

Synthesis, Characterization and A.C. Conductivity Study of Polypyrrole/Sodium Metavanadate(Ceramic) Composites

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Abstract-In-situ polymerization of pyrrole (Py) was carried out with sodium metavanadate(ceramic) in the presence of oxidizing agent ammonium persulphate to synthesize polypyrrole(PPy)/sodium metavanadate(NaVO_3) by chemical oxidation method. The PPy/ NaVO_3 composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of NaVO_3 in PPy. The surface morphologies of these composites were analyzed using Scanning Electron Microscopy (SEM), show that NaVO_3 particles are embedded in PPy chain to form multiple phases. The Fourier Transform Infra-Red Spectroscopy (FTIR) reveals the stretching frequencies were shifted towards higher frequency side. The powder X-ray diffraction (XRD) spectrograph, suggests that they exhibit semi-crystalline behavior. Thermal analysis (TG/DTA) studies/testing were done and reported. The frequency dependent A.C. conductivity reveals that, the NaVO_3 concentration in PPy is responsible for the variation of conductivity of the composites. The values of conductivity increases till wt. 50% NaVO_3 in PPy. The dimensions of NaVO_3 particles in the matrix have a greater influence on the conductivity values.

Key words: Polypyrrole; Sodium Metavanadate; Composites; Conductivity; Frequency.

I. INTRODUCTION

The discovery of electrical conductivity in molecular charge transfer promoted the development of conducting polymers which have been synthesized and show the excellent electrical properties. Conducting polymers, by virtue of their light weight and greater ease of fabrication, have replaced and are continuing to replace metals in several areas of applications. Conducting polymers have been prepared for a wide range of applications ranging from rechargeable batteries to smart windows.

Polypyrrole (PPy) has become one of the most studied electronically conducting polymer. It can be synthesized either chemically or electro-chemically. Polypyrrole is an intrinsic conducting polymer which can be made to have conductivities up to 1000 Scm^{-1}

rendering its versatile applications in batteries, electronic devices, functional electrodes, electro-chromic devices, optical switching devices, sensors and so on [1–5].

II. EXPERIMENTAL DETAILS

A. Synthesis

The AR grade [SpectroChem Pvt. Ltd.] pyrrole[6] was purified by distillation under reduced pressure. 0.3 M pyrrole solution was contained in a beaker which was placed in an ice tray mounted on a magnetic stirrer. 0.06 M ammonium persulphate[7] solution was continuously added drop-wise with the help of a burette to the above 0.3 M pyrrole solution. The reaction was allowed for 5 hours under continuous stirring by maintaining a temperature of 0°C to 3°C . The precipitated polypyrrole was filtered and dried in hot air oven and subsequently in a muffle furnace at 100°C . The yield of the polypyrrole was 3.6 g which has taken as 100 wt. %.

For 0.3M pyrrole solution, 0.36 g (wt.10%) of sodium metavanadate (NaVO_3) was added and mixed thoroughly. Further 0.06 M ammonium persulphate was continuously added drop-wise with the help of a burette to the above solution to get PPy/ NaVO_3 (wt. 10%) composite. Similarly, for 20, 30, 40 and 50 wt. %, 0.72 g, 1.08 g, 1.44 g and 1.8 g of NaVO_3 [Sisco Research Lab Ltd.] powder [8] is taken and the above procedure is followed to get PPy/ NaVO_3 composites. The pure PPy and PPy/ NaVO_3 powder was pressed in the form of pellets of 1 cm diameter using hydraulic press. The conducting silver paste was applied to the pellets of synthesized composites to act as electrodes. The A.C. conductivity of the synthesized composites was measured in the frequency range from 10 Hz to 10^7 Hz.

B. Characterization

The SEM [6-12] images of the pure PPy, PPy/ NaVO_3 (wt. 50%) composite and NaVO_3 were recorded using Scanning Electron Microscope (Jeol 6390LV). The FTIR [6-7, 10-12] spectra of were recorded on FTIR (Thermo Nicolet Avatar 370) spectrometer in

KBr medium at room temperature. The XRD patterns were recorded on X-ray Diffractometer (Bruker AXS D8 Advance) [6-11] using Cu k_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range 20° – 80° . Thermal analysis studies/testing were done in the heat range from 40°C to 740°C at $10^{\circ}\text{C}/\text{min}$ for the pure PPy PPY/NaVO₃ (wt. 50%) composite and NaVO₃ using Thermal Analysis System (TG/DTA) (Perkin Elmer Diamond TG/DTA).

