



SYNTHESIS AND OPTICAL CHARACTERIZATION OF ANTRAQUINONE-2-SULFURIC ACID SODIUM SALT AND 1,2-NAPHTHAQUINONE-4-SULFONIC ACID DOPED POLYPYRROLE-APS COMPOSITE

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Abstract:

Composite of the conducting polymer polypyrrole in Anthraquinone-2-sulfuric acid sodium salt (PPY/AQSA) and 1,2-Naphthaquinone-4-Sulfonic Acid (PPY/1,2 NQSA) were synthesized and characterized by varying the dopant concentration.

Impact of dopant and AQSA and 1,2 NQSA sodium salt on properties of polypyrrole film was then examined. The synthesized SPPY, PPY/AQSA and PPY/1,2 NQSA sodium salt were characterized by Fourier transform infrared spectroscopy (FTIR), NMR Spectroscopy, SEM analysis and XRD analysis. The conductivity of different molar ratios of doped polypyrrole was performed by a Keithley 6571B High Resistance Meter and Electrometer using a four probe-setup. The conductivity of different molar ratios of doped PPY/AQSA and PPY/1,2 NQSA increases with increasing concentration of dopant and then decreases with bulky dopant interference.

Key words - Pyrrole, ammonium peroxy disulphate, PPY/AQSA and PPY/1,2 NQSA sodium salt doped polypyrrole, chemical deposition method etc.

1. INTRODUCTION

Pyrrole may be easily converted into polypyrrole by chemical or electrochemical oxidation. When polypyrrole is created chemically, a conducting polymer is produced that contains the anion as a counterion, electrically neutralizing the partly charged polymer chain. [1]. It has been noted that the kind of anions in the polymerization solution has a significant impact on the conductivity of polypyrrole films. Doped polypyrrole has been the subject of a significant amount of research in film form, but relatively few attempts have been made in pellet form. We have concentrated on measuring the electrical conductivity of doped polypyrrole in this study. Organic sulfur-containing compounds, such as nitroxide radicals, carbonyl substance are the most studied organic cathode materials etc. [2], where an is the organic carbonyl substance A bigger conjugated system and more than two carbonyl functional groups describe this type of new electrode material, also known as quinone compounds, and it is known from the material's structure that it has more positive properties than inorganic materials. The higher specific capacity and faster reaction kinetics of polar materials [3,4].

Quinones, like traditional inorganic materials, are used for lithium ions from electrodes Detachable and intercalated "Lithium Shuttle" type, but easy to achieve high capacity. In order to realize high capacity of materials, attention has been paid to small structures as much as possible. Store electrons in and are composed of carbon (C) and oxygen (O) that are less resource-limited Constituent of ketones. However, ketones are unstable in the state where one electron is stored, So the researchers looked at a ring that connects two ketones to form a ring structure 1,2-Dione (quinone) However, quinones are electrical insulating materials with extremely poor electrical conductivity and easy to It is soluble in organic solvents, but insoluble in water, and has a high theoretical specific capacity. These The properties are just opposite to that of the polypyrrole material, so we will use the highly conductive polypyrrole. The selenium combines with quinones to form a conductive and redox. The polymer material of the original center. Scientists have previously reported the quinoidization Physical mixing of the compound with poly(3,4-ethylenedioxythiophene), the electrical conductivity of the material has been improved [5]. In this study, The PPY was prepared directly by conventional oxidative polymerization methods using AQSA and 1,2 NQSA as the doping agent. The structure of the samples was investigated by Fourier transform infrared (FTIR), NMR spectroscopy and X-ray diffraction (XRD). The conductivity of different molar ratios of doped polypyrrole was performed by a Keithley 6571B High Resistance Meter and Electrometer using a four probe-setup. Scanning electron microscopy (SEM) was used to characterize the morphology of the samples. To investigate the relationship between the PPY and composite properties. The electrical resistivity was measured using a four-probe technique.

2. EXPERIMENTAL METHODOLOGY

Chemicals: - Pyrrole (98% pure sigma Aldrich) Ammonium per sulphate (APS) (>99,8%) (Merck), as oxidant, anthraquinon-2- sulfuric acid sodium salt and 1,2 nathaquinone-4-sulfuric acid (98%) (Aldrich) used as dopants, Acetone (>99,8%) (Merck), deionized water used as solvent for synthesis.

Preparation of undoped polypyrrole powder. [SPPY]

For synthesis of polypyrrole by chemical bath method, primarily all apparatus were washed with deionized water, rinse in acetone. Pyrrole is used as monomer for preparation of polypyrrole powder. Monomer is prepared by using 1M pyrrole in deionized water. Oxidant solution was prepared 1M concentration of APS in deionized water. The ratio of monomer to oxidant was kept 1:2. which means the polymerization proceeds in excess of oxidizing agent. Firstly, Monomer solution was added dropwise in an oxidant solution reaction being carry out at room temperature at 25⁰c. During precipitation heterogenous reaction occur. Polypyrrole produced was kept unagitated for 24 hours, so that polypyrrole powder settle down at bottom. The polypyrrole powder filter out under vacuum and washed with distilled water several times to remove any impurities present. Polypyrrole dried for 2 days at room temperature. where, A- (sulfate ion) are the counter anions incorporated along polymer backbone.

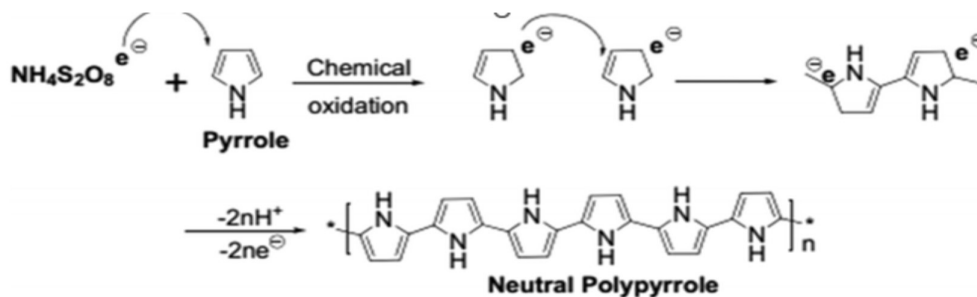


Fig1:- Chemical oxidative polymerization of pyrrole. Reference from.[6]

Preparation of dopped polypyrrole using following dopants

By using Anthraquinone sulfuric acid sodium salt.

