Synthesis and Characterization of Polyaniline/Wood and Polyaniline/Carbon Composites

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Summary: Conducting polymers have shown many applications in the field of nanoscience, nanotechnology and nuclear science. Polyaniline (PANI) is the most studied conducting polymer due to its environmental stability, easy availability of its raw materials, and simple synthesis. We have synthesized polyaniline and two of its conducting composites *i.e.*, polyaniline-carbon and polyaniline-wood in acidic medium (HCl) using $K_2Cr_2O_7$ as oxidizing agent. All samples were characterized by FTIR and four-probe d.c. conductivity methods. The synthesis was carried out at two different temperatures (0 °C and -5 °C) and it was found that the yield and conductivity were maximum at lower temperature (-5 °C). The polyaniline-carbon composites showed enhanced conductivity whereas polyaniline-wood composites showed reduced conductivity when compared with the conductivity of pure polyaniline.

Introduction

Conducting polymers have become very important in the area of nanoscience, nanotechnology and nuclear science. Studies on the synthesis, characterization and application of conducting polymers such as polyaniline, polypyrrole, polythiophene and polycarbazole have been intensified in recent years because of their great technological utility [1, 2].

Conducting polymer composites have many applications as antistatic materials, conducting adhesives, radiation shielding coatings and in electric heaters [3, 4]. Depending on the application, the specific conductivity of these conducting polymer composites can be controlled by the type and amount of the filler material. These fillers can be metallic or nonmetallic in nature.

Polyaniline (PANI) is a very important conducting polymer because of its high electrical conductivity, environmental stability, cheap raw material and simple synthetic process [5, 6]. Polyaniline can be synthesized readily by electrochemical or chemicals methods. However, the electrochemical method has an advantage over chemical method as the resulting polymer does not contain contaminant from the oxidative agents necessary for chemical synthesis [7, 8]. The chemical oxidative polymerization process is of practical importance as it is the most feasible method for the production of polyaniline.

In this paper we are reporting synthesis of pure polyaniline and its composites with carbon and guava wood by chemical method in acidic medium using $K_2Cr_2O_7$ as oxidizing agent at two different temperatures, 0 and -5 °C. The samples were characterized by FTIR and four-probe d.c. conductivity methods. It was found that maximum yield of the sample depends on the synthesis conditions.

Results and Discussion

Fourier Transform Infrared Analysis

Figs. 1-3 showed the Fourier Transform Infrared Spectra of HCl doped polyaniline and its composites prepared at 0 and -5 °C. The intense band in the range of 3400-3438 cm^{-1} is due to the stretching frequency of amino group (N-H) in the doped polyaniline [10]. The band in the region of 1472-1586 cm^{-1} is indicative of the nitrogen bonded to benzene (B), quinoid (Q) rings [11]. The band observed in the range of 1105-1136 cm^{-1} is characteristic of conducting polyaniline and is due to the charge delocalization on the polymer backbone [12]. The intensity of this peak is a measure of

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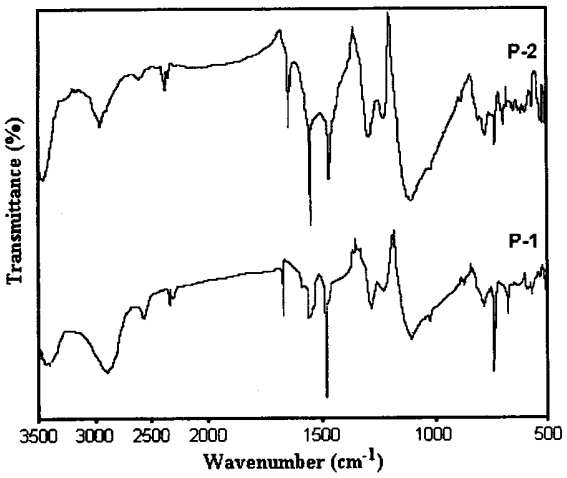

Fig. 1: FTIR spectra of PANI, P-1 and P-2, prepared at 0 and -5 °C, respectively.

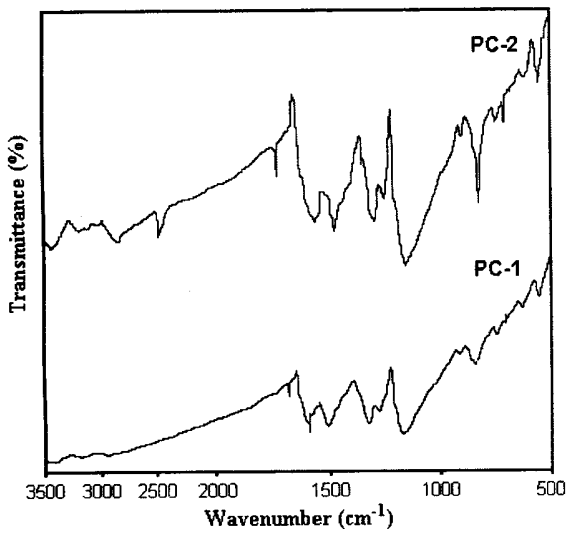

Fig. 2: FTIR spectra of PANI-carbon composites PC-1and PC-2 prepared at 0 and -5 °C, respectively.

delocalization of the electron or the conductivity [13].