III. RESULT AND DISCUSSION

A. SEM Analysis

Figure 1.a represents the SEM micrograph of pure PPy. The figure represents the size and spherical nature of PPy particles. The elongated chain pattern of the polypyrrole particles was observed. Two particles sizes were measured as 162.21 nm and 176.37 nm. Figure 1.b represents the SEM micrograph of the PPY/NaVO₃ (wt. 50%) composite. Here, particle size was increased and measured as 213.33 nm and 253.33 nm. The SEM micrograph shown that, the NaVO₃ particles were embedded uniformly in PPy chain to form multiple phases, presumably because of weak inter-particle interactions. The SEM micrograph of NaVO₃ in Figure 1.c has shown semi-crystalline nature [6-12].

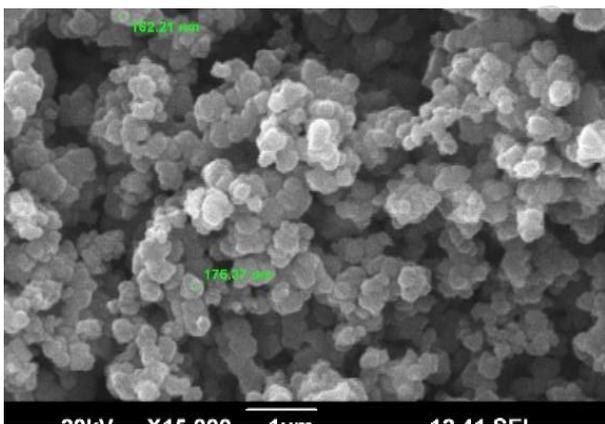


Figure 1.a SEM micrograph of the pure PPy

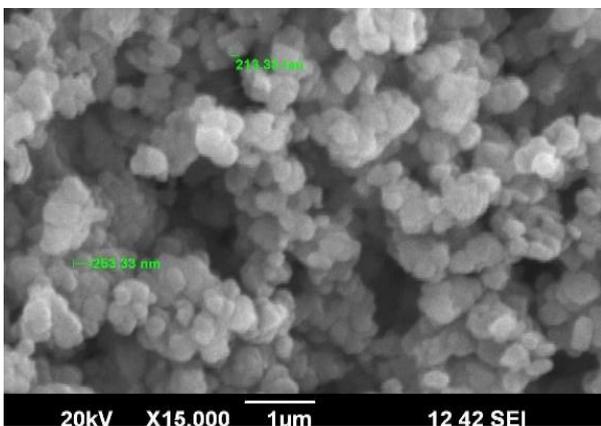


Figure 1.b SEM micrograph of the PPY/NaVO₃(wt. 50%) composite

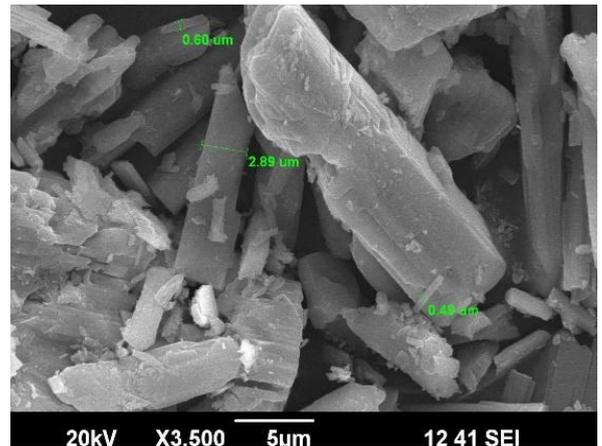


Figure 1.c SEM micrograph of the NaVO₃

B. FTIR Analysis

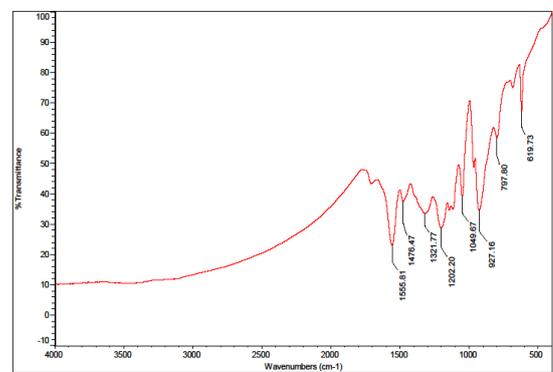


Figure 2.a FTIR spectrum of the pure PPy

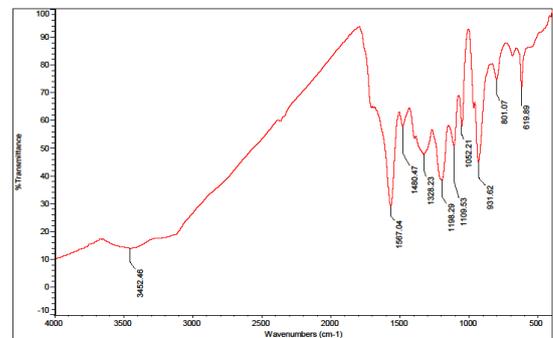


Figure 2.b FTIR spectrum of the PPY/NaVO₃(wt. 50%) composite

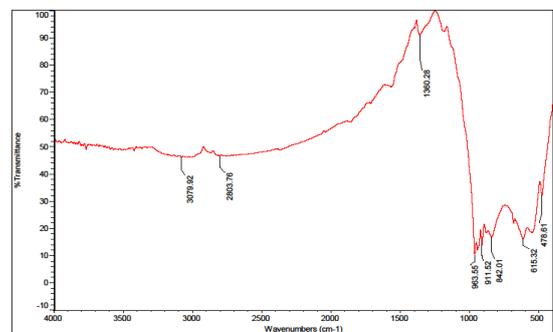


