

## Sonication Time a Salient Parameter in Shaping the Conductivity and Morphology of Polyaniline

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A novel sonochemical method has been applied to prepare Polyaniline (PANI) from aniline monomers. PANI was synthesized via ultrasonic irradiation (U.I) by varying the sonication (reaction) time. Surface morphology and electrical conductivity were studied using FESEM and Four-probe conductivity meter and structural properties were examined using FT-IR and UV-VIS. The presence of characteristic bonds of PANI was observed from FTIR spectroscopy technique. The findings of this study reveal the importance of sonication time in shaping the morphology, particle sizes and electrical conductivity of the PANI. The morphology of the generated PANI indicated granular structure. On the other hand, the electrical conductivity of the nanocomposite increased up to 1.78 S/cm at 30 min of sonication and then decreased with further increase in sonication time. Sonochemical synthesis route is a multifaceted technique using which nanostructured materials with different physical and chemical characteristics can be produced. This can be achieved by just varying the treatment condition (e.g., ultrasonic irradiation time, amplitude, temperature) during sonication. Therefore, this study provides the optimized sonication time for PANI synthesis. The output of this research clearly shows that, ultrasonication is a one of the fast, versatile, emerging, and promising non-destructive green technology which still needs to be understood completely.

### 1. Introduction

Polyaniline (PANI) is the intriguing conjugated polymeric product of aniline under acidic conditions and has been known since 1862. For a long time PANI was well known as a chemical substance. Only since 1977 it attracted interest after the discovery that iodine doped polyacetylene has a metallic conductivity. Since the discovery of PANI as a metallic conducting material is known it grabbed huge attention due to its potential to be used for various applications requiring electrical, opto-electrical and optical properties (Xia and Wang, 2002). The major drawback for conducting polymers including PANI is their non-molten nature which makes them insoluble in common solvents. Thus when prepared using conventional methods this leads to aggregation of nanoparticles due to their high surface energy (Ali Mohsin et al., 2017). Therefore, the methodology/technique to prepare conducting nanoparticles is have received much attention (Ali Mohsin et al., 2016)

Over the decades there are several reports about the polymerization of PANI. The following are the techniques which are reported in literature about polymerization of PANI. Bulk polymerization: This considered to be the easiest technique for PANI polymerization as the reaction is carried out by just using monomer and its soluble initiator. ii. Solution polymerization: This technique is adopted to counter the problems of bulk polymerization by employing the solvent to reduce the reaction viscosity, which helps in heat transfer and lowering of auto acceleration. iii. Suspension polymerization: Same as solution polymerization this technique is adopted to address heat transfer issue. However, in this method the reaction mixture is suspended in inert medium as a

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droplet. iv. Emulsion polymerization: This technique is similar to solution and suspension polymerization. The only difference is in this method the initiation is soluble in suspension media and insoluble in the monomer. Usually, two methods including chemical oxidation and electrochemical synthesis are employed for preparing PANI. Although prepared PANI via electrochemical synthesis generally has higher conductivity, this method is restricted by the size, shape and nature of the involved electrode. Therefore, this method cannot be used to prepare a large amount of PANI or to produce fine PANI powders; thus PANI used for commercial application is normally synthesized via the chemical oxidation method (Wan et al., 2004). However, there are certain limitations of PANI, those are PANI is non-biodegradable, non-flexible and non-processable, only very low amount of PANI can be and should be used for producing conductive nanocomposites (Baniasadi, 2014). In addition, the particle size of PANI should be controlled within a proper range, i.e. less than 100 nm, in order that PANI particles can be easily excreted through circulatory systems after complete degradation of polymeric matrix.

The most widely used method of PANI synthesis is oxidative polymerization, in this method doping and polymerization takes place together and this can be done either chemically or electrochemically. The limitation of using electrochemical method is lower yields as compared to chemical method (Azlinda et al., 2012). Earlier researchers have developed and reported a simple chemical polymerization method to synthesize bulk PANI. In this method aniline was polymerized with suitable oxidant in presence of a dopant (mineral or organic acid) to produce PANI (Zareh et al., 2011).