When FTIR spectras of polyaniline composites PC-1, PC-2, PW-1 and PW-2 (Figs. 2, 3) were compared with that of the pure polyaniline samples P-1 and P-2 (Fig. 1), the characteristic peaks due to N-H stretching at 3400 and 3425 cm^{-1} in P-1 and P-2 respectively are found at 3433, 3438, 3400,

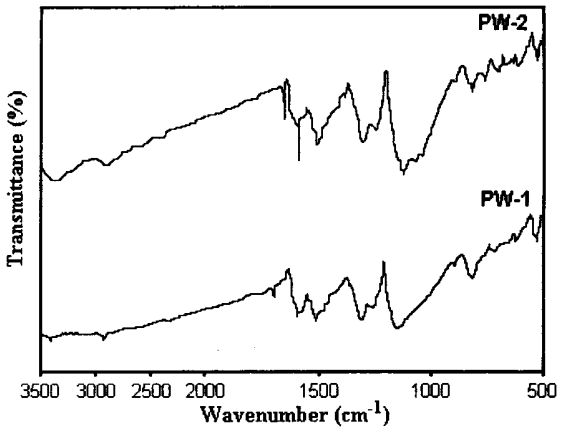

Fig. 3: FTIR spectra of PANI-wood composites PW-1 and PW-2 prepared at 0 and -5 °C, respectively.

and 3400 cm^{-1} for PC-1, PC-2, PW-1, and PW-2 respectively. The peaks due to the aromatic C-H stretching at 2905 and 2946 cm^{-1} in P-1 and P-2 respectively are found at 2928, 2920, 2900, and 2900 cm^{-1} for PC-1, PC-2, PW-1, and PW-2 respectively [3, 5]. The bands observed at 1575 and 1493 cm^{-1} in P-1 and 1570 and 1489 cm^{-1} in P-2 are due to the stretching of N=Q=N and N-B-N group respectively. In PANI-carbon composite (PC-1) these groups transition show a shift to lower wave number values (1560 and 1482 cm^{-1}) whereas a shift to higher wave number values (1586 and 1509 cm^{-1}) is found for PANI-wood composite (PW-1). In case of samples synthesized at -5 °C, the peaks due to the N=Q=N and N-B-N are found to be shifted to lower wave numbers as indicated in Table-2. These shifts in the IR band are correlated with the conductivity of the material [3, 5].

Conductivity Analysis

The conductivity of HCl doped polyaniline and its composites with carbon and wood was measured by using four-probe method [10, 11]. The

Table-1: Percentage yield of PANI (P-1, P-2), PANI-carbon composites (PC-1, PC-2) and PANI-wood composites (PW-1, PW-2).

Sample	Yield (%)
P-1	35.6
P-2	40.01
PC-1	75.04
PC-2	81.66
PW-1	51.66
PW-2	80.01

Table-2: Infrared absorptions of PANI (P-1, P-2), PANI-carbon composites (PC-1, PC-2) and PANI-wood composites (PW-1, PW-2).

Vibrational Assignment	Experimental Absorption Bands (cm^{-1})						Reference Absorption Bands (cm^{-1})
	P-1	P-2	PC-1	PC-2	PW-1	PW-2	
N-H stretching	3400	3425	3433	3438	3400	3400	3426
Aromatic C-H stretching	2905	2946	2928	2920	2900	2900	2832-2943
C=NH stretching	1683	1650	1658	1678	1689	1651	1713
N=Q=N	1575	1570	1560	1558	1586	1583	1577
N-B-N	1493	1489	1482	1472	1509	1494	1489
C-N stretching	1289	1303	1299	1287	1293	1289	1295
C=N stretching	1240	1230	1246	1235	1245	1244	1238
Aromatic C-N-C	1120	1117	1129	1126	1136	1105	1121
C-H in-plane	1036	1032	-	-	-	1050	1030
C-H out-of-plane	796	792	798	796	808	801	830
Phenazine like ring by cyclization	750	734	-	-	753	748	744
C-Cl stretching	680	681	709	707	716	679	590-700

d.c. conductivity of a conducting polymer and composites depend on morphology, type of monomer, doping level, degree of crystallinity, concentration of conducting fillers, shape of fillers, their size, orientation, and interfacial interaction with host matrix. The conductivity of protonated polyaniline is due to the presence of large ionizable groups [12].