Figure 2.c FTIR spectrum of the NaVO₃

Figures 2.a, 2.b and 2.c were shown the FTIR spectra of pure PPy, PPY/NaVO₃ (wt. 50%) composite

and NaVO_3 . Characteristic frequencies were observed at 1555.81 cm^{-1} , 1476.47 cm^{-1} , 1321.77 cm^{-1} , 1202.20 cm^{-1} , 1049.67 cm^{-1} , 927.16 cm^{-1} , 797.80 cm^{-1} 619.73 cm^{-1} for pure PPy. And characteristic frequencies were observed at 1567.04 cm^{-1} , 1480.47 cm^{-1} , 1328.23 cm^{-1} , 1198.23 cm^{-1} , 1109.53 cm^{-1} , 1052.21 cm^{-1} , 931.62 cm^{-1} , 801.07 cm^{-1} & 619.89 cm^{-1} for PPy/ NaVO_3 (wt. 50%) composite and 1518.81 cm^{-1} , 1360.28 cm^{-1} , 1049.67 cm^{-1} , 963.55 cm^{-1} , 911.52 cm^{-1} , 842.01 cm^{-1} & 615.32 cm^{-1} for NaVO_3 respectively may be attributed due to the presence of C = N stretching, N – H bending deformation, C – N stretching and C – H bending deformation frequencies. The stretching frequencies were shifted towards higher frequency side when pure PPy was compared with PPy/ NaVO_3 (wt. 50%) composite. This indicates that, there is homogeneous distribution of NaVO_3 particles in the polymeric chain due to the Van der Waals interaction between polypyrrole chain and NaVO_3 [6-7, 10-14].

