

Method Of Enhancing Polyaniline Conductivity Using Different Oxidizing Agent As Dopant

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ABSTRACT

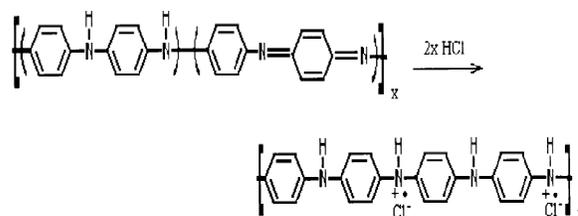
The synthesis and characterization of Polyaniline pellets has been done by using oxidizing agent Ammonium per oxy disulphate (APS). Samples of different molar ratios of Aniline Hydrochloride to oxidative agents have been analyzed. In these samples variation in the conductivity due to variation in the molar ratio is noticed, that the conductivity of Polyaniline pellets first increases up to the molar ratio of 4:1 and then start decreasing. The highest value of conductivity among the above mentioned three oxidizing agents is observed for APS i.e. 4.7 S/cm. Further Polyaniline emeraldine base film has been casted by dissolving it in Dimethylsulfoxide (DMSO). For all the samples, pellets as well as the film, variation in conductivity, XRD, and FTIR spectral variation has been studied. The thermal analysis was done for the powder form of polyaniline Emeraldine base by T.G.A and D.S.C methods indicate cross linking, melting and the decomposition of the material.

Keywords: Polyaniline, APS, DMSO, thermal degradation, conductivity, FTIR, TGA.

1. INTRODUCTION

Now a day's researchers show a great concern in the development of polymers whose strength of electrical properties can be customized for different practical application. Polyaniline is one of the conducting polymers whose electrical conductivity is enhanced upon doping of different oxidizing agents for example, Ammonium peroxy disulphate, hydrogen peroxide etc. Different conducting polymers such as poly pyrrole and poly acetylene cannot be converted into operable forms due to the infusible properties. The advance study in this field revealed that the polyaniline is the one which executes this application. [1] Such as stability and the relatively high conductivity in the doped state. The conductivity is referred to macromolecular structure and morphology and the acid used for protonation, and the stability is linked to the extrinsic factors for instance atmosphere and the temperature.

The process for controlling the conductivity is demonstrated by the slow deprotonation of the PANi salt to PANi base, which actually produces the changes at molecular level. [2] So the secondary dopants for the post polymerization can increase the conducting properties of polyaniline. Emeraldine salt films are made by their reaction with one of the solvents which are, DMSO, DMF, NMP and chloroform. But these show relatively decrease in conductivity typically ranges from 0.1-1 S/cm. So this form is converted into salt form by the acidic doping. The chemical reaction for the conversion is given as below.



The polyaniline formed through the oxidative polymerization of the monomer i.e. aniline, conducts electrically [3-4]. It is found that polymer processing is Hygroscopic in nature [5-8]. Thermal stability and temperature (T_g) are very important.

2. EXPERIMENTAL

The procedure of chemical polymerization of aniline given by the IUPAC was adopted. Ratio of 0.2 M aniline hydrochloride was oxidized to prepare Polyaniline with the variation in the molar ratio of oxidizing agent ammonium peroxy disulphate. The sample obtained was in the pallet form. Each pellet was pressed at 800 MPa. The conductivity measurements were done to know about the ratio having the best conductivity.

Further for the preparation of emeraldine base film, 0.045 M Ammonium per oxy disulphate was used. The aqueous solution of ammonium peroxy disulphate and aniline hydrochloride were prepared and left for half an hour. After this the ammonium per sulphate solution was added drop wise in Aniline

hydrochloride solution. This was kept for 24 hours and then filtered.

The precipitates were washed with distilled water and 1.5 N HCl, until the remaining became colourless. The precipitates were dehydrated in oven for 24 hours at 80 °C.

Then the emeraldine salt was converted into base by dissolving it in DMSO (Dimethyl sulfoxide). Firstly this PANi powder was put in 100 ml of 5% wt ammonia solution which was prepared from the concentrated reagent solution. After 12 hours, powder was washed with distilled water until the filtrate become colourless.

