Study of Different Acid Doped Polyaniline Nanostructures and Their Electrical Conductance Properties

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Abstract

The different acid doped polyaniline (PANI) materials were prepared in situ using mineral acids like HCl, H_2SO_4, HNO_3 and $HClO_4$ of different concentrations in presence of 0.2 M aniline solution and 0.25 M ammonium persulfate as oxidising agent by the chemical oxidation method. The synthesized materials were studied for their physico-chemical characterizations like XRD, IR and SEM. IR studies revealed the formation of emeraldine salt in all the acid doped PANI samples. XRD of samples exhibited the partly crystalline structure of which $HClO_4$ doped showed good crystallinity over other samples. SEM images displayed the formation of nanorods like structural agglomerates. The effect of acid dopants on their electrical conductivity was investigated by using the four probe set up technique. It was found that $HClO_4$ doped PANI exhibited good electrical conductivity over the other acid doped samples whereas the lowest electrical conductivity was recorded for HNO_3 doped PANI samples. The electrical conductivity of 1 M $HClO_4$ doped PANI was the highest i.e. 9.1 S cm^{-1} among all PANI samples.

1. Introduction

A new arena in the research field of polymers was begun with the discovery of intrinsically conducting polymers (ICPs) in 1960. ICPs like polypyrrole, polythiophene, polyacetylenes, and polyaniline (PANI) have been studied and investigated comprehensively [1-4]. ICPs are organic polymers that conduct electricity. The intrinsically conducting polymers (ICPs) are usually known as 'synthetic metals' [5,6]. The term 'synthetic metals' refers to the large number of organic polymers which possess not only the mechanical properties and processibility of conventional polymers, but also unique properties like electrical, electronic, magnetic, and optical properties of metals, which conventional polymers do not belong [7-10].

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PANI was initially recognized in 1835 and the term 'aniline black' was coined to it, a term used for any product obtained from oxidation of aniline. PANI is supposed to be the best candidate among ICPs due to the good processability and conductivity properties. Hence there is an abundant possibility for modifying the conductivity and processability of PANI [11,12]. Among all conducting polymer, PANI is one of the most promising conducting polymers due to properties like an ease of preparation, good environmental stability, better electronic properties, low cost, low density, and its applications in electrochromic display, electrocatalysis, rechargeable batteries, sensors and biosensors [13-17]. PANI has potential applications in the multidisciplinary field. PANI being electrically conducting in nature it can be applied in different areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electrorheological, sensors, and so on [18-23].

However, it is observed that the main difficulty related to the effective utilization of all ICPs is inherent in their lower level of conductivity compared to metal, and their infusibility and poor solubility in all available solvents [4,24]. Nonetheless, the solubility of some ICPs can be enhanced by doping with a proper dopant or modifying the starting monomer. PANI exists in three different forms viz., 1) Emeraldine base (dark green coloured), 2) Leucoemeraldine (colorless) and 3) Pernigraniline (violet colored). The salt of emeraldine base is regarded as one of the most useful forms of polyaniline due to its high conductivity and stability at room temperature. Other oxidized states leucoemeraldine and pernigraniline are not conductive because one is fully oxidized (pernigraniline) and other is fully reduced (leucoemeraldine base) [25].

The conductivity of PANI depends on two parameters viz. 1) degree of oxidation and 2) degree of protonation. Properties of PANI are dependent on the factors like concentration of monomer, dopant type, polymerization conditions (time, temperature, and pH), and mainly monomer to oxidant molar ratio. [26-28] The conductivity of polyaniline is highly influenced by doping and the nature of the doping agent. Doping with suitable dopant plays a key role in conductivity mechanism by structural modification in backbone of PANI polymer. Doping an insulating or a semiconducting polymer gives rise to a substantial increase in its electrical conductivity which can go up to the metallic regime. Electrical conductivity usually increases with the doping level due to an increase in charge carriers' concentration. A large number of synthesis routes and types of dopants have been identified for producing polyaniline, its derivatives and composites. Doping with different inorganic and organic acids is extensively studied in the case of polyaniline [29-31].

