Dielectric and conduction behaviour of H$_2$SO$_4$ doped conducting Polyaniline

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Abstract: We report the effect of H$_2$SO$_4$ doping on the dielectric and conduction behaviour of Polyaniline (PANI) samples. The PANI salt prepared by oxidising aniline hydrochloride in distilled water with the oxidant ammonium persulphate with continuous stirring at room temperature and PANI base is produced by subjecting PANI salt to a reaction with 0.5M NaOH. H$_2$SO$_4$ doped PANI is prepared by subjecting PANI base to reaction with 1M H$_2$SO$_4$ at room temperature under constant stirring for 1h. The synthesized PANI along with the doped samples were further washed with acetone to study the effect of acetone washing on the electrical behaviour. It is observed that the dielectric constant as well as the dielectric loss decreases with frequency in the entire studied sample. The frequency dependent AC conductivity at room temperature obeys the power law and the DC conductivity was obtained from the fitting parameter. It is found that the non acetone washed PANI doped in 1M H$_2$SO$_4$ shows highest dielectric constant and conductivity.

Key Words: PANI, H$_2$SO$_4$, dielectric study, Impedance study, Conductivity

1. Introduction

Conducting polymers have potential applications in many areas such as electrochemistry, electromagnetic systems, electronics, electromechanical systems, electroluminescence and sensors. Out of most semiconducting/conducting polymers, the charge transfer polymers like polypyrrole, polythiphene, poly paraphenylene and polyaniline, show excellent electrical and optical properties. Among these semiconducting/conducting polymers the most widely studied polymer is polyaniline due to its easy preparation method, environmental stability, low cost with applications in molecular electronics [1]. The conductivity in PANI arises due to the delocalisation of electrons in a continuously overlapped pi orbital in the polymer backbone. Because of this reason it has interesting optoelectronic properties and finds applications like photo-voltaic cells, organic light emitting devices, solid state laser, electromagnetic shielding, rechargeable battery electrodes, light emitting diode, transparent electrodes, inorganic semiconductors and sensors like gas sensors and humidity sensors [2-13]. There are several methods to improve the dielectric and conductivity properties of PANI by doping. The doping can be achieved either by chemical means involving partial oxidation or reduction of the polymer, electrochemical doping by applying a DC source, photo doping involving photogenerated charge carriers, charge-injection doping as well as non-redox doping carried out by proton doping of
PANI base with protonic acids [12-18]. Among them aid doping is found to be most suitable. The polymer in doped state shows semiconducting to metallic-like conductivity because doping incorporates charge carriers like polaron and bipolaron to the polymer backbone. With increasing the doping level, the localised polaron and bipolaron near to the dopant can overlap to produce new energy bands which lie in between the valence and conduction bands through which electron can flow.

The conducting polymers synthesis method and chemical modifications provides unlimited opportunities for their potential applications [19]. The preparation condition of PANI, dopant concentration, environmental parameters like humidity, use of various solvents and oxidants during preparation of polymer, presence of residual water creating hydrogen bonding between water and PANI during preparation, extent of disorder and cross linking in polymer, the reaction time can affect the electrical properties of PANI [20-26]. Apart from this the incorporation of various functional groups on the polymer backbone, can increase the processibility in comparison to the pristine polymer. Besides the above mentioned parameters, the presence of short chain oligomers which lack polycouination and other reactive intermediates produced during polymerisation are undesirable for the electrical properties of the polymer. In order to get oligomers free highly conducting form of PANI, it is recommended to wash the polymer by acetone after polymerisation, because by acetone washing of the polymer, short chain oligomers and other reactive intermediates are removed [IUPAC]. However, to study regarding the electrical properties of conjugated polymers it is required to focus on the properties of more well defined oligomers to avoid problems such as defects in ideal polymer chain or disorder. In short oligomers molecules, the polaron wave functions are forced to overlap due to spatial confinement whereas in longer polymer molecule the polaron are free to move apart sufficiently and the wave functions do not overlap. In the non-degenerate ground state conjugated oligomers of varying length, in the absence of extrinsic effects bipolarons may be unstable than that of the formation of two independent polaron. Hence, the use of oligomers will increase both as test structures for studies of the formation of species such as polaron and bipolaron and their direct use in electronic applications making them to play the important roles in organic-based electronic applications. Overall, the bulk conductivity of conducting polymers consists of contributions from intra-chain, inter-chain and inter-domain electron transportation.