Fig. 4 shows current-voltage (*I-V*) curves of pure and composite polyaniline samples. The voltage is measured with varying current (I) at room temperature which follows a linear relationship to ensure that the samples follow an ohmic behavior. From the initial slope, the average room temperature conductivity of pure polyaniline samples was determined as 3.749 S cm^{-1} and 4.078 S cm^{-1} corresponding to samples prepared at 0 and -5 ^{o}C respectively. The average conductivities of pure and composites polyaniline are shown in Table-3 having the following order of conductivity:

PC-2 > PC-1 > P-2 > P-1 > PW-2 > PW-1

The conductivity in polymers is explained in terms of the presence of crystalline and amorphous regions. It is believed that a conducting region behaves like a metallic region. These metallic regions in polymers are physically connected by relatively less ordered bridging chains through amorphous regions. In a crystalline region the electronic wave function is localized over 50-150 Å whereas it is well localized in an amorphous region. The charge delocalization on bridging chains is less compared to that in crystalline regions. It is clear from Table-3, that the conductivity of both PC-1 and PC-2 is greater than P-1 and P-2. The higher conductivity in PC-1 and PC-2 is due to the combined effects of small

Table-3: Conductivity of PANI (P-1, P-2), PANI-carbon composites (PC-1, PC-2) and PANI-wood composites (PW-1, PW-2).

Sample	Average Room Temperature Conductivity (S cm^{-1})
P-1	3.749
P-2	4.078
PC-1	7.146
PC-2	12.959
PW-1	0.599
PW-2	1.915

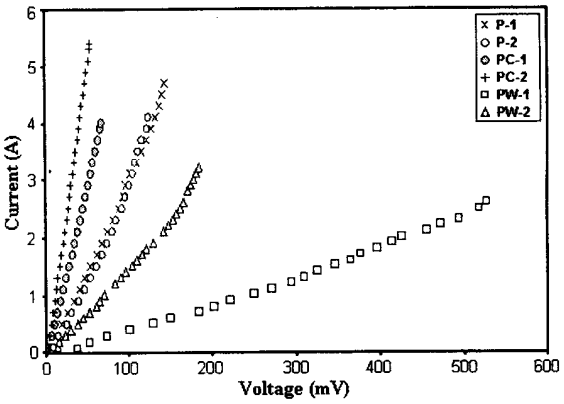

Fig. 4: Current vs. Voltage curves of pure PANI (P-1, P-2), PANI-carbon composites (PC-1, PC-2) and PANI-wood composites (PW-1, PW-2).

potential barrier in the disordered regions and increased charge delocalization in the ordered regions [13]. During preparation of PANI-wood composite, wood fills the spaces in polyaniline structure and promotes a more coiled and complex structure which results in decreased conductivity of PW-1 and PW-2 samples. Also wood is an insulator and introduces insulating inorganic islands in the conductive matrix

of PANI which disrupts the chain linearity / planarity [14]. This causes the (partial) blocking of charge carrier hopping as the charge carriers are unable to hop between favorable localized sites and thus decreases the conductivity [15].

The conductivity versus temperature relation is shown in Fig. 5. It is observed that there is a clear fall and rise in the conductivity of all samples with increase in temperature. The initial fall in the conductivity is more prominent in pure PANI samples P-1 and P-2. The conductivity of P-1 and P-2 falls significantly up to around 333 K after which it decreases slowly and then starts to increase gradually as the temperature rises. At about 352 K, we see a sharp increase in the conductivity with increase in temperature for both samples P-1 and P-2. The wood composites of polyaniline PW-1 and PW-2, show the same behavior but in these samples the initial decrease and then increase in conductivity with temperature is not as pronounced as is observed for pure polyaniline samples.

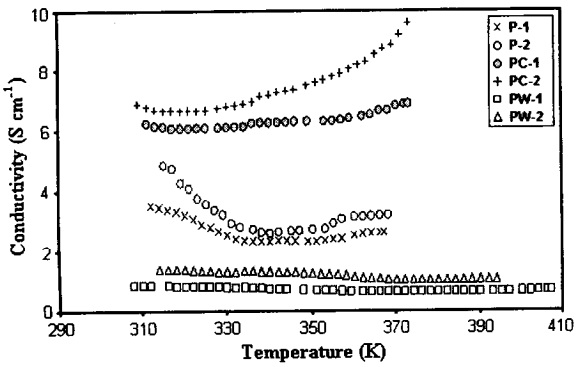

Fig. 5: Conductivity vs. Temperature plot of pure PANI (P-1, P-2), PANI-carbon composites (PC-1, PC-2) and PANI-wood composites (PW-1, PW-2).