In the present study, the effect of different doping agents mainly acids and their counter ions on the electrical conductivity of PANI has been studied along with characterization to investigate the morphology of synthesized polyaniline samples. The effect of concentration of acid has been also studied to see the conductivity of PANI material. Keeping in mind the useful properties of inorganic acids such as handling ease, solubility, we have chosen inorganic acids as a dopant for PANI.

2. Experimental

2.1. *Materials*

Aniline, ammonium persulfate (APS), hydrochloric acid (HCl), nitric acid (HNO$_3$)), sulphuric acid (H$_2$SO$_4$), perchloric acid (HClO$_4$) and acetone, all these chemicals used were of analytical reagent grade and procured from MERCK, India. All the chemicals and reagents were used as received without further purification. Deionized (double distilled) water was used throughout the studies for preparation and filtration.

2.2. *Preparation of PANI using different acids*

PANI materials were prepared and doped in situ by using different acids of 0.5 M, 1.0 M and 1.5 M concentrations. 0.2 M Aniline was prepared from aniline while 0.25 M ammonium persulfate was prepared from ammonium persulfate. The solutions were prepared from different acids having different concentrations (see Table 1). The aniline, APS (oxidizing agent) ratio was kept 1:1.25. First, 0.2 M aniline in a beaker was kept on the magnetic stirrer surrounded by ice for about 10 min maintaining the temperature 0-5 °C. After that 0.25 M APS solution was added to aniline solution dropwise under constant stirring very carefully. The reaction was carried out at low temperature in an ice bath because polymerization reaction is an exothermic reaction. The color of the reaction mixture gradually changed from blue to violet to dark green color. The green colour confirmed the conducting emeraldine salt form of PANI. It was stirred for 24 h on the magnetic stirrer with 450 rpm. The dark green coloured PANI precipitate was filtered and washed with the same strength of the corresrponding acid which was used during the preparation. It was washed thoroughly with double distilled water several times followed by acetone.

Table 1. Different doping acids and their concentrations.

Sr. No.	Doping acid	Concentrations of doping acid		
1	HClO$_4$	0.5 M (PANI-1)	1.0 M (PANI-5)	1.5 M (PANI-9)
2	HCl	0.5 M (PANI-2)	1.0 M (PANI-6)	1.5 M (PANI-10)
3	H$_2$SO$_4$	0.5 M (PANI-3)	1.0 M (PANI-7)	1.5 M (PANI-11)
4	HNO$_3$	0.5 M (PANI-4)	1.0 M (PANI-8)	1.5 M (PANI-12)

This final washing with acetone would help to remove low molecular weight impurities like oligomer and organic intermediates. It was washed until the filtrate became colourless. The precipitate of PANI was dried in oven at 60 °C for 16 h.
One batch of PANI was synthesized as follows,
The acid solution of required strength was prepared from double distilled water say 400 mL. From the stock solution of 400 mL, 0.2 M aniline (200 mL) and 0.25 M APS (200 mL) solutions were prepared.

2.3. *Physico-chemical characterization*

IR spectra were recorded on an instrument a JASCO FT-IR 4600 spectrum spectrophotometer. SEM images were recorded on FESEM model S-4800 Type II Make Hitachi Technologies Corp. Japan with EDXS detector X Flash 5030 Bruker Nano Berlyn, Germany on gold coat ion sputter. XRD patterns of various PANI samples were recorded on Bruker Germany Model D8 Advance X-ray diffractometer.

2.4. *Electrical conductivity*

For the measurement of electrical conductivity, pellets were prepared from the dried powdered PANI samples. The pellets of 10 mm diameter and 1-2 mm thickness were prepared under 12 Mpa pressure for 3 min. The pellets were dried prior the measurement in oven at 60 °C to remove the absorbed moisture from it. After cooling the pellet, the conductivity was measured by four probe set up at room temperature.