The charge transport mechanism in conducting polymers has been widely studied using different experimental techniques such as AC conductivity, dielectric relaxation and photoconductivity [27, 28]. Complex Impedance Spectroscopy (CIS) is a powerful technique for understanding the charge transport mechanism in disordered conducting polymer nanostructures. Its main advantage over other techniques is the use of wide frequency range [27]. It has been reported that the relaxation of electric field in a charge carrier system is due to the hopping of mobile charge carriers, which leads to both short-range AC conductivity and long-range DC conductivity [28, 29]. The frequency dependent conductivity and dielectric permittivity provide important information on the electronic transport mechanism in disordered materials. It gives an insight in to the molecular structure of the materials, since the localized electronic states within the material are created due to the presence of disorder in the molecular configurations [30]. In this manuscript we report the electrical behaviour (dielectric relaxation, impedance and conductivity) of PANI base, PANI doped in 1M H$_2$SO$_4$ with and without washed with acetone. Since the acetone washing removes various reaction intermediates as well as oligomers, hence the presence of these species on the PANI electrical properties has been analysed. The frequency dependences of the dielectric constant and the AC conductivity are analyzed in terms of a dipolar- or a conductivity-relaxation mechanism and pair approximation.

2. Experimental

The PANI salt was synthesised through the conventional method of oxidative polymerisation of aniline hydrochloride with the oxidant ammonium persulphate. Aniline hydrochloride (2.592gm) was dissolved in distilled water (50ml) to which ammonium persulfate solution (prepared by dissolving 5.704gm in 50 ml. of distilled water) was added slowly with continuous stirring at room temperature to prepare PANI salt. Then the reaction mixture was allowed to stand for three hour at room temperature followed by filtration. After filtration the washing of the samples was carried out in two different procedures. In the first procedure the residues were washed with 0.2M HCl followed by distilled water and in another procedure after washing the residue with 0.2M HCl and distilled water it was washed
with acetone. The PANI samples prepared in the above experiments were air dried whole night followed by drying at 60°C in an oven for one day. The resulting PANI salt samples were subjected to a reaction with 0.5M NaOH solution followed by air drying as well as drying at 60°C in an oven for one day. The produced dried PANI base is powdered and doped in 1M H₂SO₄ by stirring PANI base with 1M H₂SO₄ for one hour at room temperature. The synthesized PANI base and 1M H₂SO₄ doped PANI samples with and without washed with acetone were structurally characterized by X-ray diffraction (XRD) using a Philips diffractometer model PW-1830 with Cu-Kα (k=1.5418 Å) radiation. In order to analyse the electrical properties, the samples were made in the form of circular disc having diameter 10mm and thickness 1mm using a hydraulic press. For electrical contact measurements the ends of the PANI pellets were coated with silver paints. The frequency dependent dielectric and impedance study was carried out by using a N4L-NumetriQ (model PSM1735) connected to a computer.

3. Result and Discussion

3.1 XRD Analysis

The X-ray diffraction pattern for PANI base and PANI doped in H₂SO₄, with and without acetone washing are given in Figure 1 (a,b). The XRD plot for PANI base shows a semicrystalline nature whereas the H₂SO₄ doped PANI samples show a more crystalline nature. The semicrystalline characteristics of PANI base is due to repetition of benzenoid and quinoid rings in the polymer chain whereas the crystallinity in these PANI samples may be due to the systematic alignment of polymer chains by chain folding or due to the formation of single or multiple helices [32]. Peaks appeared at positions 2θ = 20° corresponds to (020) plane of PANI which is due to the periodicity parallel to polymer chain and 2θ =25.6° corresponds to (200) plane of the polymer and it is due to the occurrence of periodicity perpendicular to the polymer chain [34]. For acid doped PANI, the peak observed at 2θ = 20° is diminished and prominent peak is observed at 2θ =25.6° suggesting the formation of PANI salt and it represents the extent of conjugation for delocalisation of π electrons in the polymeric chain structure.

