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Effect of variation in preparation temperature on the conductivity of PANI

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An attempt has been made to investigate the effect of temperature on the conductivity of polyaniline (PANI). The synthesis of conducting polymer is done by a chemical route in an aqueous medium. The polymer was grown from aqueous solutions employing a range of temperatures (5^0C –30^0C). The film was deposited by the Sol Gel technique. The change in conductivity is studied by the two probe method. The result shows that with increase in temperature, the conductivity of PANI film decreased. An I-V characterization of PANI film shows ohmic behaviour of the film. The physical properties of synthesized PANI film were characterized by analyzing the results obtained by IR Spectroscopy and to understand the electrochromic window and non linear optical material UV-visible spectroscopy is studied.

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1. Introduction

Interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene etc. has increased tremendously during the last decade because of their electronic properties for use in electronic devices, functional electrodes, electro chromic devices, optical switching devices, sensors, batteries, and so on [1-7].Conducting polymers can be prepared by chemical or electrochemical polymerization. In the chemical polymerization process, monomers are oxidized by oxidizing agents or catalysts to produce conducting polymers [7,8].The advantage of chemical synthesis is that, it offers mass production of conducting polymer at low cost. This makes them suitable for use in electronic devices, Organic Light Emitting Diodes, Capacitors, electrochemical (bio) sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference shielding, anti-static coating and drug delivery systems [8]. On the other hand, the electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology but by this method the mass production is not possible. [9, 10]

Therefore, Polyaniline (PANI) a conducting polymer of the semi-flexible rod polymer family has been prepared through chemical polymerization. In recent years the Polyaniline captured the attention of the scientific community due to the discovery of its high electrical conductivity and its rich chemistry. Amongst the family of conducting polymers, polyaniline is unique due to its ease of synthesis, environmental stability, and simple doping/dedoping chemistry [11,12] .Although the synthetic methods to produce polyaniline are quite simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex.It has been found that polyaniline is inexpensive to produce, relatively lightweight, corrosion resistant, possesses environmental stability, good redox properties and exhibits good matrix adhesion[9]. In addition, the electrical and optical properties of polyaniline conducting polymers are highly dependent on the presence of substituent, the nature of the dopant, other synthetic conditions (temperature, time, etc.)[9].

In Polyaniline thin film, the properties of the resultant films depend on a number of parameters, such as the type of solvent and their molar concentrations, temperature and on other synthesis conditions, research on the preparation and characterization of conducting polymers is still continuing. Hence, effort has been to investigate the effect of preparation temperature on conducting polymer Polyaniline, by chemical polymerization process [10–13].

The present paper focuses on the effects of temperature on the conductivity during the polymerization process of aniline in aqueous medium. The detail of chemicals and instruments used for the formation and characterization of the conducting polymer is given second section. The third of this paper deals with the experimental section in which the first part illustrates the steps involving in the synthesis of conducting polymer polyaniline and the latter part of this section deals with the formation of the conducting film with the help of spin coater. The Result are Discussed in the fourth section and fifth section conclude the paper.

2. Materials and instruments

2.1 Chemicals

All the chemicals and solvents used were dried and purified by standard methods. Analytical grade Aniline hydrochloride (Ranbaxy New Delhi) Ammonium peroxodisulphate (APS) and Hydrochloric acid (HCL) (SD - fine chem.), Acetone and DMF are (Loba chemicals) and for filtration of precipitate What man's filter paper No.60 are used .

2.2 Polymer characterization

The polyaniline films produced were characterized by FTIR spectroscopy (Nicolet-380), UV-spectrophotometer (SHIMADZU-1601), and conductivity measurement is done by the two-probe technique at 25^0C.