The composites powder was prepared by same procedure mention above only dopant Anthraquinone sulfuric acid with 10%,20%,30%, 40%, 50%,60% w/v added in pyrrole solution before addition of oxidant solution. For example, synthesis A₄,B₄,C₄,D₄,E₄,F₄ in Table 1. Then doped powder were obtained. After 24hrs it was filtered and washed with distilled water several times to remove any impurities present in it. Doped polypyrrole powder dried for 2 days at room temperature.

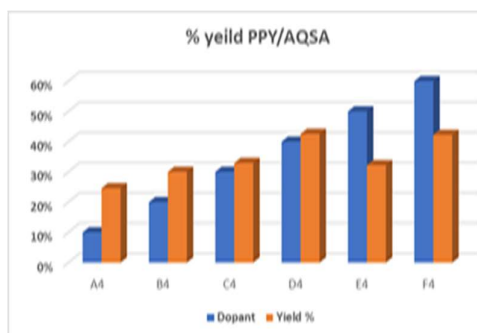
By using 1,2naphthaquinone-4-SulfonicAcidsodiumsalt

The polymerization was carried out either in neutral solution such as deionized water. An overview of synthesized materials is summarized in Table 2. Dopant 1,2 naphthoquinone -4-Sulfonic Acid sodium salt with 10%, 20%, 30%, 40%, 50%, 60% w/v, which means the polymerization proceeds in excess of oxidizing agent. For example, synthesis A₅, B₅, C₅, D₅, E₅, F₅ in Table 1 proceeds as follows:

The yield is given as follows in Table no. 1 **Monomer: oxidant =1:2 ratio**

Sr No.	Dopant	Colour of product	Yield % of PPY/AQSA	Sr No.	Dopant	Colour of product	Yield % of PPY/1,2NQSA
A4	10 %	Black	12.40%	A5	10 %	Black	24.59%
B4	20%	Black	20.78%	B5	20%	Black	30.02%
C4	30%	Grey	17.49%	C5	30%	Black	32.92%
D4	40%	Black	23.49%	D5	40%	Black	42.54%
E4	50%	Black	23.71%	E5	50%	Black	32.19%
F4	60%	Black	21.87%	F5	60%	Black	42.22%

a)



b)

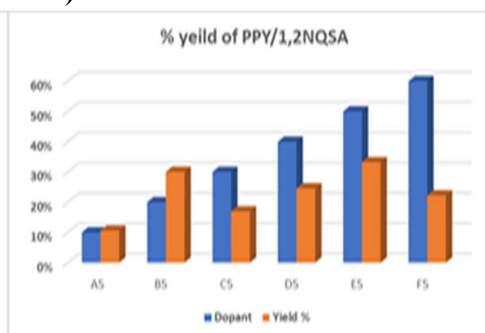


Fig.2: Effect of % of dopant on yield of (a) PPY/AQSA (b) ppy/1,2NQSA

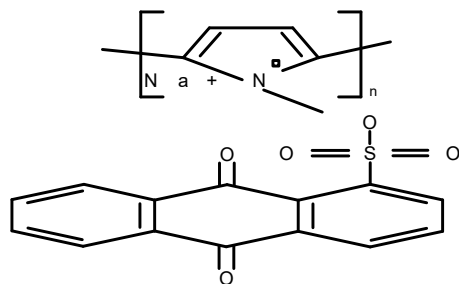


Fig:3. PPY doped with AQSA

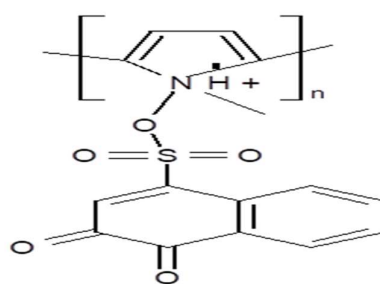


Fig: 4. PPY doped with 1,2 NQSA

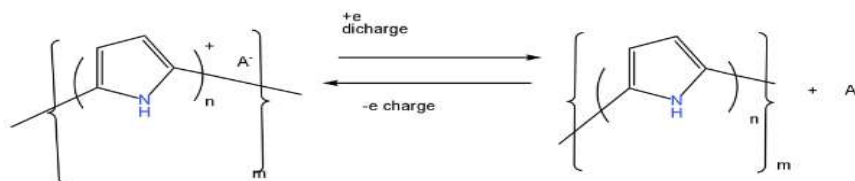


Fig:5 Chemical Reaction with anion

Analysis and Measurements

FTIR spectra of all synthesized composite materials under investigation were recorded on Shimadzu FTIR-02634 (Serial no. A13749) Spectrophotometer between 400 and 4000 cm^{-1} . NMR spectra of all synthesized composite materials under investigation were recorded on BRUKER ADVANCED II 400 NMR Spectrometer, SAIF, Punjab University, Chandigarh. The Polypyrrole was characterized by XRD using Analytical (Philips), model miniflex 600. The XRD patterns were recorded between $2\theta = 10^\circ$ to 40° . The X-ray diffractometer uses $\text{CuK}\alpha$ radiation of $\lambda = 1.5418 \text{ \AA}$ generated at 40 kV/20 ma. The morphology of Polypyrrole was examined using Scanning Electron Microscope (SEM) JEOL make JSM- IT200 model. The conductivity of different molar ratios of doped polypyrrole was performed by a Keithley 6571B High Resistance Meter and Electrometer using a four probe-setup (DFP.2 model).