![Figure 1. X-Ray diffraction pattern for the (a) PANI with and with acetone washing (b) 1M H₂SO₄ doped PANI with and with acetone washing](image)

3.2 Frequency dependent dielectric study

The variation of dielectric permittivity at room temperature with frequency for PANI base and 1M H₂SO₄ doped PANI samples without and with acetone washing is shown in Figures 2(a,b) respectively. In all cases, a relatively high dielectric permittivity is achieved at low frequency region which is a characteristic of polymer as well other dielectric material and it is due to the space charge.
polarisation produced due to the free charges at the interface [14] and the nature of the dielectric constant \( \varepsilon' \) can be expressed as follows

\[
\varepsilon'(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{[1 + (i\omega\tau)^{1-\alpha}]
\]

(1)

For very low frequency the charge carriers get sufficient time to move over macroscopic distances and build up at the interfaces between the sample and the electrodes within half a cycle of the applied AC field, resulting in high value of the dielectric permittivity [33]. After getting a high dielectric permittivity value at low frequency, the plot becomes asymptotic at higher frequency which is the characteristics of disordered conducting polymer like PANI and it occurs due to hopping of electrons between isolated polarons and bipolarons [34]. The decrease in the dielectric constant with increasing frequency is due to by dielectric relaxation, phenomena that tells that the charge carrier localization is not stable and frequency disturbances effect the charge carrier localization [35].

![Figure 2](image)

Figure 2. Frequency dependent dielectric constant of (a) PANI with and without acetone (b) 1M H\(_2\)SO\(_4\) doped PANI with and with acetone washing

Figure 3 (a,b) shows the variation of dielectric loss with frequency for the PANI base and acid doped samples without and with acetone washing respectively. A high dielectric loss is observed in all the samples at low frequency signifies the increased conductivity occurs due to free mobility of the charge carriers in the polymer arising by the creation of percolation path by long conducting clusters present in the polymer [36]. Among the samples without acetone washed PANI base shows comparatively lower dielectric permittivity as well as loss. However, when the sample is doped with 1M H\(_2\)SO\(_4\) the sample without washed with acetone has higher dielectric permittivity whereas for the same sample that is washed with acetone the loss factor is more in comparison to that of non acetone washed sample showing the decrease in capacitive nature and increased in conductivity in acetone washed acid doped sample. The higher dielectric permittivity of non acetone washed acid doped polymer may be due to the extra charge carriers contribution from the small chain oligomers present in non acetone washed sample.
3.3 Complex Impedance Analysis

Figure 4 (a,b) shows the variation of real part of impedance with frequency for without acetone washed and with acetone washed PANI base and acid doped PANI samples respectively. It is observed that for PANI base (both without and with acetone washing) the magnitude of $Z'$ decreases with increase in frequency and reaches an asymptotic value in the high frequency range. For acid doped samples the enhancement of impedance with frequency shows that the AC conductivity increases with frequency. A comparatively lower value of real part of impedance is observed in 1M H$_2$SO$_4$ doped PANI that is not washed with acetone than that of the doped polymer washed with acetone. Again, it is observed that the real part of impedance of acid doped in non acetone and acetone washed PANI sample is almost frequency independent which shows that the materials have no AC conductivity for a wide range of frequency.

Figure 5 (a,b) shows the variation of imaginary part of impedance with frequency for without acetone washed and with acetone washed PANI base and acid doped PANI samples respectively. The curves show that the $Z''$ values reach a maxima peak ($Z''_{\text{max}}$) in all the samples. The broadening of peaks suggests that there is a spread of relaxation times, i.e., the existence of electrical relaxation phenomenon in the material. The relaxation process may be due to the presence of immobile species. For PANI base in acetone washed sample the frequency corresponding to the $Z''_{\text{max}}$ values move to the higher side than that of the non acetone washed sample which implies that the relaxation time decreases for PANI base when it is washed with acetone. For acid doped sample, the opposite observation has been found i.e. the
relaxation time decreases for the sample when it is not washed with acetone. Again, maximum $Z''_{\text{max}}$ is obtained for PANI base and least $Z''_{\text{max}}$ value is obtained for acid doped PANI that is not washed with acetone.