3. Experimental

In present paper the conducting polymer have been synthesized by chemical method by oxidizing the corresponding monomer. The thin film of polyaniline has been prepared successfully by chemical oxidatiative polymerization and Sol-Gel technique. The physical properties of the film are characterised by the FTIR spectroscopy, the FTIR spectroscopy gives details of stretching bond in the prepared polymer film. The UV-vis spectrum is useful for gauging the extent of conjugation - highly conjugated, providing information about the extent of conjugation, the electronic spectrum is indicative of polymer morphology, the presence of a free carrier tail. The change in conductivity due to temperature variations were observed with two probe method at room temperature.

3.1 Synthesis of Polyaniline conducting polymer

To oxidized 0.2M Aniline hydrochloride with 0.25M Ammonium peroxidisulphate aqueous medium Aniline Hydrochloride (purum: 2.5 gram, 20 mmole) was dissolved in deionized water in volumetric flask to 50 ml. of solution. Ammonium peroxidisulphate (purum: 5.79gram, 2.5 mmole) was dissolved in deionized water in volumetric flask to 50 ml. of solution. Both solutions are kept at room temperature for 1 hour, then mixed in beaker, briefly stirred and left to polymerize. During the polymerization the solution was kept in a salt ice bath to maintain the temperature in the desired range 5^0C to30^0C. Next day Polyaniline precipitate was formed and collected on Whatman's filter paper, washed with three 100 ml portion of 0.2M HCL and thereafter with Acetone. Polyaniline (emerdine) powder was formed and dried in air and vaco at 60^0 C. [15]. Oxidation of aniline hydrochloride with ammonium Peroxidisulphate yields Polyaniline [16, 17] as shown in Fig. 1.

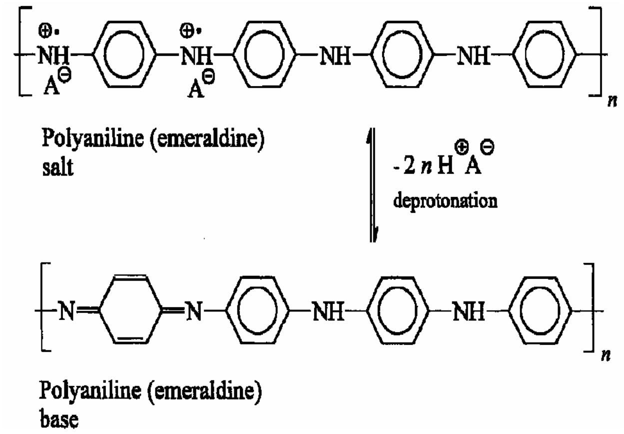

Fig . 1. Oxidation of aniline hydrochloride with ammonium Peroxidisulphate yields Polyaniline..

3.2 Preparation of the polymer thin film

For the measurement of conductivity, the film of Polyaniline is deposited by spin coating technique. In this process, the purified polymer was dissolved in DMF to form the Gel. The Polyaniline emerdine salt will dissolve in DMF with 0.5g: 10ml with 2 hrs stirring. The solution of Polyaniline is spread on rotating substrate, repeating this process for two / three times the uniform film will be obtained. After evaporation of solvent a thin film is formed. [6]. During the deposition of the film the temperature of the spinning machine assembly and surrounding is maintain below the room temperature throught the deposition process [2]. Initially the speed of machine is at the 500 rpm for 20 second and 1200 rpm for 50 second.

4. Results and discussion

4.1 Electrical characterization

The synthesized PANI films with optimised concentration of monomer, dopant, and oxidant and on different temperatures are subjected to I - V characterization to study the effect of temperature on the ohmic behaviour of the film. Aniline monomer doped with hydrochloric acid in aqueous medium produced uniform thin film of Polyaniline. The electrical characterization of film is done by the two-probe method at room temperature. Fig. 2 shows the I-V characteristics PANI film which gives the linear relation ship. As we increase the applied voltage the current is increase in proportion with the applied voltage. This reveals that the Polyaniline film has an ohmic behaviour [18, 19].