3. RESULTS AND DISCUSSION

Percentage Yield

Preliminary results show that PPY doped with AQSA and 1,2 NQSA sulfonic acid could be chemically prepared. The simplicity of PPY synthesis was further confirmed by the preparation of the polymer from when a dopant is not used. The results of the apparent yield obtained from the chemically synthesized PPY are as shown in Table 1. There is a trend of higher yield from the polymerization carried out at lower temperature with the doped system having more yield.

Table 2

Overview of synthesized PPY materials.

Synthesis no.	Oxidizing agent	Doping agent	Dopants awaited in product
SPPY	APS	-----	SO_4^{-2}
A_4 to F_4	APS	Na^+ (AQSA)	Anion AQSA, SO_4^{-2}
A_5 to F_5	APS	1,2NQSA	Anion 1,2NQSA, SO_4^{-2}

The SO_4^{2-} dopants are residuals

This higher yield of the doped system is due to the ability of AQSA and 1,2NQSA to generate enough radicals through protonation of the pyrrole monomers that initiates the cationic polymerization of PPY. The AQSA and 1,2NQSA equally forms micelles in aqueous solution using its hydrophilic sulfonic acid group to combine with the hydrophobic pyrrole monomers. The result shows that the efficiency of the polymerization reaction is highest at the w/v (40%) dopant ratio obtained an apparent PPY yield of 23.49 % for AQSA, lower yield value of 42.54 % for PPY/1,2 NQSA w/v (40%) ratio for the same length of polymerization time. This result is quite comparable. The lower yield value of 23.49 % for PPY/AQSA with w/v (40%) compared to the 42.54 % for PPY/1,2 NQSA w/v (40%) might be due to the higher steric hindrance associated with the bulkier trinuclear anthraquinone moiety compared to the dinuclear naphthaquinone group.

Fouries transform infrared (FTIR) investigation

The Polypyrrole powders prepared in different ways were analyzed by FTIR. In fig (6) FTIR spectra showed the main characteristic peaks in between 1700-1500 corresponding to Aromatic C=C stretching of polypyrrole ring. Low intensity peaks are observed at around 2804.4 cm^{-1} which can be attributed to aromatic C-H stretching vibrations. The peaks at 1695.43 cm^{-1} and 1126.43 cm^{-1} represents C=N and C-N bonds respectively, the bond of C-H in plane deformation vibration is pointed at 821.68 cm^{-1} and of the C-C out of plane ring deformation vibrations or C-H rocking is at 677.01 cm^{-1} which occurs at 619.15 cm^{-1} in spectrum. This range of absorption peak agrees well with literature, confirming the formation of Polypyrrole. [7,8] FT-IR spectra of PPY/AQSA, (Fig. 7) characteristic peaks of PPY were at 1670 cm^{-1} for the C=C and the absorption peak of the stretching vibration 1211.35 cm^{-1} for C—N stretching vibration absorption peak. Aromatic Ar-H strength was observed at $2935.78, 2870.20, 2353.26 \text{ cm}^{-1}$. The sulfonic acid presence in the doped polymer was provided by the absorption bands at 1311 cm^{-1} and 1211 cm^{-1} , assigned to the asymmetric stretch of the O=S=O group. FTIR spectra of 1,2NQSA -doped polypyrrole in fig 8 shows that A shift of the baseline was evident in the spectra obtained shows that when the spectra were viewed over the extended scale, covering the complete wave number range experimentally available, i.e., 5000 cm^{-1} to 1000 cm^{-1} .