One of the technologies that have grabbed huge attention for producing PANI by chemical synthesis method is Ultrasonic irradiation (U.I). U.I is relatively new technology. It works on the principle that when an ultrasonic wave passes through a reaction mixture, huge microbubbles will form then grow and eventually collapse and all this happens in very short span time (few microseconds), this phenomenon is called ultrasonic cavitation (Neelgund and Oki, 2011). During cavitation extreme conditions take place inside a cavitating bubble this extreme conditions leads to cavitation. Upon successful cavitation nanostructured nanomaterials are produced. Sonochemical synthesis route is a multifaceted technique using which versatile method that can be satisfactorily used to produce nanostructured materials with different physical and chemical characteristics can be produced. This can be achieved by just varying the by changing the treatment condition (e.g., ultrasonic irradiation time, amplitude, temperature) during sonication. (Yang et al., 2017). Also, the sonochemical method that uses ultrasound irradiation has shown promise because it is a green and feasible technique that is fast and simple (Husin et al., 2015). Sonochemistry is the application of ultrasound to chemical reactions and processes. Besides, ultrasonic irradiation route could enhance the rate of reaction for many homogeneous and heterogeneous chemical reactions (Aziz et al., 2011). Therefore, in the present work, a simple sonochemical method was used to prepare PANI nanoparticles and study the effect of sonication time on its properties. In order to investigate the effect of sonication time, electrical conductivity, morphological, FT-IR and UV-VIS characterizations were carried out. To the best of our knowledge, the effect of ultrasonic irradiation time on electrical conductivity and structural properties of PANI has not been reported in previous investigations.

## 2. Materials and methods

### 2.1 Synthesis of PANI

Aniline and ammonium persulfate (APS) were procured from Sigma Aldrich, Malaysia. Hydrochloric acid (HCl) 1.0 M was purchased from TOLSA. The PANI nanoparticles were prepared using ultrasonic irradiation by in situ polymerization of aniline (Azlinda et al., 2012). The typical procedure involves the addition of, 100 mL HCl (1.0 M) and 4 mL (0.0439 mol) of double distilled aniline in a 250 mL three-necked flask equipped with inlet and outlet of inert gas was added. This solution was left for few minutes and the temperature of the ice bath was maintained 0-3 °C during the reaction. This was followed by addition of oxidant solution which was prepared by dissolving measured amount of APS in deionized water. The solutions were degassed with inert gas and the prepared APS solution was added dropwise over a period of time. After the complete addition of oxidant the solution was left for sonication by varying the time as shown in Table 1. The obtained solution was kept aside for 24 h for reaction to complete. Only the sonication time was varied all other parameters were kept same as the molar ratio of aniline to APS was kept at 1:1. The obtained product was purified by washing with water three times followed by ethanol until pH 7 was achieved. The dark green powder was collected on a filter paper using vacuum filtration. The filtrate was dried in vacuum (50 °C) for 12 h. The same procedure was repeated for preparation of PANI nanoparticles with different ultrasonic irradiation times (15, 30, 60 and 120 min) as shown in Table 1.

### 2.1 Characterizations

Electrical conductivity was measured by using four probe Keithley meter (Model 6517 A), which comes along with a resistivity chamber (Model 8009). This comes in a shielded box protecting the electrodes, the protection

will reduce the stray electrostatic pick-up to avoid measurement errors. The electrodes are built as per ASTM standards and are made up of stainless steel. The electrodes in the resistivity chamber are coated with conductive rubber for better sample electrode contact. Each sample was tested for at least three times to ensure repeatability and reproducibility. The sample for electrical conductivity measurement was prepared by taking 5 g of PANI nanoparticles in a Carver model C press and made into a pellet (diameter: 13 mm, thickness: 1 mm). Morphology of the PANI nanoparticles was studied by using FE-SEM JSM-6701F. The high resolution was consisted of 1.0 nm at 15 kV and 2.2 nm at 1 kV. The samples were coated using JFC-1600 Auto Fine Coater before they were scanned by FE SEM JSM-6701F. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet (Madison, WI, USA) 170SX FTIR spectrometer in the wavelength range of 4,000–400  $\text{cm}^{-1}$  in the attenuated total reflection mode.