C. XRD Analysis

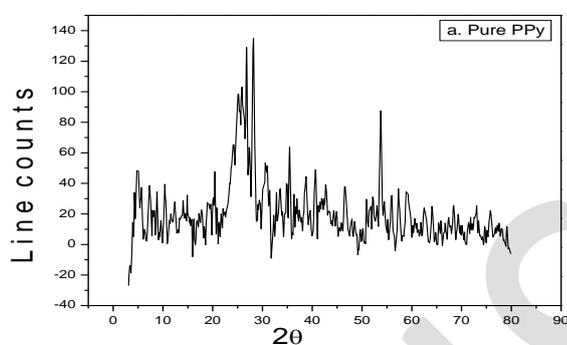


Figure 3.a XRD pattern of the pure PPy

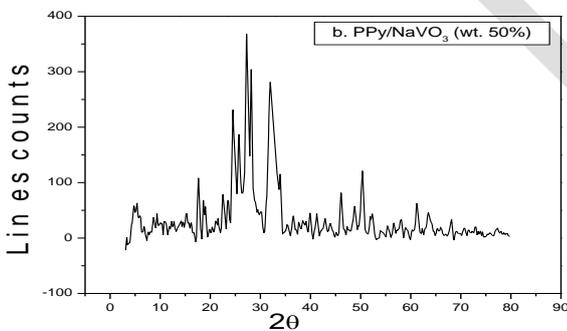


Figure 3.b XRD pattern of the PPy/ NaVO_3 (wt. 50%) composite

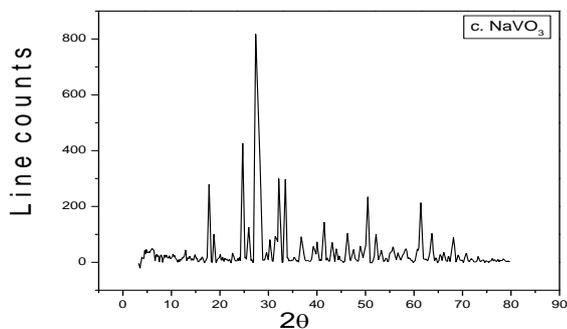


Figure 3.c XRD pattern of the NaVO_3

The Figure 3.a represents the XRD pattern of pure PPy. This has a broad peak at about $2\theta=25^\circ$, shown a characteristic peak of amorphous PPy. The XRD pattern of PPy/ NaVO_3 (50 wt. %) composite shown in the Figure 3.b. The characteristic peaks were indexed by lattice parameter values. The main peaks were observed with 2θ at 17.6° , 22.53° , 24.53° , 25.72° , 27.21° , 28.18° , 31.93° , 33.9° , 46.09° , 48.78° and 50.36° with respect to inter-planar spacing (d) 5.03 \AA , 3.94 \AA , 3.62 \AA , 3.46 \AA , 3.27 \AA , 3.16 \AA , 2.8 \AA , 2.64 \AA , 1.96 \AA , 1.86 \AA and 1.81 \AA respectively. Careful analysis of the XRD of the PPy/ NaVO_3 (50 wt. %) composite suggests that, it exhibits semi-crystalline behavior. The Figure 3.c represents the XRD pattern of the NaVO_3 revealing the semi-crystalline nature [6-11].