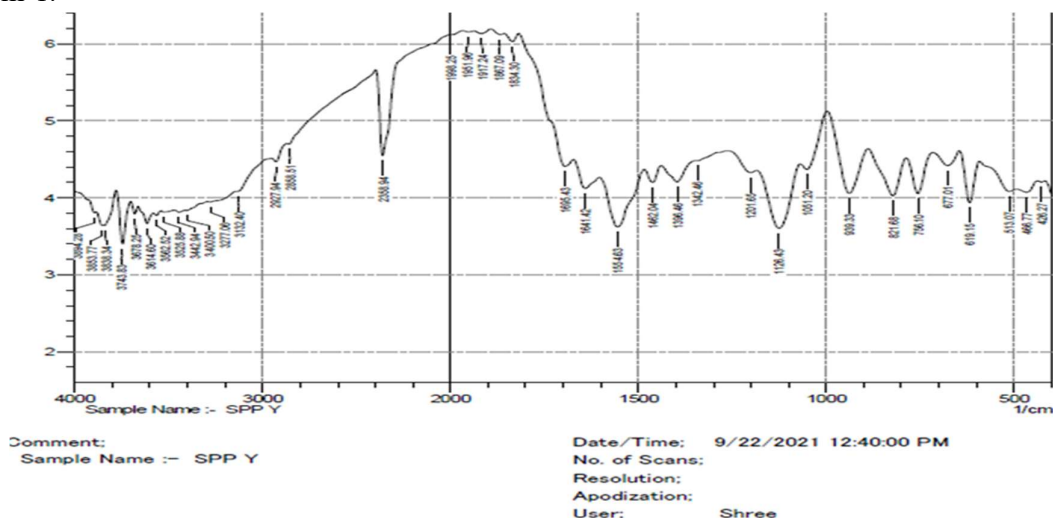


Fig: -:-6 IR representation of SPPY

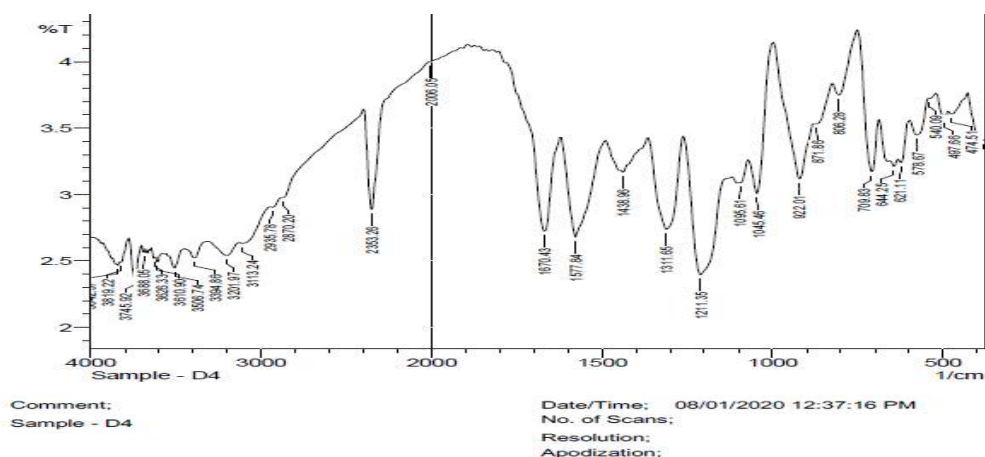


Fig: -:-7: IR representation of doped PPY/AQSA composite.

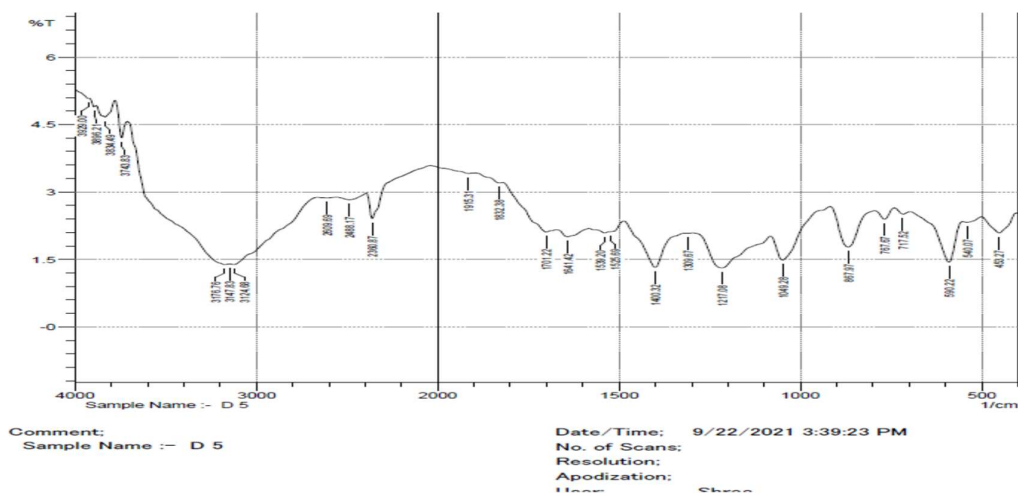


Fig: -:-8: IR representation of doped PPY/1,2 NQSA composite.

The downward bands at 1577.84, 1438.96 cm^{-1} were assigned to C=C and C=N vibrations. The band at 1294 cm^{-1} was assigned to N-H in plane contributions. Sulfonic acid present in the doped polymer was evidence the absorption bands at 1309.67 cm^{-1} , 1217.08 cm^{-1} , assigned to the asymmetric stretch of the O=S=O group. As this range is evidence on one available literature [9] The presence of CO₂ is indicated by an absorption band at 2360.87 cm^{-1} that increased in intensity int is observed in IR spectral image. This agrees well with literature, confirming the formation of doped Polypyrrole. [10,11] The following table no.3 lists the significant peak range.

Table.3

Polymer composite	Position of absorption maxima (cm ⁻¹)						
	N-H stretching (Reference value 3500-3300cm ⁻¹)	Ar-H	Aromatic C=C stretching (Reference value 1700-1500cm ⁻¹)	C=N stretching (Reference value 1690-1640cm ⁻¹)	C-N stretching (Reference value 1350-1000cm ⁻¹)	C=C-H bending (Reference value 900-690cm ⁻¹)	S=O Stretching (Reference value 1375-1300cm ⁻¹ & 1350-1140cm ⁻¹)
Pure PPY (SPPY)	intensity peak in between 3743.83 - 3277.06 cm ⁻¹	2358.94 cm ⁻¹	1554.63, 1641.42 cm ⁻¹	1695.43 cm ⁻¹	1126.43 cm ⁻¹	821.68 cm ⁻¹	1342.46 & 1201.65 cm ⁻¹
PPY/AQSA (D4) 40% doped Anthraquinone-2-sulfuric acid sodium salt	Intensity peak in between 3500-3300 cm ⁻¹	2353.26 cm ⁻¹	1577.84 cm ⁻¹	1670 cm ⁻¹	1095.61, 1045.46 cm ⁻¹	709.83cm ⁻¹	1311.65 cm ⁻¹ & 1211.35 cm ⁻¹
PPY/NQSA (D5) 40% doped 1,2Naphthaquinon-sulfuric acid sodium salt	Intensity peak in between 3500-3176.76 cm ⁻¹	2360.87	1701.22, 1539.20, 1525.69 cm ⁻¹	1641.42 cm ⁻¹	1049.28 cm ⁻¹	867.97cm ⁻¹	1309.67 cm ⁻¹ & 1217.08 cm ⁻¹

NMR spectra of SPPY/ doped PPY

The NMR spectra given in the fig.9,10,11. Which revealed that NMR spectra of SPPY, PPY/AQSA, PPY/1,2NQSA shows three distinct peaks. In SPPY, the first peak is obtained for C=C-H proton at 2.50. The second peak corresponding to N-H proton is obtained at 3.9. This

peak is deshielded because the proton is attached to more electronegative nitrogen atom. The peaks corresponding to aromatic protons is assigned at 7.1. In PPY/AQSA, the first peak is obtained for C=C-H proton at 2.50-2.51. The second peak corresponding to N-H proton is obtained at 3.56. The peaks corresponding to aromatic protons is assigned at 1H NMR (400 MHz; CDCl₃) δ:7.53 (dd, J=6.0, 3.6 Hz, 2H), 7.61-7.65 (m, 2H), 7.84 (d, J=7.6 Hz, 1H), 7.99 (dd, J=8.0, 2.0 Hz, 1H), 8.04 (d, J=1.2 Hz, 1H); The peak corresponding to aromatic proton is observed that δ 7.1002 in SPPY, 7.100 (t), 6.9(dd), 7.5(d), 8.5(d) indicate that dopant 1,2 naphthaquinone-4-sulfuric acid sodium salt may present in the structure. The increase in aromaticity may be a consequence which highly affects the conductivity of the sample.

