield of sulfuric

acid as by-product.[43] With the inclusion of a 0.01 M–10 M HCl as doping agent, the pH of the final synthesising medium was found to be pH 2.05. Despite that, it was found that the amount of PANI produced is inversely related to the medium pH in which the lower the medium pH (increasing acidity), the higher the amount of PANI yield. A similar trend was reported in previous literature;[31,44] one of the possible reasons for such observation is the insertion of more dopants into the polymer chain, hence, increasing the total mass.[45] In addition, it was reported that an increase in medium acidity may enhance the polymerisation reaction by promoting the generation of additional dissociated ions (H_3O^+), thus improving the nucleation stage and subsequently leading to higher coupling efficiency.[36]

Table 1: The pH of the synthesising medium and the amount of PANI yielded using different concentrations of HCl.

Molarity of HCl used (M)	pH of the final synthesising medium	PANI yield (g)
0	2.35	7.283
0.01	2.05	8.415
0.1	1.95	9.518
1	1.41	15.236
10	0.80	23.306

From the physical appearance of the formed PANIs (see Figure 1), there were slight changes in the colour of the formed PANI with the variation of HCl concentrations. For the 0 M HCl sample, the PANI had a light brownish colour, and upon increasing the HCl concentration, the colour of the PANI darkened and a green shade became apparent. This was also observed during the polymerisation of aniline, where the mixture turned to dark green colour, indicating the formation of the emeraldine form.[46] The colour change in PANI in the emeraldine state is due to an acid-base reaction, specifically protonation with HCl leading to formation of green PANI.[47]

Figure 1: The physical appearance of PANI yielded using different concentrations of HCl. (Bottle arranged from left to right is for PANI produced using 0 M, 0.01 M, 0.1 M, 1 M, and 10 M of HCl).

3.2   Effect of Medium Acidity on the Morphological Properties of PANI

SEM analysis was performed on the as-made PANI sample to identify the changes in morphological characteristics across the synthesis medium acidity variation. As shown in Figure 2(a–c), the as-made PANIs appeared in a mixture of shapes under low acidity mediums. In specific, the PANIs formed at 0 M HCl consist of plate-like, tube-like and a small quantity of globule-like structures. In few spots, the PANIs were found to form clusters that resemble nanoflowers. These observations were also seen on the PANI prepared at 0.01 M and 0.1 M HCl, as shown in Figure 2(b, c). However, the number of plate-like and tube-like PANIs has been gradually replaced by globule-like PANIs. Apparently, the increase in acidity of the synthesising medium has led to a higher granulation of PANI. When the medium acidity was further increased by using 1 M HCl (see Figure 2[d]) and 10 M HCl (see Figure 2[e]), a defined and smoother globule-like PANIs were found to monopoly the whole sample.
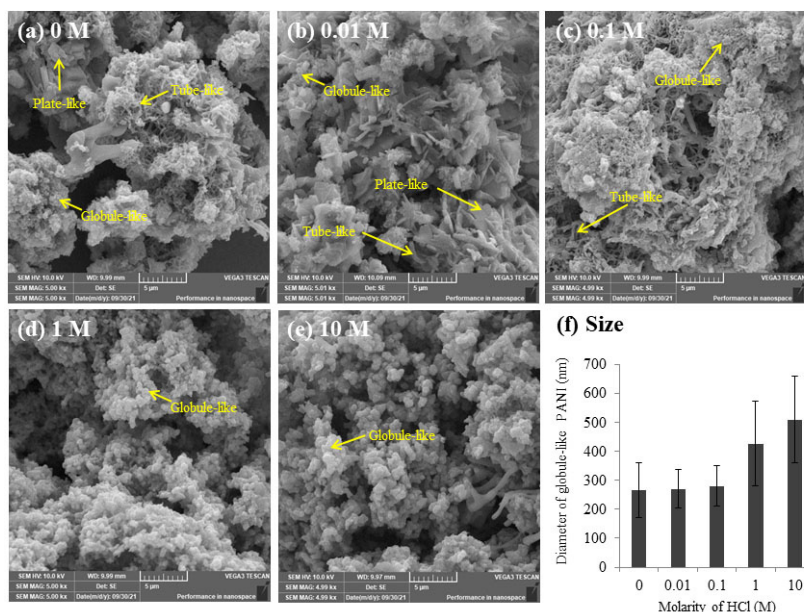

Figure 2: SEM images of PANI formed using (a) 0 M HCl, (b) 0.01 M HCl, (c) 0.1 M HCl, (d) 1 M HCl, and (e) 10 M HCl. (f) Average diameter of ten randomly selected globule-like PANIs. (Magnification: 5,000×).

Theoretically, the initial step in the COP of aniline is called the induction period which produces aromatic phenazine rings. Clusters of these phenazine ring subsequently turn into polymer sphere in the stage of polymer chain growth.[43] At low acidity mediums, the induction period is longer which favours

the assembly of phenazine into columns and thus, forming one-dimensional PANI.[48] This explains the presence of tube-like PANI in the 0 M 0.01 M and 0.1 M samples. On the other side, under strong acidity mediums (1 M and 10 M HCl), the induction period was shortened and the chain growth happens quickly. Under such conditions, PANI of globular shape is favourably formed, as seen in Figure 2(d, e). Similarly, in several reported works, the formation of globular-shaped PANI was found to be favourably formed in a strong acid medium;[36,39] for instance Koh et al. reported that synthesis of PANI in strong acid, weak acid, water and alkaline mediums produced PANI of globular shape, tubular shape, plate shape and flake shape, respectively.[39] In addition to the changes in morphological structure, it was found that the diameter of globule-like PANI has increased from ~266.67 nm, to ~270.49 nm, ~281.67 nm, ~425.83 nm and ~508.33 nm, when the HCl concentration was set at 0 M, 0.01 M, 0.1 M, 1 M and 10 M, correspondingly (Figure 2[f]). Evidently, increasing the acidity of the COP medium promotes enlargement of the PANI size.