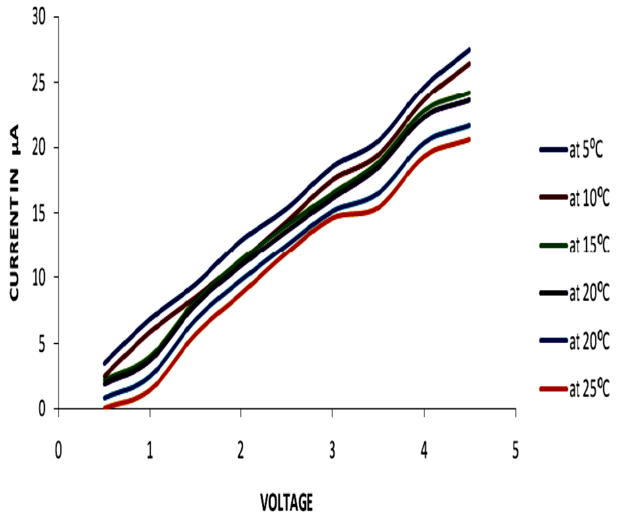

Fig.2. I-V characteristics of PANI.

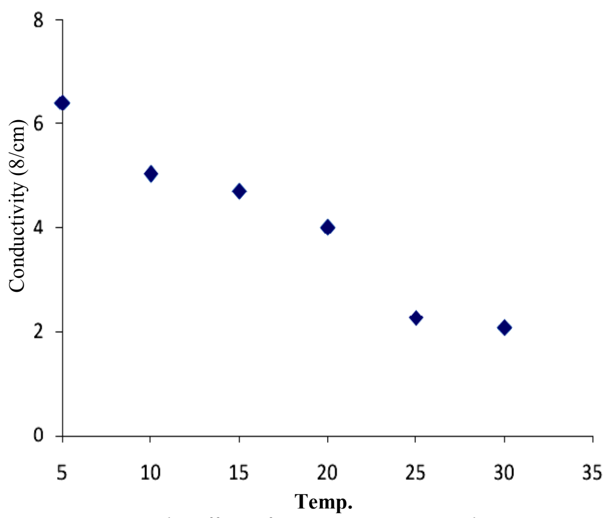

Fig. 3. The effect of temperature on conductivity.

Fig. 2 shows the I-V characteristics of PANI film on different temperatures. It reveals from the curve that, as we increase the temperature during the transition of polymer to conducting polymer Polyaniline, the conductivity of the resulting PANI decreases. The PANI gives higher conductivity at lower preparation temperature.

4.2 FTIR analysis of synthesized PANI films

The molecular structure of the synthesized PANI film was studied using the FTIR spectroscopy. Formation of the polymers, presence of a functional group on the polymer backbone or change in the protonation-deprotonation equilibrium of emeraldine can be deduced from the presence of corresponding bands in the FTIR spectrum. All these characteristic of polyaniline prepared at different temperature are shown in Table.1. This confirms the presence of conducting ES phase of the conducting polymer Polyaniline, and our results are in good agreement with earlier reported work [19-21]. Fig. 4 shows the FTIR spectrum of synthesized PANI film prepared at 5^0C only. The FTIR- spectrum of PANI films was recorded in the range of 400-4000 cm^{-1}(Nicolet-380). The point at which absorption occurs indicates the type of functional group present in the polymer. At the lower temperature the bond frequency is higher because the bond is stronger as we increase the temperature the bond becomes weak due to the elongation process, therefore the frequency deviate from their standard value. In the presence of primary amino function two characteristics of frequency are observed for N-H bond due to symmetric asymmetric stretching of N-H bond [14, 22, 24].

Table. 1. The characteristics of polyaniline prepared at various temperatures.