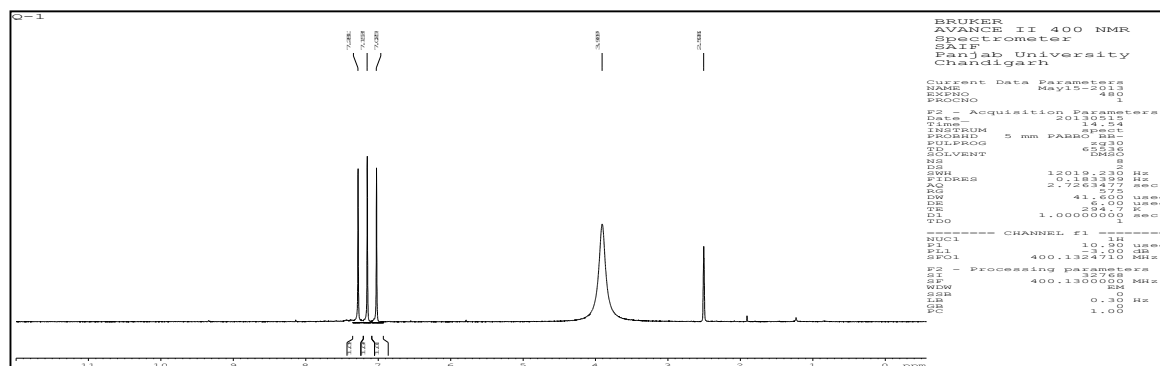


Fig: -9: NMR spectra of SPPY (undoped polypyrrole)

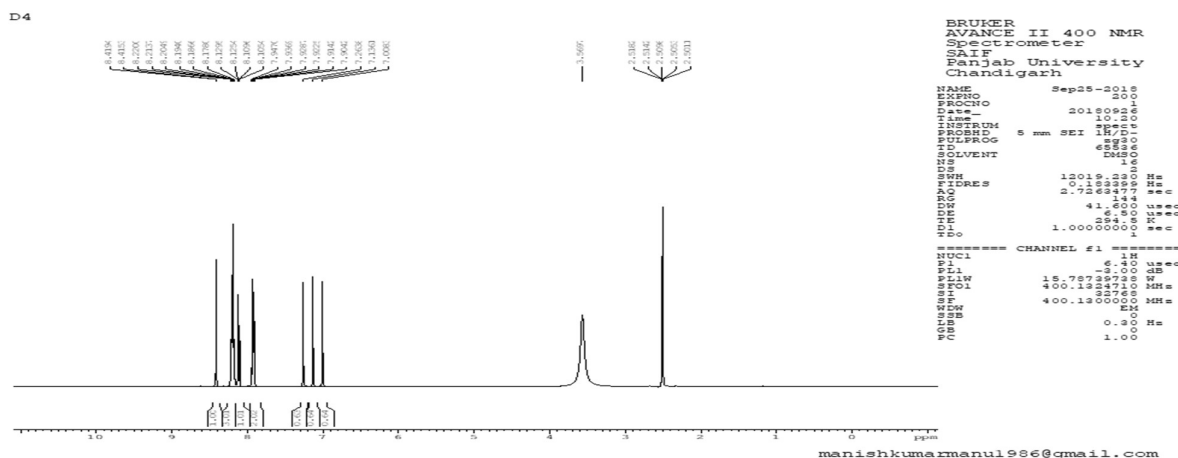


Fig: -10-NMR spectra of PPY/AQSA (D4).

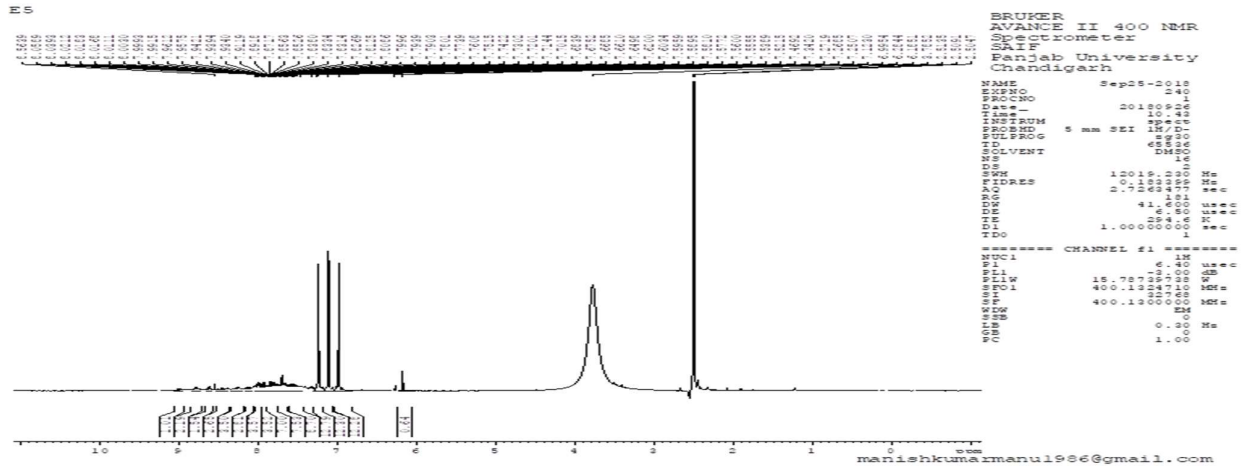


Fig: -11-NMR spectra of PPY/1,2NQSA (D5) .