3. Results and Discussion

3.1. *Yield of PANI*

PANI materials were synthesized and doped in situ by using different acids of 0.5 M, 1.0 M and 1.5 M concentrations as shown in Table 1 and their yields are recorded in Table 2 given below. The yield of PANI depends on the reaction conditions, the acid used and its concentration or its pH. As a ratio of the aniline (monomer) and APS (oxidizing agent) was maintained the same for the synthesis of all PANI samples, the role of their concentration could be neglected. During the polymerization process, the protonation of aniline to form an anilinium ion is an important step that facilitates polymerization process. As all the acids are strong inorganic acids the rate of protonation of aniline and hence the rate of reaction is fast. It was also observed that at lower pH or at higher concentration of acid, the yield was increased to greater extent. The yield of PANI reflects the protonating power of the acid. As the polymerization reaction is exothermic the synthesis was carried out at low temperature range 0-10 °C which is favourable for the reaction. The yield of PANI was increased in all the PANI samples when acid concentration was increased from 0.5 M to 1.0 M. However, there was not much significant change in PANI yield when acid concentration was increased from 1.0 M to 1.5 M as can be seen in Table 2.

As the aniline/APS ratio is fixed for all PANI samples the yield of PANI is most likely dependent on the concentration of acid and dopant ion. It was observed that for 0.5 M HNO_3 the yield of PANI was low i.e. 52 %. In fact, there was not much increase in the yield of PANI when the concentration of HNO_3 increased to 1.0 M giving rise to merely 55 % yield and slight decrease in yield i.e. 53 % was observed for 1.5 M HNO_3 concentration. This low yield could be attributed to the low protonation power of HNO_3

acid. The yield of PANI for acids HCl and H_2SO_4 are comparable. That was clearly understood from the yield recorded in the given Table 2. The highest yield was obtained when $HClO_4$ was used as doping agent. The PANI yield 73 % , 85 % and 86 % were recorded for 0.5 M, 1.0 M and 1.5 M perchloric acid respectively. The strength of perchloric acid is greater than other acids. It is indeed, reflected in PANI yield for $HClO_4$. The protonation of aniline is enhanced in the case of perchloric acid leading to the increase in the extent of the polymerization. Thus the highest yield is attributed to the strong protonation power of $HClO_4$ acid.

Table 2. Yields of acid doped PANI materials.

Sr. No.	Acid (M)	% Yield of acid doped PANI			
		$HClO_4$	HCl	H_2SO_4	HNO_3
1	0.5	73	65	61	52
2	1.0	85	77	74	55
3	1.5	86	75	72	53

