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ARTICLE

Synthesis, Electrical Conductivity, and Dielectric Behaviour of Polyaniline Doped with H_2SO_4; HCl and (HCl + $NaNO_2$) Mixture

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ABSTRACT

Acid doped Polyaniline (PANI) due to their increased electrical conductivity, are considered to be the most promising conducting filler materials. Hence, the present study, reports the synthesis of the PANI followed by acid doping, electrical conductivity and dielectric properties measurements of H_2SO_4; HCl and (Conc. HCl + $NaNO_2$mixture) doped PANI. In order to know the effect of acetone washing on the electrical properties of acid doped PANI samples, the electrical properties of the non-acetone washed acid doped PANI samples are compared with that of their acetone washed counterparts. The PANI salt was prepared by conventional route using aniline hydrochloride and ammonium persulphate as an oxidant. PANI salt was subjected to 0.5M NaOH to form PANI base, which was further doped separately with H_2SO_4; HCl and (Conc. HCl + $NaNO_2$mixture) respectively followed by acetone washing. A comparative electrical conductivity study between the acetone washed and unwashed PANI salt and H_2SO_4, HCl and Conc. HCl + $NaNO_2$ mixture doped PANI were characterized by dielectric and impedance study.

1. Introduction

Numerous electrically conductive polymers like polypyrrole, polythiphene, polyparaphenylene and polyaniline though available, but due to the easy synthesis process, greater environmental stability, low cost, polaniline (PANI) is the most studied conducting polymers finding potential electronic applications such as solar cell, light emitting devices, solid state laser, energy storage devices, sensors etc [1-11]. The properties of PANI are determined by the regular structure of polymer chains. The presence of alternating phenyl and nitrogen containing groups as well as the lone pair on nitrogen atom impart polyconjugation, which provides the transport path for charge carrier (formed during oxidation) mobility [12]. The acid doping of polyaniline generates suitable soluble counter-ions which improves the processibility of such conducting polymers. The acid doping of PANI is capable of polyaniline protonation along with providing suitable functional groups to the polymer backbone, making the polymer chemically stable, electrically conductive along with increasing the solubility factor of the polymer [13-16]. The degree of protonation can affect the dielectric, electrical conductivity, and other properties of PANI. The polymerisation of aniline can effectively takes place in acid medium where aniline is present as anilinium ion.

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Again, the methodology adopted for preparation of conducting polymers and chemical modifications make them promising candidates for various potential applications. In case of PANI, the polymer is washed with acetone after synthesis for removal of oligomers and other reactive intermediates [17] whose presence is considered to be undesirable in conducting point of view. However, to get an in depth knowledge regarding electrical and optical properties of such conjugated polymer it is essential to study on the short chain oligomers formed during the course of polymerisation and their effects on the overall electrical and optical characteristics of the polymer [2].

In such kind of disordered polymeric system the charge transfer phenomenon is best explained by Complex Impedance Spectroscopy (CIS). It is reported that the hopping of mobile charge carriers is responsible for the electrical conductivity in such a polymeric charge carrier system [18,19]. The variation of electrical conductivity with respect to frequency and dielectric property provide information regarding electronic transport phenomenon in disordered polymeric materials along with the molecular structure of the materials, because due to disorder structure within the material localized electronic states are resulted [20]. In the current manuscript, we have focused the effect of various acids i.e. H_2SO_4; HCl and mixture of HCl + $NaNO_2$ as well as the role of short chain oligomers on the electrical behaviour of PANI via complex impedance spectroscopy.

2. Experimental

The PANI salt was synthesised through the chemical oxidative polymerisation of aniline hydrochloride using oxidant ammonium persulphate. Aniline hydrochloride solution was prepared by dissolving 2.592gm of aniline hydrochloride in 50 ml distilled water. Ammonium persulfate solution was prepared by dissolving 5.704gm in 50 ml. of distilled water. To the aniline hydrochloride solution oxidant ammonium persulfate solution was added slowly with continuous stirring at room temperature and the reaction mixture was allowed to stand for three hour at room temperature followed by filtration. After filtration one part of the residue was washed with 0.2M HCl followed by distilled water and another part was washed with 0.2M HCl and distilled water followed by acetone. The resulting washed PANI samples were dried in air whole night and then at 60^0C in an oven for one day. The resulting dried polymer salt samples were treated with 0.5M NaOH solution and the resulting samples were dried in the similar manner as described for polymer salt samples to prepare PANI base samples. The resulting dried samples were powdered and treated with 1M H_2SO_4, HCl and mixture of HCl and $NaNO_3$. The electrical properties of the synthesized PANI base samples and acid doped PANI samples were measured through making compacted form of circular discs having diameter 10mm and thickness 1mm using a hydraulic press. For electrical contact the ends of the 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. Results and discussion

3.1 *Frequency Dependent* Dielectric Study

The variation of dielectric constant with frequency for PANI base and acid doped PANI samples with and without acetone washing are shown in Figure 1 (a,b). In all the compositions the dielectric constant decreases with increase in frequency which is due to the space charge polarisation produced because of the free charges at the interface [21]. When the frequency is low, the charge carriers get sufficient time to cross the macroscopic distances and accumulates at the interfaces between the sample and the electrodes within half a cycle of the applied AC field, consequently results a high dielectric permittivity [22]. At higher frequencies the plot becomes asymptotic, as expected in case of disordered conducting polymer like PANI, and such trend is occurred due to hopping of electrons between isolated polarons and bipolarons [23]. It is observed from the figure that the acid doping enhances the dielectric constant in the PANI base. In presence of acid the charge carriers are stabilised by the counter ions of the acid which increases the dielectric constant. Again, it can be observed that acetone washing has a great impact on the modification of dielectric behaviour of the doped samples. The acetone washed samples are showing higher dielectric constant in all doped samples. It is also found that for without acetone washed samples maximum dielectric constant was observed for $1MH_2SO_4$ doped sample where as for acetone washed composition 1M HCl doped sample is showing highest dielectric constant.