SEM Morphology

SEM images were used to determine the size of the PPY molecule (SEM). At a magnification of 20, Figure 12 depicts the spherical shape of PPY samples using ammonium persulphate as an oxidant. As a result, the morphological changes of the PPY were highly influenced by the type of the chemical polymerization process, when an oxidant is utilized. Thus, the morphological change of the PPY was strongly dependent on the type of oxidant used during the chemical polymerization process is reported [12].

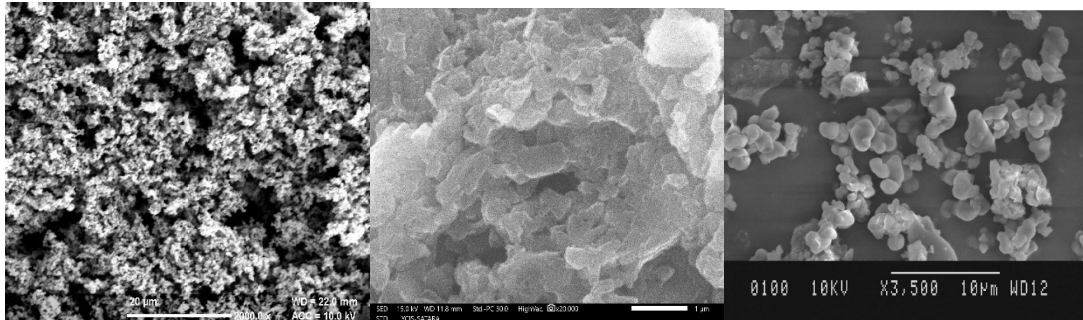


Fig.12: SEM (SPPY) Fig.13: SEM (PPY/AQSA) Fig.14: SEM (PPY/1,2NQSA)

The PPY/AQSA, PPY/1,2NQAS (fig.13-14) particles are clearly larger than the undoped PPY particles. The PPY/AQSA composite's continuous film structure, which resembled a cauliflower like structure, was visible in the SEM picture of Fig. 13. It is built on PPY because of its outstanding electrical conductivity. This continuous conductive network helps in enhancing the conductivity of PPY/AQSA materials, and after that It can somewhat make up for PPY when coupled with the high-capacity properties of AQSA. It is reported that the specific capacity of a single material is expected to exhibit higher specific capacity than PPY in Li-ion batteries. [8] (Fig. 14) The tubular and regularly arranged PPY/1,2NQSA granules are visible at a 1 magnification. This fibrillar structure of the polymer chains guarantees that the polymer chains are sequentially ordered or densely packed, improving conductivity and facilitating the simple transfer of load carriers.

X-Ray Diffraction Analysis

X-ray diffraction tests for SPPY samples with APS oxidants as shown in (Fig. 15). The intermolecular stacking structure and amorphous character of the polymer are indicated by the large peaks in the region $2\theta=20^{\circ}-30^{\circ}$. This is consistent with earlier information provided in

the literature. [13,14]. Since structure of PPY/AQSA displayed clear diffraction peaks in its XRD pattern (w/v 20%, 40%) Fig.16, demonstrating its strong crystallinity as sharp peak observed. The PPY/1,2 NQSA's XRD pattern is amorphous and exposed in between $20^{\circ} - 30^{\circ}$ degrees (Fig.17 a, b) PPY and nanoparticles of 1,2 NQSA were placed in contact during the synthesis, the XRD pattern of the PPY/1,2 NQSA composite was moved towards a higher angle. It is discovered that the XRD pattern of pure PPY/1,2NQSA displays no sharp peak except for a wide peak at $2\theta = 22^{\circ}-28^{\circ}$ (Fig. 1), which is a characteristic peak of PPY and It implies that the nature of PPY/1,2NQSA is amorphous. which is typical peak of PPY and suggests that the nature of PPY is amorphous has been reported [15].

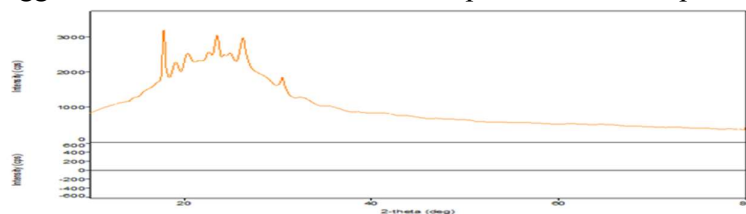


Fig:15: X-ray diffraction patterns of SPPY

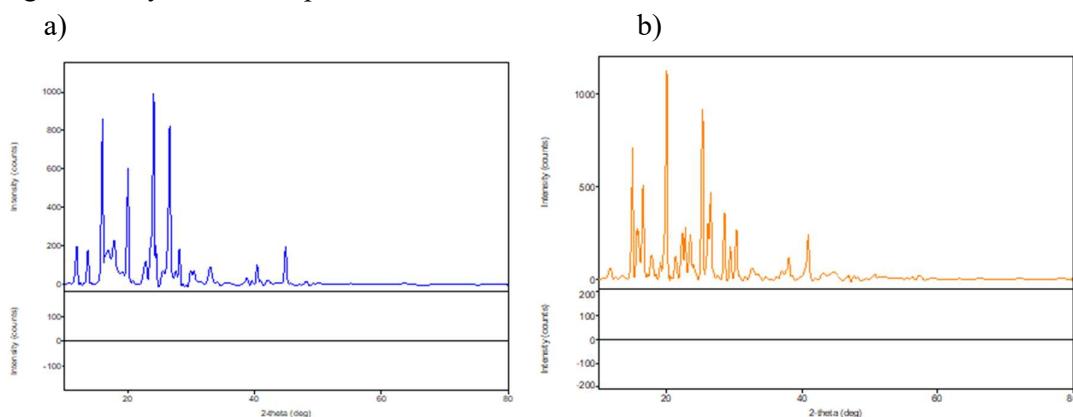


Fig:16: XRD pattern of (a) PPY /AQSA (20% Doped) and (b) PPY /AQSA(40%Doped)