3.2. *Characterization of PANI samples*

XRD patterns of PANI samples doped with 1 M acid concentration are shown in Fig. 1. The diffraction patterns show amorphous as well as crystalline components. PANI is basically not perfectly crystalline in nature. The crystallinity indicates the higher molecular alignment. The PANI-5 sample exhibits two Bragg's peaks for $2\theta \approx 18.4°$ and at $2\theta \approx 23.6°$. The PANI-6 sample exhibits the two peaks at $2\theta \approx 18.1°$ and $2\theta \approx 24.6°$ with slightly greater intensity as compared to PANI-5. The decrease in the crystallinity of PANI-7 and PANI-8 can be seen in Fig. 1. It is evident from XRD spectra of PANI samples doped with H_2SO_4 and HNO_3 that they showed either partial, low crystallinity or amorphous nature. The PANI-7 and PANI-8 show one low intensity peak at $2\theta \approx 24°$ whereas the intensity of the same peak gets further diminished for PANI-8 sample. Thus the PANI-8 sample doped with HNO_3 reveals more amorphous nature and less molecular alignment as compared to other samples. The low crystallinity and more amorphous character could affect electrical conductivity for HNO_3 doped PANI samples. The intensities of the peaks are greater for the PANI-5 sample obtained using $HClO_4$ acid, which suggests higher molecular alignment and crystallinity as compared to other PANI samples. So, it can be assumed that presence of ClO_4^- groups in the polymer phenyl rings formed more ordered regions through interchain hydrogen bonding which is responsible for increased crystallinity in $HClO_4$ doped samples. The increased intensity at $2\theta \approx 18.4°$ and $2\theta = 23.6°$ peak in $HClO_4$ doped PANI-5 can be attributed to the better π–π interchain stacking and assembling of the dopant molecules in the tunnels between the polymer chains. It is found that aligned segments of conducting polymer molecules facilitate easy electron transport which results in enhanced electrical conductivity [32]. The XRD studies revealed the effect of dopant ions which is one of the important factors in achieving crystallinity.
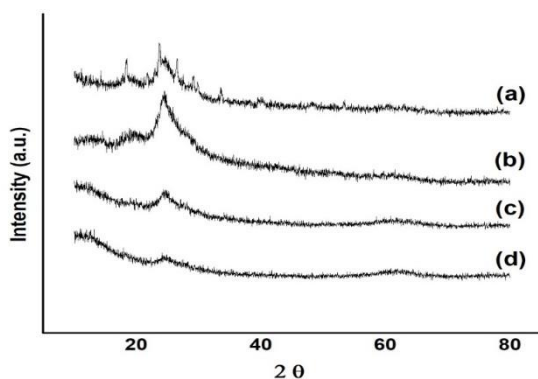
Fig. 1. XRD patterns of different acid (1 M) doped PANI samples: a) PANI-5, b) PANI-6, c) PANI-7, and d) PANI-8.

Fig. 2 shows FTIR spectra of 1 M acid doped PANI samples. It is found that IR spectra are in good agreement with the previously reported literature [33]. From IR spectra, certain peaks which are associated with different bonds of PANI structure could be easily recognized, thereby confirming the formation of PANI material. IR studies reveal the interactions among different atoms or ions in the molecules which induce changes in the vibrational levels of the atoms affecting the nature of spectrum. The values of IR absorption frequencies for different samples could be correlated with each other. The presence of peaks at around 610-750 cm^{-1} is due to C-N-C bonding mode of vibration. The absorption band at frequency around 810-850 cm^{-1} can be attributed to C–H out of plane bonding in benzenoid ring. The appearance of bands at around 1501-1511 cm^{-1} is consistent with quinonoid C-N stretching and 1450-1485 cm^{-1} bands in spectra are ascribed to benzenoid ring C-N stretching vibration. The protonated form of conducting PANI samples gives rise to absorption band characteristic at 1240-1249 cm^{-1}. It can be interpreted as corresponding to a C–N$^{+\bullet}$ stretching vibration in the polaron structure. The effect of dopant ions on polaron structure is also reflected in the intensity of peaks. Dopant ions play the important role in the stabilization of polaron structure. The intensity of peaks depends upon the polarization of bond i.e. dipole moment and concentration of molecular structures. Hence it can be assumed that the strong dopant ions ClO_4^-, Cl^- and HSO_4^- are responsible for intense peaks for quinonoid and benzenoid structures whereas weak intensity peaks are observed for HNO_3 doped PANI sample. The $HClO_4$ acid doped PANI-5 sample shows distinct and prominent absorption peaks indicating extensive protonation along the long chain of the polymer. The prominent absorption band appearing at around 1100-1160 cm^{-1} can be assigned to –NH$^+$= structure in the PANI backbone which suggests the high degree of protonation. The absorption frequency band at around 1600-1680 cm^{-1} in the spectra is attributed to C=C ring vibration in the polymer chain.
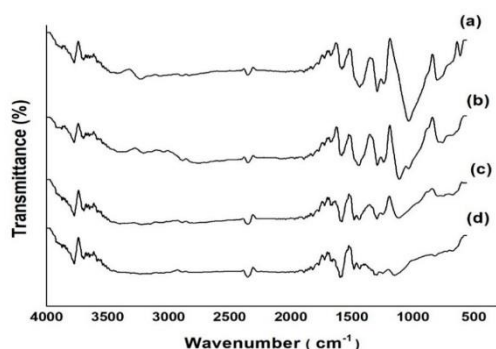
Fig. 2. FTIR spectra of different acids (1.0 M) doped PANI samples: a) PANI-5, b) PANI-6, c) PANI-7, and d) PANI-8.