### 3. Result and discussion

#### 3.1 Electrical conductivity

The electrical conductivity of the nanocomposite depends on PANI chains, and the formation of the PANI chains is initiated by sonication, so the duration of sonication affects the conductivity of the nanocomposites. Table 1 shows variation of conductivities of PANI nanoparticles obtained through ultrasonic irradiation at room temperature (27 °C). The conductivities of nanocomposites are in the range of 0.0067 – 1.78  $\text{S cm}^{-1}$ . When the U.I time exceeds 30 min, the conductivity of PANI decreases drastically. The conductivity for PANI at U.I time of 60 min is 0.041  $\text{S cm}^{-1}$  and for U.I time of 120 min is 0.0067  $\text{S cm}^{-1}$ . The electrical conductivity of the nanocomposites increases with the increase in ultrasonic irradiation time from 15 to 30 min, beyond that the conductivity decreases. Clearly, at less than 30 min not enough crosslink points are produced to construct PANI chains and conducting channels, which results in the decline of the electrical conductivity of the nanocomposite. Increase in irradiation time beyond 30 min causes a side reaction for oxidizing PANI, which leads to the devastation of the PANI chain in some extent, a conducting channel be formed effectively, therefore, the conductivity of the PANI decreases (Neelgund and Oki, 2011). Upon increasing the U.I time beyond 30 min, the PANI chains are dispersed and the conducting channels are weakened which results in smaller conductivity for the PANI (Tang et al., 2008). Clearly, showing ultrasonic irradiation time contributes to the variation in conductivity of the nanoparticles prepared.

*Table 1: Preparation conditions, electrical conductivity and morphology of synthesized PANI.*

Sample ID	Reaction Time (min)	HCl Concentration ( $\text{mol.L}^{-1}$ )	Electrical Conductivity ( $\text{S cm}^{-1}$ )	Primary morphology
P1	15	1	1.01	Semi-Spherical
P2	30	1	1.78	Spherical
P3	60	1	0.041	non- Spherical
P4	120	1	0.0067	non- Spherical

#### 3.2 Morphology

The morphology of PANI nanoparticles were investigated by FE-SEM. In fact PANI nanoparticles show three types of shape distribution: spherical type (ca. 10 nm mean diameter of nanocrystals), semi-spherical and non-spherical shape (around 30 nm) or irregular. Figure 1a to 1d show the morphology of the generated PANI nanoparticles synthesized for 15, 30, 60 and 120 min. There were morphological evolutions from semi-spherical to spherical to non-spherical structures with increase in ultrasonic irradiation time. It is evident from Figure 1 polymerization preferably occurs in the bulk with spherical structure. The regulated spherical structure began to break into non-spherical when ultrasonic irradiation time was increased to 60 and 120 min. The PANI particles of these samples (60 and 120 min) tend to agglomerate and form bigger particles with non-spherical shape as the ultrasonic irradiation time is increased.

With the increase in ultrasonic irradiation time overgrowth of polyaniline is noticed, similar results were reported but for varying concentration of aniline (Saikia et al., 2010). This indicates that the particle morphologies were influenced only by the sonication times. Increasing sonication times meant increasing the energy transfer from the sonication generator to the precursor, which changed the morphological structure, as reported in the previous investigation (Widiyastuti et al., 2016). It may be due to the continuous ultrasonic irradiation provides higher local temperatures that are a consequence of low energy cavity collapse due to acoustic cavitation. Thus, there is bigger particles of PANI were observed for sample synthesized under longer ultrasonic irradiation time (Aziz et al., 2011). This bigger particle formation of PANI is due to the coalesce of smaller particles. Addition of that, longer time ultrasonic irradiation was also expected to provide better dispersion of PANI particles. Similar

behaviour was observed on the study of the effect of ultrasonication duration on colloidal structure of alumina–water nanofluid by Mahbulul et al. (2014).