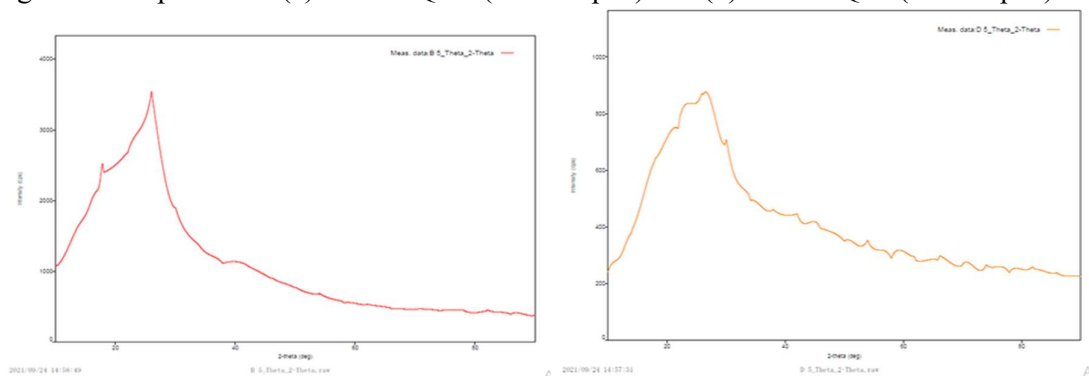


Fig:17: XRD of PPY /1,2NQSA (20% Doped) and PPY /1,2NQSA(40%Doped)

Conductivity measurements for various molar ratios of PPY/AQSA and PPY/1,2NQSA

In this arrangement, the samples were sandwiched between the copper electrodes by pressure contact [16]. The temperature was adjusted from room temperature (313 K) to 343 K while the

voltage, V, was kept constant. The current values were taken as the temperature increases. Using the relation, the resistivity at various temperatures was calculated.

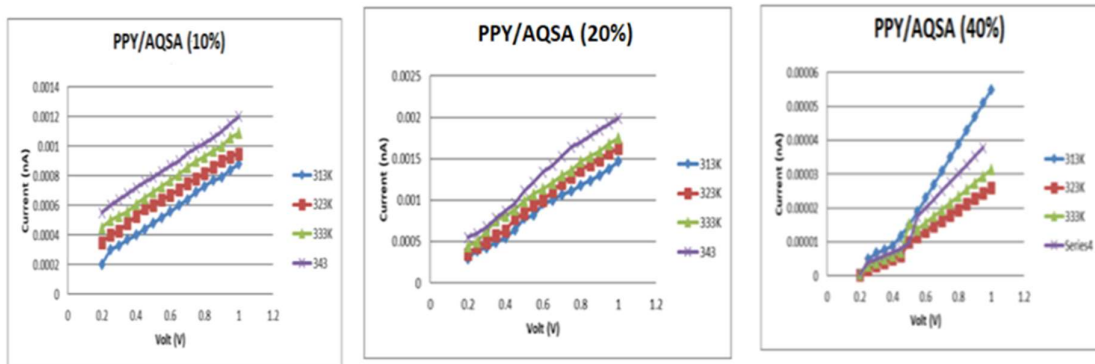
$$\rho = 4.5324 \times V \times d/I \times F$$

where, $F = d/s$ and I is current, V is voltage, d is thickness of the pellet (2.434 mm), F is correction factor and s are distance between two probes and distance of the probe which was 1.8 mm. The conductivity was calculated using the relation.

$$\sigma = 1/\rho$$

where ρ is resistivity; the correction factor depends on the sample geometry, thickness, borders and location of points in the sample.

Figure 18 displays the I-V characteristics for the polypyrrole powders produced with a dopant-to-monomer ratio of PPY of 10–60% when AQSA is present in varied concentrations. The current exhibits linear behaviour as the temperature rises. Lower resistance caused by thermal impacts enables more current to flow through the sample. The conductivity rapidly rises to a maximum metal-conducting at the ratio up to 40% in the dopant concentration region. When the ratio rises from 50% to 60%, it doesn't get saturated but rather lowers slowly before unexpectedly dropping to low levels. while the ratio keeps going up. Average particle size dominates the change in conductivity and thermal stability for the resulted polypyrrole at different dopant concentration. The strong association of the average particle size and the conductivity could be interpreted as follows. On the one hand, in perspective of the theoretical model proposed by Baughman and Shacklette [17], the conductivity being the lowest accompanies the average particle size being the lowest as small dopant concentration in between w/v 10-20%; for 20-30% their conductivities being the highest corresponds to the average particle size being the highest, also the conductivities and average particle size drop down coincidentally from 40-60% as particle size again goes on decreases with dopant concentration. It is reported in literature that the conductivities and average particle size drop down coincidentally with increasing dopant concentration.[18] The conductivity measurement of PPY with various concentration of 1,2 NQSA is shown in Fig. 19. The variation of PPY/1,2NQSA monomer-dopant ratio w/v from 10 to 40% led to a greater yield and conductivity of the doped PPY and from 40% it began to decrease.