In case of polyaniline-carbon composites, PC-1 and PC-2, decrease in the conductivity for a very short range of temperature that is up to 315 K and then increase in conductivity with increase in temperature is observed. It is noticeable that in PC-1 and PC-2 conductivity increases at much faster rate than all other samples. However, the rate of increase in the conductivity of all samples except PC-2 tends to slow down at higher temperature.

Table-3 shows that the samples prepared at low temperature (-5 °C) have higher conductivities than those prepared at higher temperature (0 °C). X-ray scattering studies on the structural characterization of conjugated polymers have shown that the interlayer distance between the polymer chains increases as the temperature of preparation of polymer increases and reaches a maximum value. Morphological studies of conducting polymer films by scanning electron microscope (SEM) suggest that the change in conductivity is due to compactness in the molecular packing. The presence of large spacing between monomer rings makes it more difficult for the electrons to "hop" from one layer to the next and hence reduces the conductivity. The compactness of the film is also greater at lower temperature of synthesis and helps to enhance the conductivity [16].

In summary, we prepared conducting polyaniline and its composites with carbon and wood by single stage polymerization. The yield of polyaniline (PANI) and its composites depends on the temperature of polymerization reaction. The lower temperature of preparation gives higher yield of polyaniline and its composites. Conductivity of PANI-carbon increased whereas PANI-wood composite decreased compared with pure PANI.

Experimental

Materials

Aniline (Riedel-De-Haen) was distilled before use and stored under Nitrogen gas. HCl (United Lab Chemical), DMF (Merck), $K_2Cr_2O_7$ and acetone (Riedel -De-Haen) were used without further treatment.

Synthesis of polyaniline (PANI)

10 ml of distilled aniline was added to 100 ml of 2 M HCl with constant stirring until complete mixing. This mixture was placed in freezing mixture in an ice bath followed by addition of 0.1 M potassium dichromate ($K_2Cr_2O_7$) drop wise over a period of 1 hour. The mixture became dark green indicating polymerization of aniline. The resulting polymerization mixture was placed for 24 hours in refrigerator. After this the precipitate was filtered and washed with acetone and 2M HCl to remove any residual monomer, oxidant and different decomposed products. The product was dried in an oven at 40-50 °C for 48 hours. The same process was repeated for the synthesis of PANI at -5 °C. Both 0 and -5 °C temperatures were attained using freezing mixture in an ice bath. These prepared PANI samples were

labeled as P-1 and P-2 representing synthesis at 0 and -5 °C, respectively.

Synthesis of PANI Composites

PANI-wood (Guava) composites were prepared by adding 2 g of milled guava wood in polymerization solution of aniline simultaneously during the addition of oxidizing agent over a period of 60 minutes while stirring, following the same procedure at two different temperatures 0 and -5 °C. The resulting composites were labeled as PW-1 and PW-2 representing synthesis at 0 and -5 °C, respectively.

PANI-carbon composites were prepared by adding 2 g of activated carbon following the same procedure as mentioned above for the PANI-wood composites at two different temperatures 0 and -5 °C. The resulting composites were labeled as PC-1 and PC-2 at 0 and -5 °C, respectively.

Characterization

FTIR spectra were recorded using Perkin Elmer RX1 FTIR spectrophotometer in the range 4000-700 cm^{-1}. The resolution of the spectrometer was set to 4 cm^{-1} and operating temperature was 25 °C. FTIR spectra of polyaniline samples were taken after mixing it with KBr powder and compressed into pellets.

Electrical resistance of the pellets was measured by four-probe method. A Professional Pro's kit multimeter was used as an ammeter and a digital multimeter M 2007 AVO was used as a voltmeter. Four needle-like electrodes of very thin copper (Cu) wires were pasted on the surface of sample parallel to each other with silver paint. Voltage was applied to the sample pellet with a d.c. power supply and the corresponding voltage and current developed across the sample were noted with voltmeter and ammeter, respectively. The current was passed in the range of 0.1 A (min) to 5.4 A (max) and voltage was measured for each of the corresponding value of current. The conductivity was determined from the current and voltage using equation:

$$\sigma = S\, I / V\, A \qquad (1)$$

where S is the mean distance between probes, I is applied current, V is measured voltage, and A is area of the sample.

To study the temperature dependent conductivity, each sample was put into the same circuit of four-probe method. Then the sample was heated in a furnace specially made for this purpose. The temperature of the furnace was firstly raised to 110 °C (383 K) keeping it below the melting point and degradation point of PANI. The current was set to a constant value of 1 A. After holding the temperature at 110 °C for a while the voltage was noted and then the temperature was slowly decreased to room temperature with small intervals of 1 °C. For every value of temperature, the corresponding value of the voltage drop across the sample was noted and conductivity was calculated for each set of reading using equation (1). Conductivity was plotted for each sample as shown in Fig. 5.

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