a. TG/DTA Analysis

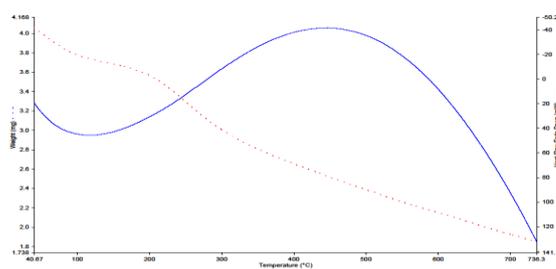


Figure 4.a TG/DTA thermograph of the pure PPy

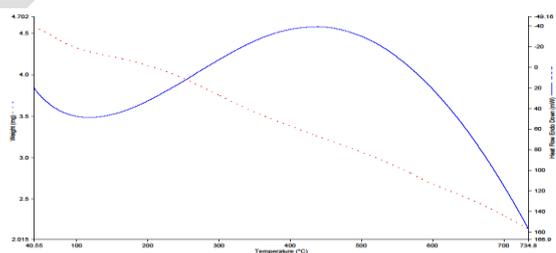


Figure 4.b TG/DTA thermograph of the PPy/ NaVO_3 (wt. 50%) composite

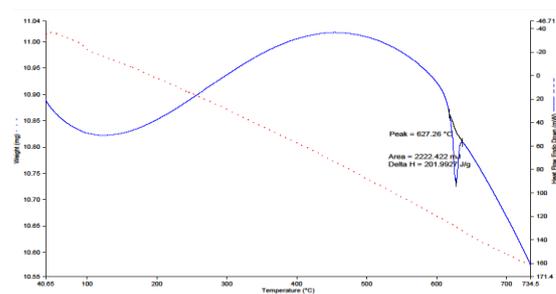


Figure 4.c TG/DTA thermograph of the NaVO_3

The most important and reliable factor in the study of heat stable polymers is the measurement or evaluation of thermal stability. Thermal properties and interaction between the polymers can also be noted from the oxidative degradation curves through thermogravimetric analysis (TG/DTA) studies. DTA is most commonly used to determine transition temperatures such as glass transitions, melting cross-linking reactions and decomposition. However, it measures only the total heat flow and the sum of all thermal transitions in the sample.

The representative TG/DTA curves for pure PPy, PPy/NaVO₃ (wt. 50%) composite NaVO₃ are shown in Figures 4.a-4.c respectively. The residual weights (γ_c) of the pure PPy, PPy/NaVO₃ (wt. 50%) composite and NaVO₃ were reported at 736.3 °C, 734.8°C and 734.5°C respectively. The materials have been heated from 40 °C to 740 °C under a constant heating rate of 10 °C/min and in the inert atmosphere of nitrogen gas. Variation of weight is almost linear and the maximum polymer decomposition temperature is there from 40 °C to 740 °C for all. In the Figure 4.a, two major weight loss stages for PPy were observed at 110 °C to 130°C and 736.3°C. In the Figure 4.b, two major weight loss stages for PPy/NaVO₃ were observed at 120°C to 140°C and 734.8°C. And in the Figure 4.c, three major weight loss stages for PPy/NaVO₃ were observed at 120°C to 140°C, 625.26 °C and 734.5 °C.

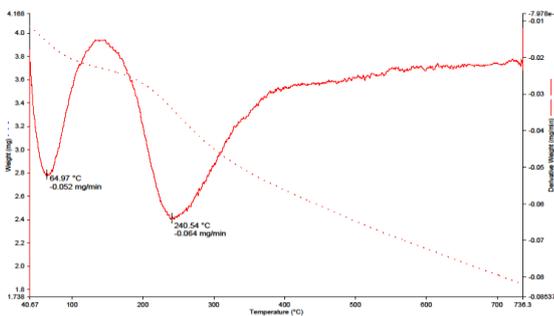


Figure 5.a TG/DTA thermograph of the pure PPy

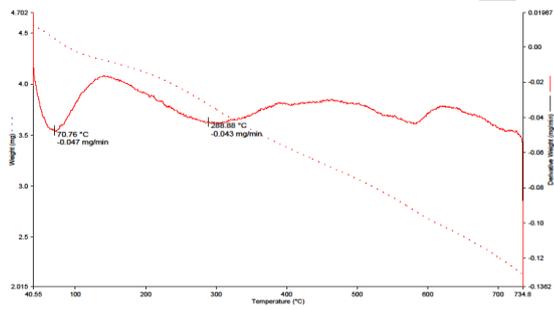


Figure 5.b TG/DTA thermograph of the PPy/NaVO₃ (wt. 50%) composite

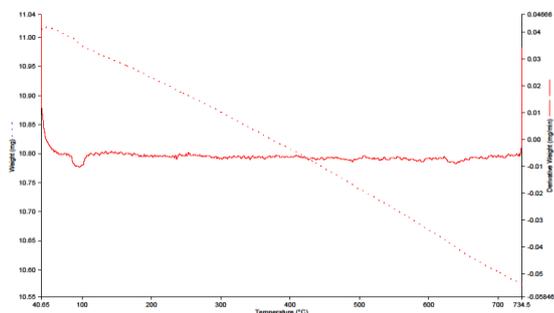


Figure 5.c TG/DTA thermograph of the NaVO₃

Derivative weight (mg/min) versus temperature is shown in Figures 5.a-5.c for the pure PPy, PPy/NaVO₃ (wt. 50%) composite and NaVO₃ respectively. For pure PPy, 0.052 mg/min is decomposed at 64.97 °C mg/min and 0.064 mg/min is decomposed at 240.54 °C with