**Figure 5.** Frequency dependent imaginary part of impedance of (a) PANI with and without acetone (b) 1M $\text{H}_2\text{SO}_4$ doped PANI with and with acetone washing

### 3.4 AC conductivity studies

Figure 6 (a,b) shows the variation of AC conductivity with frequency at room temperature of all the samples without acetone and with acetone washing respectively. The AC conductivity is calculated using a relation $\sigma_{ac} = \omega \varepsilon \varepsilon_0 \tan \delta$, where $\omega$ is angular frequency, $\varepsilon_0$ is the dielectric permittivity of vacuum and $\tan \delta$ is the loss factor. The AC conductivity $\sigma(\omega)$ obeys the Jonscher’s power law [37] as given by $\sigma(\omega) = \sigma_{dc} + A\omega^n$ where $n$ is the frequency exponent in the range of $0 = n = 1$. Here $A$ and $n$ are temperature dependent parameters and indicates that the electrical conduction is a thermally activated process. Funke [38] explained that the value of $n$ might have a physical meaning (i.e., $n \leq 1$ would mean that the hopping motion involved is a translational motion with a sudden hopping). On the other hand, value of $n$ greater than 1 would mean that the motion involved is a localized hopping of the species with a small hopping without leaving the neighbourhood. The frequency at which change in slope takes place is known as hopping frequency ($\omega_p$) of the polarons, which is temperature dependent. It is a function of both temperature as well as frequency, and corresponds to short-range hopping of charge carriers through trap sites separated by energy barriers of varied heights. The dispersion in conductivity at low frequency can be explained due to non-adiabatic hopping of charge carriers between impurity sites. In disordered polymers like PANI, various conduction mechanisms contribute to the total conductivity where there is movement of electrical charges when it is subjected into an alternating electric field [21].

The DC conductivity of the samples was obtained by fitting the frequency dependent AC conductivity with the Jonscher’s power law. Basically, there are two types of charge carriers are present in case of PANI, one bound charges, responsible for dipole moment and another non-bound charges (polarons and bipolarons) responsible for DC conductivity [39]. In case of PANI base (both non acetone and acetone washed) there is no DC conductivity was observed with the measured frequency range and the conductivity increases with increase in frequency which shows that the materials are devoid of capacitive behaviour in the mentioned frequency range. This type of characteristics may be due to the presence of long conducting clusters present in the polymer [36]. In PANI base both without and with acetone washing, there is very less electrical conductivity and dielectric constant was observed which signifies the absence of proton in PANI Chain [22]. For acid doped samples, a comparatively higher conductivity was observed in case of sample that is not washed with acetone than that of the acetone washed sample. When the polymer is not washed with acetone it may contain some low molecular
weight oligomers which can be fully doped by acids than that of the high molecular weight polymers [18], consequently increasing the charge carriers that may contribute to the PANI electrical properties with increase in electrical conductivity.

![Graph](image)

**Figure 6.** Frequency dependent AC conductivity of (a) PANI with and without acetone (b) 1M H2SO4 doped PANI with and with acetone washing

### 4. Conclusion

The PANI base was prepared by oxidising aniline hydrochloride with the oxidant ammonium persulphate with continuous stirring at room temperature. The samples were again washed with acetone to study the effect of acetone washing that removes the short chain oligomers on the electrical behaviour of the polymer. The incorporation of H2SO4 in the polymer increases the crystallinity as observed in the XRD study. The electrical properties were observed via dielectric and impedance measurement for all the samples and a comparative study with respect to acetone washing was presented. Among all acid doped samples, the sample without acetone washed shows higher dielectric as well as conductivity than that of acetone washed sample due to the stable charge carriers and extra electrical conductivity contribution from the small chain oligomers present in the polymer. Whereas for PANI base there is lowering in dielectric and conductivity value in without acetone washed sample than that of the acetone washed sample. From the above study, we can conclude that acetone washing has a significant role in the electrical behaviour of PANI especially in acid doped polymer. Hence, the presence of short chain PANI oligomers increases the electrical conductivity as well as dielectric permittivity of the acid doped polymer. The higher value of dielectric permittivity and electrical conductivity of non acetone washed acid doped PANI may find promising applications in various industrial applications.

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