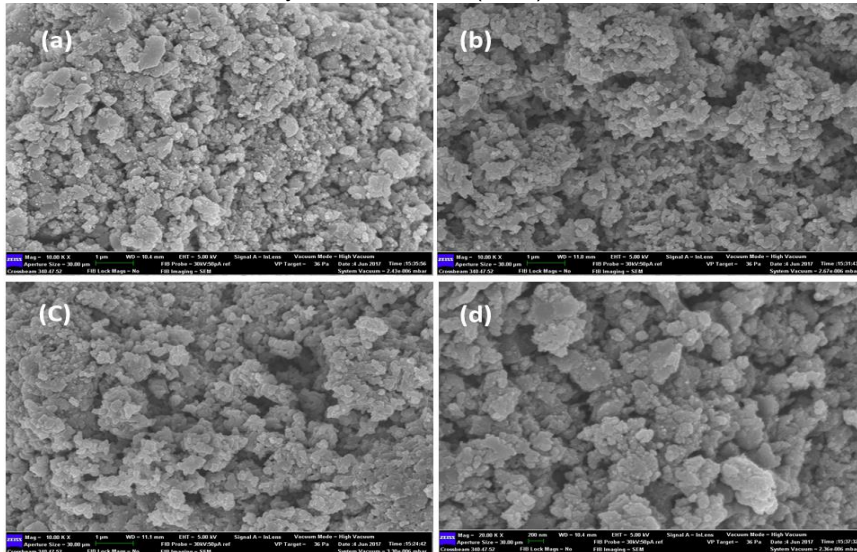


Figure 1: PANI nanoparticles synthesized for (a) 15, (b) 30, (c) 60 and (d) 120 min.

### 3.3 FT-IR analysis

As depicted in Figure 2 the peaks at  $1,567\text{ cm}^{-1}$  and  $1,483\text{ cm}^{-1}$  are the characteristic peaks of PANI.

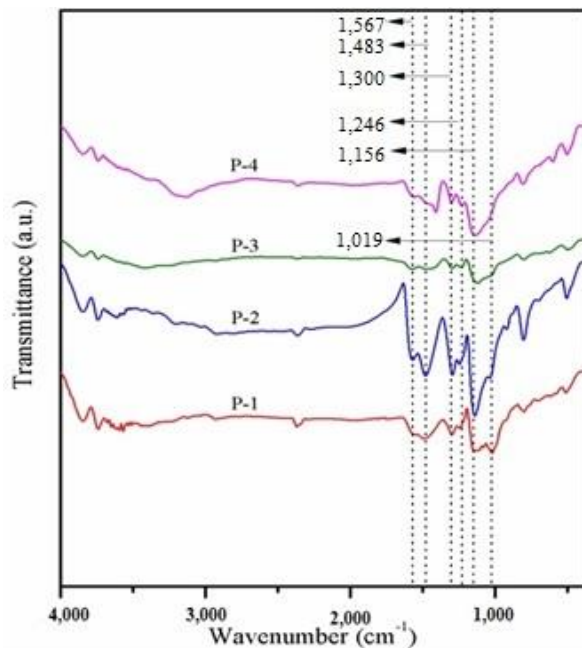


Figure 2: IR spectra of PANI nanoparticles at varying times

The peak at  $1,567\text{ cm}^{-1}$  can be assigned to the C=C and the peak at  $1,483\text{ cm}^{-1}$  can be assigned to C=N stretching vibrations. These peaks are the indication of the deformation of quinoid and benzenoid ring. The peak at  $3,210\text{ cm}^{-1}$  is the characteristic peak of emeraldine base form, this is due to the N-H stretching with hydrogen bonded  $2^\circ$  amino groups (Parveen et al., 2016). The peak at  $3,210\text{ cm}^{-1}$  is apparent in sample P4, while no peak can be observed for P1 to P3 samples at  $3,210\text{ cm}^{-1}$ . Electrical conductivities values have been used to proof and support the claim that sample P4 is emeraldine base. On top of that, the conductivity of emeraldine base is very less compare to emeraldine salt, which can be noticed from the electrical conductivity values presented in

Table 1. Thus, indicating upon increasing the sonication time the PANI is changing from emeraldine salt to emeraldine base which is aptly supported by electrical conductivity results. Another characteristic peak of PANI can be attributed to the peak at  $1,300\text{ cm}^{-1}$ . The above argument provides an evidence that conductive PANI nanoparticles is successfully formed.