Filtrate was dried for 48 hrs at 50-60 °C. Then 0.6 g of EB was dissolved in 50 ml of DMSO and stirred for 5 hrs using magnetic stirrer. The dark blue solution was filtered and used to cast the film on glass strip, dried and then peeled off from the glass by immersing it in water. Then film was pressed between the glossy weighing papers and dried in air for few days.

The results showed that the conductivity of base is very low, so the film was dipped in 1N aqueous solution of HCl. For the complete doping the film was immersed in solution for half day.

An FTIR spectrum was taken SHIMADZU 8400S, XRD to confirm the sample prepared, conductivity measurements were made. And the T.G.A and D.S.C analysis was done of the powder form of emeraldine base.

3. RESULT AND DISCUSSION

3.1 Conductivity measurement

Conductivity of the various oxidants to monomer ratio was measured using the four point probe method and it was found that the best ratio having the highest concentration is 4:1 and the value of conductivity was 4.7 S/cm. And the conductivity of the polyaniline (emeraldine base) film was of the order of 10^{-10} S/cm. After doping in HCl, the value of the conductivity was found to be 11.7 S/cm.

3.2 XRD Analysis:

It was done just to find the structure of PANI base sample. It was done by using Regaku Geiger Flex D-MAX/A diffractometer of Company.

The value of the operating voltage was 35 kV and current was 225 mA. The source of radiation used was copper.

The diffraction patterns were taken counts verses incident angle (2θ). The graph is shown in the figure 1. It is obvious from the graph that the chains are perturbed. The polyaniline EB shows the peaks at almost $2\theta = 27.7^\circ$.

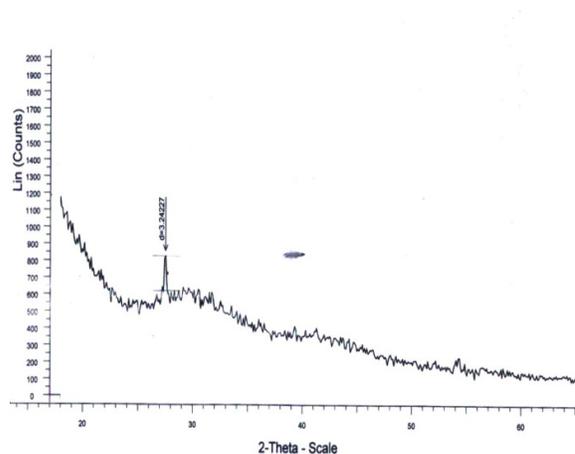


Fig.1: X-Ray diffraction of polyaniline base.

3.3 FTIR Analysis:

Figure 2 represents the spectra of PANI base film.

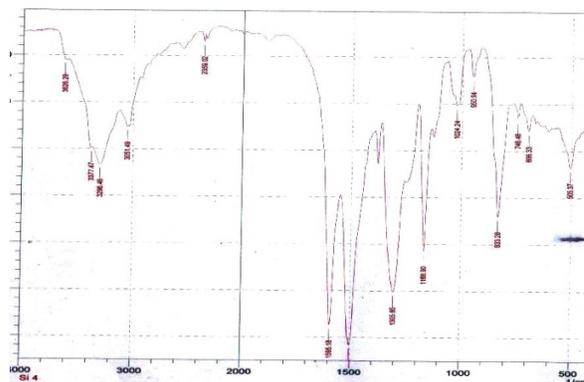


Fig. 2 FTIR of PANi base film.

The spectrum exhibits the 9 main absorption peaks at 3377.47, 3037, 1595, 1504, 1305.85, 1168.90, 1024.24, 950.94 and 833.28 /cm. the peaks at 3377.47 is allotted to N-H(H free). The band corresponding to 3037 is due to C-H aromatic ring vibrations. The peaks at 1595 and 1504 /cm are attributed to C=C (Q) and C=C (benzenic). The peak at 1305.85 is assigned to C-N from aromatic amines. The band at 1168.90/cm

represents N=Q=N. And the peaks 1024.24, 950.94 and 833.28 /cm are assigned to aromatic ring. The C-Cl stretching peaks originates in the region 590 to 700 /cm. [9]

The absorption characteristics of the PANI film are found to match with the literature [10].