SEM images of PANI samples reveal the morphology of PANI samples as displayed in Fig. 3. The morphology of PANI samples is also one of the important factors which can affect the conductivity property of polyaniline. The most striking feature about all these samples is that they exhibit nanorods like structural assembly or agglomerates. It is evident from SEM image that using $HClO_4$ and H_2SO_4, the nanorods assembly is obtained predominantly. $HClO_4$ doped PANI-5 sample displays the distinct nanorods structure of the average size of 150-250 nm. HCl doped PANI-6 sample shows globular agglomerates to some extent. The method of preparation and reaction conditions affect the morphology of PANI materials that resulted in the formation of nanostructures in PANI samples.
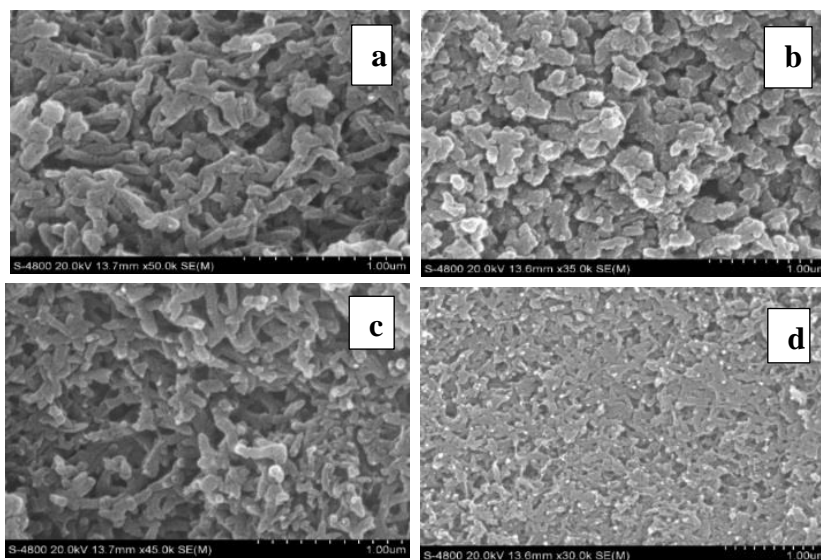

Fig. 3. SEM images of Different Acid (1.0 M) Doped PANI samples showing nanostructures a) PANI-5, b) PANI-6, c) PANI- 7, and d) PANI-8.

3.3. *Electrical conductivity of acid doped PANI samples*

As we have used different inorganic acids, the electrical conductivity reflects the extent of doping and the effect of dopant ions. The electrical conductivity of PANI samples were measured by four probe method. The conductivity was calculated by following Eq. (1).

$$\sigma \; = \; \frac{I}{V \,.2\pi S} \tag{1}$$

Where σ is electrical condutivityt in S/cm, I is current through the outer pair of probe in ampere, V is floating potential difference between inner probes in volt and S is spacing between adjacent point probes

The influence of doping on the electrical conductivity is clearly evident and traced. There are factors like the degree of conjugation, the length of polymer chain, the alignment of fibers and the formation of polarons and bipolarons which play crucial roles in the electrical conductivity of polyaniline. The increase in conductivity with increased doping concentration is a familiar phenomenon. The conductive homogeneous polymer phase can be created by varying oxidant species, oxidant to monomer molar ratio, dopant species and processing conditions like temperature, pH, mixing mechanism etc. [34-35].