The peak at  $1,300\text{ cm}^{-1}$  suggests that the PANI is in doped state and conducting in nature as this peak is the quantification of the degree of electron delocalization as an “electronic-like bond”. The peak at  $1,300\text{ cm}^{-1}$  is due to the electron delocalization in the C-N stretching vibrations of the quinoid rings. The next peak at  $1156\text{ cm}^{-1}$  was assigned to the vibration mode of the  $-\text{NH}^+=$ . The films with better performance in electric conductivity were located in these peak regions (Park et al., 2016). For PANI, the peak at  $1,483\text{ cm}^{-1}$  representing the stretching vibration of benzenoid ring becomes less prominent for P2 and almost disappears for P-3 to P-4 suggesting the decrease of PANI property (Saikia et al., 2010). Similarly, the bands at  $1,300\text{ cm}^{-1}$  and  $1,246\text{ cm}^{-1}$  correspond to C-H stretching vibration with aromatic conjugation, suggesting presence of PANI but with varying intensities. This is also supported by the electrical conductivity values for the respective nanoparticles. The final characteristic peak for PANI which confirms its successful synthesis is at  $821\text{ cm}^{-1}$  attributed to C-H out of plane deformation bending of the benzene ring. Previous study found similar findings that was no significant different of the PANI characteristics when the polymerization is exposed to different ultrasonic wave and time (Husin et al., 2015).

### 3.4 UV-VIS analysis

UV-VIS spectroscopy is a simple yet effective technique for governing the quality of nanoparticles prepared from conductivity point of view. The characteristics absorption peaks of PANI are at  $\sim 315$ ,  $\sim 420$  and  $\sim 600\text{ nm}$  as shown in Figure 3.

The absorption peak at  $\sim 315\text{ nm}$  is corresponding to the  $\pi$ - $\pi$  transition of the benzenoid structure. The peak at  $\sim 420$  is attributed to the polaron band transitions. The final absorption peak at  $\sim 600\text{ nm}$  which can be assigned to  $\pi$ - $n$  which is as a result of excitons formation in the quinoid rings and doping level. These three peaks are typical characteristic peaks of emeraldine salt. These observations are consistent with literature reports of PANI (Parveen et al., 2016). The wavelength of the quinoid band plays an important role in switching polyaniline from an electric insulator to a conductor upon doping. For PANI, the last two bands are related to the doping process that is responsible for the polymer conductivity (Zareh et al., 2011). Upon increasing the U.I time the exciton formation in the quinoid ring reduces (as seen by reduction in band intensity at all the three peaks) and ultimately disappearing. Thus, reducing the conductivity of the PANI nanoparticles. Similar finding was found that thermal conductivity enhancement of nano-fluids ( $\text{TiO}_2$ -water,  $\text{TiO}_2$ -ethylene glycol and  $\text{TiO}_2$ -paraffin oil) increased with the increase of sonication time during exposure (Sonawane et al., 2015).

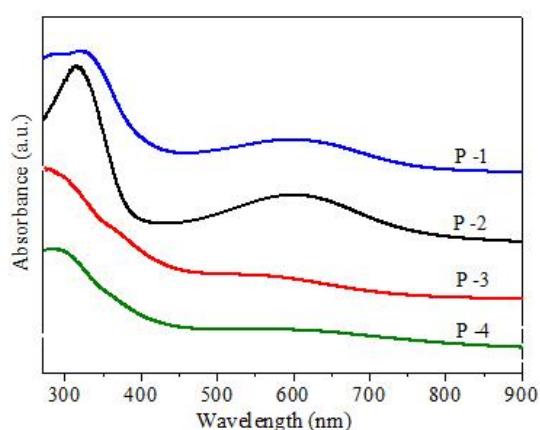


Figure 3: UV-VIS spectra of PANI nanoparticles at varying times

## 4. Conclusion

Polyaniline was synthesized using ultrasonic irradiation technique by varying the sonication time. The obtained results showed that sonication time is one of the salient parameter modifying which results in PANI's characteristic properties. The electrical conductivity of the synthesized PANI shows the importance of sonication time as the conductivity of the PANI varies exponentially upon changing the sonication time. Also, the morphology of the PANI nanoparticles varies from semi-spherical to spherical and non-spherical as the

sonication time increases from 15 to 120 min. These results were ably supported by FT-IR and UV-VIS. As the characteristics peaks of PANI were observed in FT-IR analysis. The FT-IR and UV-VIS results showed that change in sonication time have very less impact on them as the peaks shifted very little. Finally, it can be concluded apart from type of dopant, dopant concentration, oxidant concentration etc., sonication time plays a vital role in determining the conductivity of the PANI nanoparticles. These results will be useful for future researchers as it shows how by varying the sonication time, electrical conductivity and morphology of PANI changes.

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