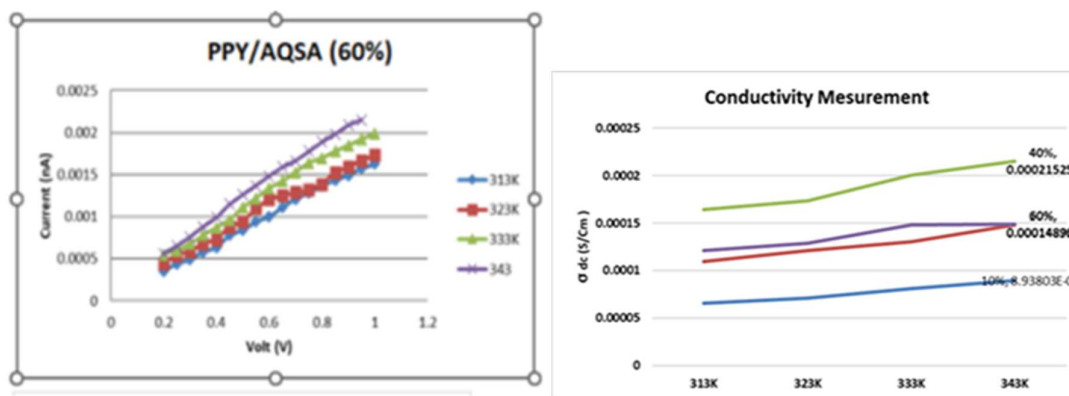


Fig.18. Current-voltage characteristics for various concentration of PPY/AQSA

By higher amount of 1,2 NQSA, as depicted in Fig. 18(c,d) It could be because a so-called protective envelope was forming around the products at a greater rate when an excess of 1,2 NQSA was absorbed onto the surface of hydrophobic pyrrole. Increasing molecular concentrations of bulky dopants stopped further polymerization. As a result, the molar ratio of 1,2NQSA increased, the conductivity of PPY/1,2NQSA dropped. It is observed that the conductivity of polypyrrole is due to dopant concentration.

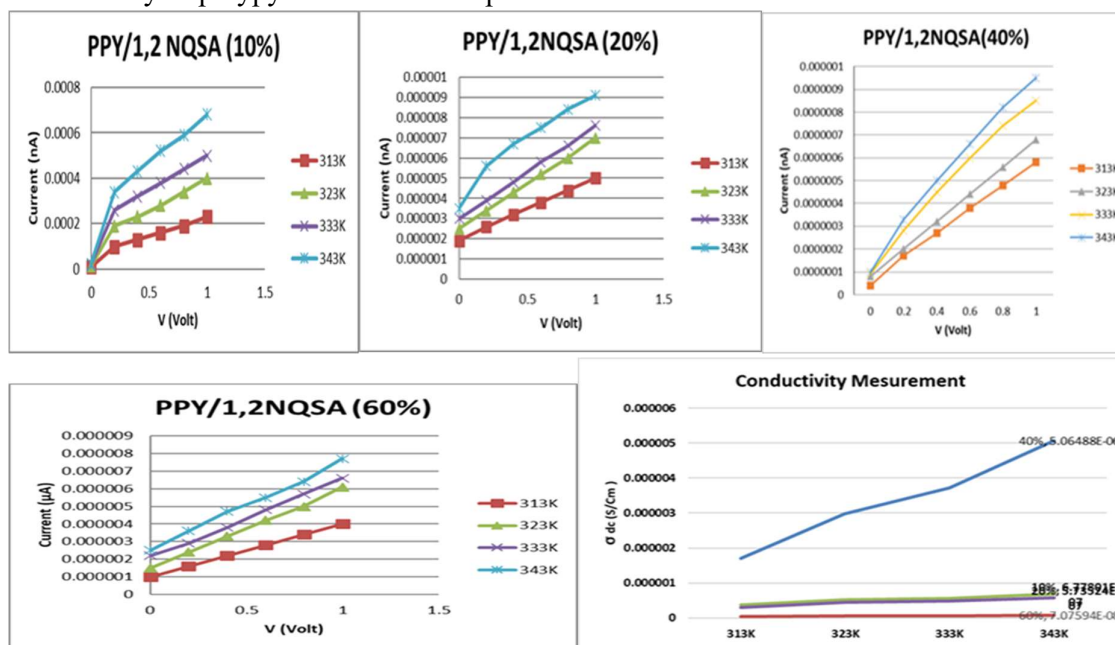


Fig.19. Current-voltage characteristics for various concentration of PPY/1,2NQSA

Comparison between conductivity of PPY/AQSA and PPY/1,2 NQSA composite

The conductivity is determined by the intrinsic conjugation length, and the greater the conjugation length, the simpler it is for carriers to move about inside and/or between chains. Therefore, AQSA dopant has a longer conjugation length than 1,2NQSA dopant. It is observed that the conductivity of PPY/AQSA composite is more than PPY/1,2NQSA composite is due to longer conjugation length. The average conjugation length, on the other hand, has a positive relationship with average particle size because the longer the conjugation, the longer the chain, and hence, the greater the particle size.

4. CONCLUSION

- SPPY, PPY/AQSA and PPY/1,2NQSA composite were successfully synthesized by chemical oxidation. The % of yield increases with dopant concentration.
- FT-IR and NMR studies confirm that doping causes structural changes in the polymer chains supported by SEM Image.
- XRD Patterns demonstrated the amorphous, semi crystallinity of the PPY/1,2NQSA. The stacking structure of PPY/AQSA, in its XRD pattern showed obvious diffraction peaks, indicating its high crystallinity.
- When the particle size is changed (increases) as aromatic ring conjugation increases in AQSA as compared to 1,2NQSA used as dopants. So, the longer conjugation length, the longer chain length, and causing the larger particle size. Ground on this reasoning the positive dependence of the conductivity on the average particle size is understood. The conductivity value of PPY/AQSA is more than PPY/1,2NQSA as aromatic conjugation length is more. It is observed.
- AQSA, 1,2NQSA doping PPY provided both high conductivity and better solubility. Organic acids (sulfonic) were found to be suitable for use as dopants to produce more stable, more soluble (improved processability) and more conductive polypyrrole.
- As a result, conductive PPY/AQSA and PPY/1,2NQSA polymers with advanced optical properties seem to have a good interface potential for the pro devices such as diodes and transistors.
- When bulky dopant molecular concentration increases which prevented further polymerization. So, the conductivity of doped PPY decreased.

ACKNOWLEDGMENTS

The researchers give many thanks in appreciation to Government Vidarbha Mahavidyalay, Amravati for providing suitable environment for research work. Researchers also say thank you to the Directors of G V I S H Amravati.

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