Table 3 shows the conductivities of 0.5 M, 1.0 M and 1.5 M acid doped PANI samples. All the PANI samples exhibited increase in electrical conductivity as the concentration of acid increased from 0.5 M to 1.0 M. However further increase in acid concentration to 1.5 M could not affect electrical conductivity significantly. This shifting of conductivity can be ascribed to different oxidation levels of polyaniline backbone. The increased concentration of acid from 0.5 to 1.0 M facilitates the formation of emeraldine salt and hence the increase in polaron and bipolaron in polyaniline backbone. As the oxidant to monomer molar ratio is 1.25 which is kept constant for all acid doped PANI samples, it becomes obvious that it is the strength and nature of acid and dopant ions that play major roles in conductivities of PANI samples. PANI-1 sample doped with 0.5 M $HClO_4$ exhibited electrical conductivity 8.2 S/cm while PANI-5 sample doped with 1M $HClO_4$ showed 9.1 S/cm which is highest among all PANI samples. PANI-9 sample doped with 1.5 M $HClO_4$ acid exhibited slight decrease in conductivity to 8.7 S/cm which indicates the further higher concentration of acid could not facilitate molecular alignment in polyaniline backbone. PANI-8 doped with 1 M HNO_3 displayed 3.1 S/cm conductivity and PANI-4 doped with 0.5 M HNO_3 exhibited 2.7 S/cm which is the lowest electrical conductivity among all the PANI samples. This low electrical conductivity is indeed due to the less ordered molecular structure showing more amorphous character as revealed in XRD pattern and the weaker strength of HNO_3 acid leading to less doping level. HCl doped PANI samples exhibited better electrical conductivity over H_2SO_4 doped PANI samples. The effect of dopant ions i.e. Cl^- and HSO_4^- could be understood from the conductivities of HCl and H_2SO_4 doped PANI samples. The PANI-10, PANI-11 and PANI-12 samples doped at acid concentration 1.5 M could not show any significant increase in electrical conductivity.

The highest electrical conductivity of $HClO_4$ doped sample can be attributed to the structural morphology and extent of doping. Thus it seems that the factors like percentage of crystallinity, inter-chain separation, oxidation level, molecular arrangement, percentage of doping and type of dopant affect the electrical conductivity of different acid doped PANI samples. XRD and IR studies revealed the better structural morphology for $HClO_4$ doped PANI samples as compared to other acid doped PANI samples. The conductivity of PANI also depends on bridging among conductive regions. Thus, these structural changes lead to such morphology of chains which have charge transitions resulting into enhanced electrical conductivity through the process of delocalization and hopping along the polymer chain.

Table 3. Electrical conductivity of PANI samples.

Sr. No.	Concentration of acid (M)	Conductivity of acid doped PANI (S/cm)			
		$HClO_4$	HCl	H_2SO_4	HNO_3
1	0.5	8.2	7.4	6.4	2.7
2	1.0	9.1	8.6	7.4	3.1
3	1.5	8.7	8.4	7.4	3.2

4. Conclusion

In the present study, different acid doped PANI samples were prepared using chemical oxidation method with 0.5 M and 1.0 M acid concentrations and maintaining the APS /aniline ratio as constant. All the PANI samples revealed nanorods like structural agglomerates in 150-250 nm range. The electrical conductivity of PANI samples get affected by concentration of acid and dopant ions. PANI samples doped at acid concentration of 1.5 M did not show any significant increase in electrical conductivity. The enhanced electrical conductivity of $HClO_4$ doped PANI samples over other acid doped PANI samples could be attributed to the strength of acid, better crystallinity, molecular alignment and formation of polaron structures in PANI backbone due to the doping of acid as is revealed in XRD, IR and SEM characterizations.

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