3.4 Thermal analysis

3.4.1 Thermal Gravimetric Analysis (TGA)

The main points or the levels at which the weight losses of polyaniline base occurs are two, no matter whatever the environment is, when the experimental work is carried out. The first one is at smaller temperature at which the dehydration and possible evaporation of other unknown minor molecules occurs.

The second weight loss is the more important one which is actually at high temperatures and tells us about the degradation of the polymer.

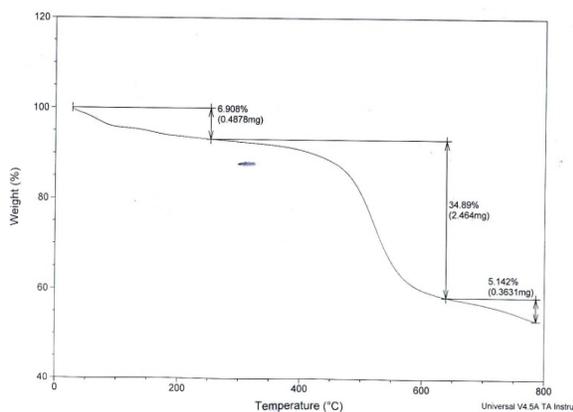


Fig.3 TGA curve of polyaniline base powder.

TGA curve is shown the figure 3, So in our case the initial weight loss of 6.908 % was observed up to the temperature 350 °C due to the moisture contents and due to the other solvents present. The major weight loss was observed between the temperature 400 to 650 °C, which was about 34.89 %. After this the further decomposition was 5.142 % observed up to 800 °C. This almost completed the polymer decomposition. So, it can be said that polyaniline base was thermally stable at least to 300 °C.

The weight loss detected after 350°C is due to volatile and evaporable products leading from the oxidation of polymer. There are some important factors on which thermal stability depends, such as,

acid used for doping purpose, state of oxidation, heat treatment environment and the conditions of preparation. So the Polyaniline base has the steady and stable behavior among all form of polyaniline. [11]

3.4.2 Differential Scanning Calorimeter (DSC):

DSC is the commonly used technique to determine the transition temperature, cross linking, melting and the decomposition of the material.

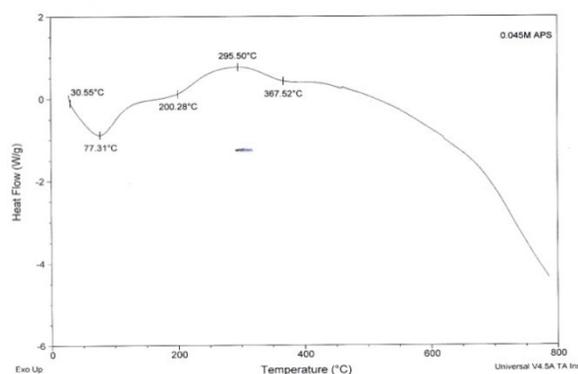


Fig.4: Differential Scanning Calorimeter trace of pani base powder.

Figure represents the DSC curve exhibiting the total heat flow and thermal conversions. The peak for endothermic reaction is there from 30.55°C to almost 500°C. and the exothermic peak is from 200 to 360°C was found, which is similar to the work already reported about the moisture contents of polyaniline base powder [12]. The glass transition temperature is 30.55°C.

The first exothermic peak representing the evaporation of water is logical in accordance with the TGA results. The next exothermic peak may be for the chemical process associated with the recrystallization [13] or the cross linking reaction [14]

4. CONCLUSION

The method of producing the polyaniline salt and base from the monomer, electrical, structural and the thermal stability of the samples was done. It is concluded that the best ratio of oxidant to monomer is 4:1. The increase in conductivity from base to salt form is in the order of 10^{-11} to 10 S/cm. Thermal analysis curves indicate, temperatures corresponding to the exothermic and endothermic peaks illustrates the decomposition of the polyaniline.

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