Interesting to note that as compared to the findings by Sapurina et al., which showing plate-like, tube-like, and globule-like PANI can be prepared by using different types of acid dopants,[48] the present work showed that the shape of the PANI can also be varied by using a single type of dopant (HCl) by with varying concentrations. Hence, it is convincing to claim that the acidity of the COP medium plays a critical role in determining the morphological properties of the formed PANIs.

3.3   Effect of Medium Acidity on the Surface Functionalities of PANI

Figure 3 shows the FTIR spectra of the PANI samples produced using different HCl concentrations and their corresponding characteristic absorption bands. The bands around 1,556 cm^{-1} and 1,480 cm^{-1} are attributed to the main peak consistent with quinone and benzene ring deformations of PANI, respectively.[49–52] The broad band of the amine group (N-H stretching vibration) is apparent at 3,214 cm^{-1}, 3,226 cm^{-1}, 3,220 cm^{-1}, 3,215 cm^{-1} and 3,211 cm^{-1}, for PANI produced using 0 M, 0.01 M, 0.1 M, 1 M and 10 M HCl, respectively.[53] The N-H stretching vibration is contributed from the primary aniline monomer amine.[54] The presence of a broader absorption band in the 3,500 cm^{-1}–3,000 cm^{-1} range, as indicated in Figure 3 of the FTIR spectra for the 0.1 M sample, is indeed an outlier observation but a definitive explanation for its origin has not been reached. The absorption band located around 2,989 cm^{-1}–2,823 cm^{-1} can be assigned to the aromatic sp^2 hybridised C-H stretching vibration as well as the aliphatic hydrocarbon

C-H stretching of aniline.[53,55] In addition, the absorption band at 1,038 cm^{-1} and 1,090 cm^{-1} for the 0 M sample can be ascribed to the in-plane bending motion of C-H bonds;[56,57] these peaks were slightly shifted and changed in intensity for PANIs formed using different concentrations of HCl.
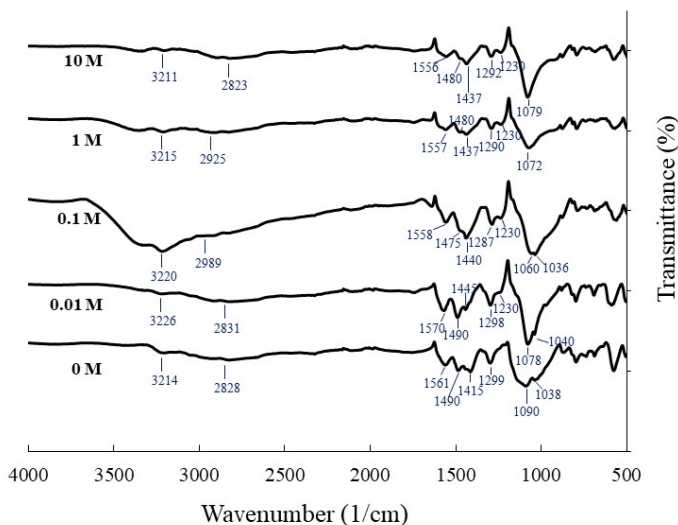

Figure 3: FTIR spectra of PANI formed using various concentrations of HCl.

By comparing the FTIR spectrum of PANI produced without HCl (0 M HCl) and those formed with HCl (0.01 M–10 M), a weak band located at 1,230 cm^{-1} was found in all of the PANIs formed with HCl. This specific peak is the characteristics band of the conducting protonated form of PANI and can be assigned to C-N$^{+•}$ stretching vibration.[51,58] The intensity of this specific peak is more pronounced upon increased in the HCl concentration.

4.   CONCLUSION

This study has successfully investigated the effects of medium acidity during PANI synthesis on the physicochemical properties of the product. The synthesis procedure was carried out through the COP method and five PANI samples were formed using varying HCl concentrations. It was found that increasing the medium acidity increased the amount of PANI produced. Specifically, the mass of PANI produced was recorded as 7.283 g and 23.306 g when the COP was conducted at 0 M and 10 M HCl, respectively. This increase in yield was owed to the higher conversion rate caused by the addition of HCl acid, which prompted the formation of additional PANI chains. The colour of the PANI yields differed

as well, whereas the 0 M HCl sample produced a light brownish colour. Upon the increase of HCl concentration, the solutions darkened and a dark green shade appeared which indicating the formation of the emeraldine form of PANI. SEM analysis proved that the morphology of PANI is strongly affected by the medium acidity with a mix of random structures (globule, tube, and plate-like structures) formed when the COP was performed in low acidity medium. In contrast, PANI of a more defined globule-like structure was formed when the COP was conducted in high acidity medium. Meanwhile, the acidity of COP medium has insignificant effect on the surface functionalities of the formed PANI except for an increase in the intensity of C-N$^{+\bullet}$ stretching vibration with the increase in HCl concentration.

5.   ACKNOWLEDGEMENTS

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