respect to total weight of the sample i.e. 4.057 mg. For PPy/NaVO₃ (wt. 50%) composite, 0.047 mg/min is decomposed at 70.76 °C mg/min and 0.043 mg/min is decomposed at 288.88 °C with respect to total weight of the sample i.e. 4.580 mg. It is found that, the weight loss caused by the volatilization of the small molecules in PPy/NaVO₃ (wt. 50%) composite at different temperatures is slow compared to that of pure PPy and indicates its higher stability, which clearly proves that NaVO₃ was inserted into the PPy to form composite and has increased the thermal stability of the composite material [15-23].

b. A.C. Conductivity Study

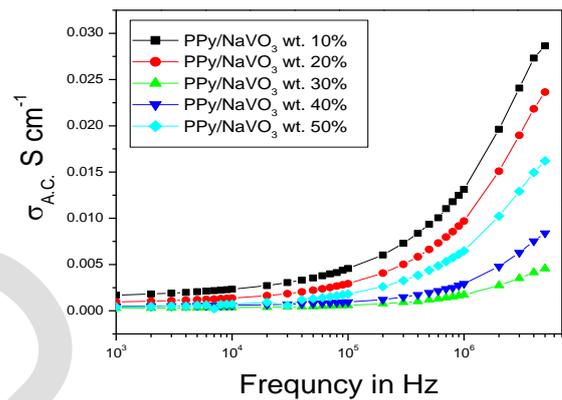


Figure 6.a Variation of A.C. conductivity as a function of frequency for PPy/NaVO₃ composites

The variation of A.C. conductivity as a function of frequency for PPy/NaVO₃ composites is shown in Figure 6.a. It is observed that, the conductivity increases with frequency showing multiple phases of conductivity. It can also be seen that, the value of conductivity increases for 30 wt. % of NaVO₃ in polypyrrole. This may be due to the extended chain length of polypyrrole which facilitate the hopping of charge carriers when the content of NaVO₃ is increased up to 30 wt. %. Further the conductivity decreases for 50 wt. % composite. The increase in conductivity for 30 wt. % may be due to the variation in the distribution of NaVO₃ particles which may support more number of charge carriers to hop between favorable localized sites causing increase in conductivity.

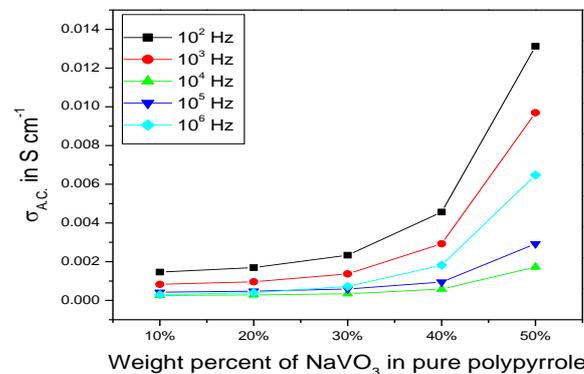


Figure 6.b Variation of A.C. conductivity as a function of wt. % of NaVO₃ in pure PPy

The variation of A.C. conductivity as a function of the wt. % of NaVO₃ in the pure PPy at different frequencies is shown in Figure 6.b. In all the composites, the conductivity increases with respect to the frequency as compared to the pure PPy. The values of the conductivity increase up to 50 wt. % of NaVO₃ in PPy. This percent weight is the percolation threshold for these composites. The composites obey percolation theory. This can be attributed due to the distribution of NaVO₃ particles in PPy due to hopping of the charge carriers [9-10, 24-26].

CONCLUSION

The PPy/NaVO₃ composites were synthesized to tailor the transport properties. Detailed characterizations of the composites were carried out using SEM, FTIR, XRD and TG/DTA techniques. The results of A.C. conductivity of PPy/NaVO₃ composites show a strong dependence on the weight percent of NaVO₃ in polypyrrole. PPy/NaVO₃ composites may find applications in sensors.

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