Assignment	5^0C	10 ^{0}C	15^0C	20 ^{0}C	20 ^{0}C	30 ^{0}C
N-H str. and C-H aromatic str	3440	3440	3320	3350	3232	3140
Stretch of quinoid ring	1653	1653	2853.4	2753.76	2854	1682
C=C benzenoid ring stretch	1423	1423	1463.5	1463.4	1463	1320
C-N stretch of benzenoid ring	1315	1315	1377.3	1377.25	1377	1299
In-plane C-H bending	1024	1024	1153.08	1145.32	1145.34	1050
Out-of-plane C-H bending	952	952	722	721.2	722.1	720

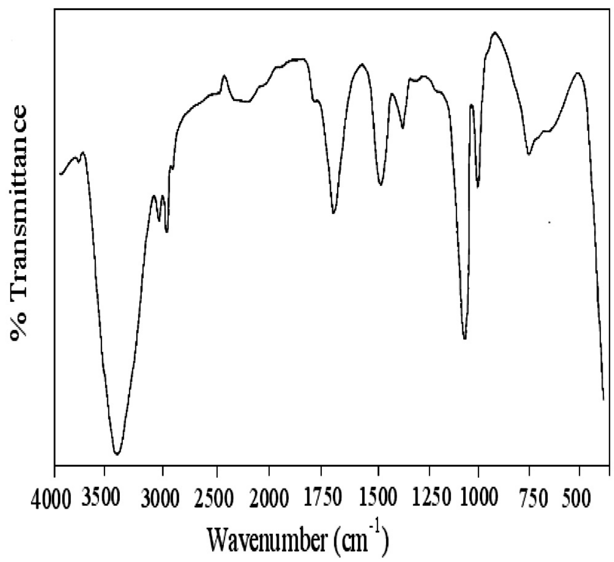

Fig. 4. FTIR spectra of synthesised polyaniline film prepared AT 5^0C.

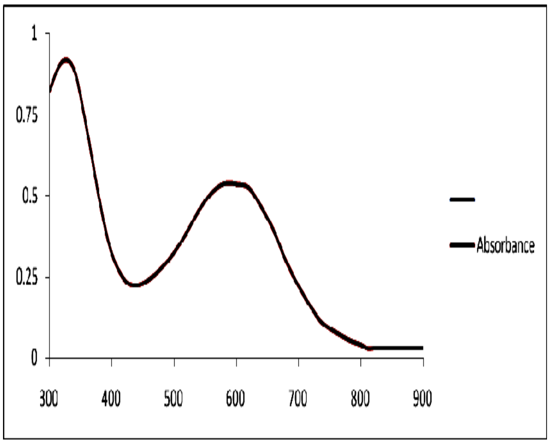

Fig. 5. U-V Spectra of polyaniline film prepared AT 5^0C.

4.3 UV-visible spectra

The UV-Visible absorption spectra of PANI films were recorded using UV-Visible 1601 Shimaduzu spectrophotometer in the range of 300-800nm. Typically, emeraldine base exhibits absorbance at approximately 330 nm, due to the Benzenoid π-π* transition, and at approximately 635 nm, which is attributed to the quinoid excitons absorption .Upon doping, the quinoid transition disappears, and two new absorbance appear. Therefore, to realize these transitions, UV analysis has been carried out for prepared PANI films and the results reported in our paper shows good agreement with earlier reported work [20]. Fig. 4 shows the UV spectra of PANI film prepared at 5^0C .The peak at 328 nm corresponds to π-π* transition of the Benzenoid ring, while the sharp valley at 445 nm can be assigned to the localized polarons which are characteristics of the protonated polyaniline, together with the extended tail at 800 nm representing the conducting ES form of the polymer film [23, 24].

5. Conclusions

In the present work conducting polymer polyaniline is prepared by chemical synthesis technique at different temperatures. Stretching bonds of N-H, C-H of PANI films show great dependence on temperature, which are investigated through FTIR spectroscopy. It is observed that the conductivity of PANI film enhances at lower temperature i.e. 5^0C. Further, it can be conclude that the deposited film can be used to prepare efficient active layer for sensors because of its ease in synthesis and environmental stability. Its redox behaviour (doped/dedoped) makes it a potential candidate for chemical sensing element, chemiresistors and Schottky diode etc.

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