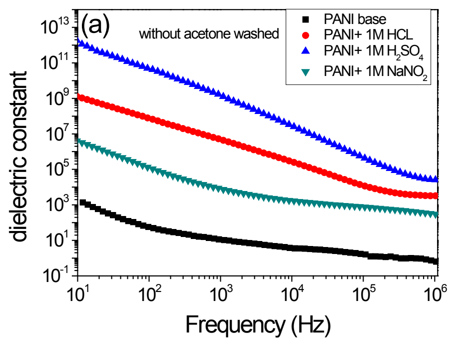

Figure 1 (a). Frequency dependent dielectric constant of without acetone washed acid doped PANI

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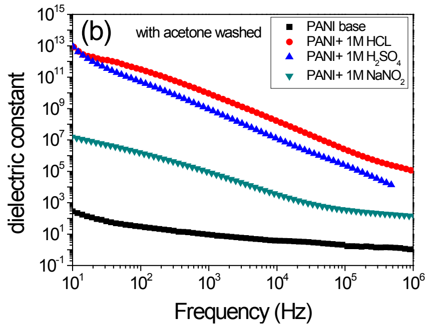

Figure 1 (b). Frequency dependent dielectric constant of acetone washed acid doped PANI

3.2 *AC Conductivity Study*

The frequency dependent AC conductivity of all the non acetone and acetone washed samples respectively are shown in Figure 2(a,b). Using a relation $\sigma ac = \omega\varepsilon\varepsilon_0 \tan\delta$ the AC conductivity is calculated. It has been found that the ac conductivity $\sigma(\omega)$ obeys the Jonscher's power law ($\sigma(\omega) = \sigma_{dc} + A\omega^n$) [24] where n is the frequency exponent in the range of $0 = n = 1$. The factors A and n are temperature dependent parameters suggesting that the electrical conduction is a thermally activated process. Temperature and frequency dependent hopping frequency (ω_p) of the polarons is the frequency at which change in slope takes place and corresponds to short-range hopping of charge carriers through trap sites separated by energy barriers of varied heights. Moreover, non-adiabatic hopping of charge carriers between impurity sites is responsible for the dispersion in conductivity at low frequency. For disordered systems like PANI, movement of electrical charges takes place when it is subjected to an alternating electric field and total conductivity is due to the different types of conduction mechanisms [25]. Such polymers consist of conducting clusters of varying length with random orientation in the absence of the electric field. When the clusters are long enough they can create a percolation path and the charges are free enough to move, hence shows electrical conductivity.

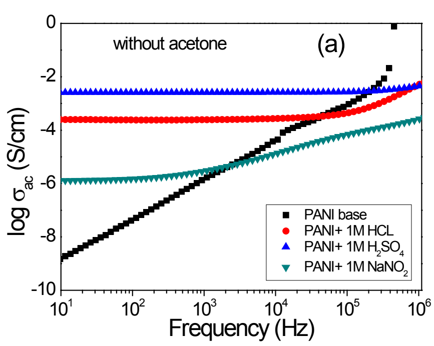

Figure 2 (a). Frequency dependent ac conductivity of without acetone washed acid doped PANI

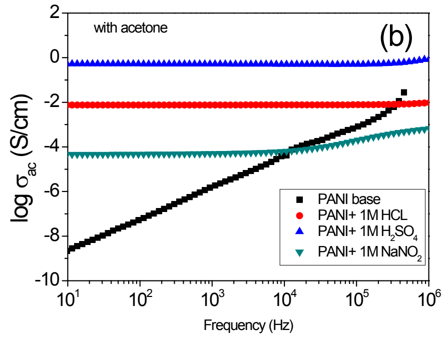

Figure 2 (b). Frequency dependent ac conductivity of with acetone washed acid doped PANI

From Figure 2, it can be observed that for both acetone washed and without acetone washed the doped samples have higher conductivity then that of PANI base. Again, in all doped samples the AC conductivity increases with acetone washing. Another important phenomenon observed with acetone doping is that the hopping frequency move towards the higher frequency side showing that various transport mechanisms are involved in conductivity process. The figure also reveals that with acetone washing there is hardly any decrement of conductivity with frequency in the doped samples which makes the sample more suitable for industrial application then that of the counterpart. Among all the samples, H_2SO_4 doped sample shows highest conductivity for both acetone washed and without acetone washed.

4. Conclusion

Acetone washing has significant effect on the dielectric permittivity of the samples. Among the acid doped samples without acetone washed 1M H_2SO_4 and acetone washed 1M HCl doped PANI samples are considered to be potential dielectric materials. In terms of the electrical conductivity, there is no significant decrement of conductivity with increase in frequency showing their prospects in industrial applications.

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