



INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

Synthesis, Characterization and Dielectric Study of Polypyrrole/Sodium Metavanadate (Ceramic) Composites

Sangappa K Ganiger¹, Chaluvvaraju B V² and Murugendrappa M V³

¹Department of Physics, Government Engineering College, Raichur-584134, Karnataka, India

²Department of Physics, Bangalore Institute of Technology, Bangalore-560004, Karnataka, India

³Department of Physics, BMS College of Engineering, Bangalore-560019, Karnataka, India

sangappaganiger1973@gmail.com

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 (NaVO₃) by chemical oxidation method. The PPy/NaVO₃ composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of NaVO₃ in Py. The surface morphologies of these composites were analyzed using Scanning Electron Microscopy (SEM), show that NaVO₃ particles are embedded in PPy chain to form multiple phases. The Fourier Transform Infra-Red Spectroscopy (FTIR) reveals the stretching frequencies are 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 ϵ^1 , ϵ^{11} and tangent loss reveals that, concentration of the NaVO₃ in PPy is responsible for the variation in value of ϵ^1 and ϵ^{11} of the composites. The dimensions of sodium metavanadate particles in the matrix have a greater influence on the ϵ^1 and ϵ^{11} .

Keywords: Polypyrrole; Sodium Metavanadate; Composites; Conductivity; Frequency.

Introduction

The discovery of electrical conductivity in molecular charge transfer promoted the development of conducting polymers. Conducting polymers have been synthesized which show 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 S cm⁻¹ rendering its versatile applications in batteries, electronic devices, functional electrodes, electro-chromic devices, optical switching devices, sensors and so on [1–5].

Experimental Details

Synthesis

The AR grade [Spectro Chem 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 PPy 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 0.3 M pyrrole solution, 0.36 g (wt. 10%) of sodium metavanadate (NaVO₃) 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/NaVO₃ (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 NaVO₃ [Sisco Research Lab Ltd.] powder [8] is

taken and the above procedure is followed to get PPy/NaVO₃ composites. The pure PPy and PPy/NaVO₃ 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 dielectric relative permittivity (ϵ') and dielectric loss (ϵ'') for the dielectric properties of the synthesized composites were measured in the frequency range from 10 Hz to 10⁷ Hz.

Characterization

The SEM [6-12] images of the PPy, PPy/NaVO₃ (wt. 50%) composite and NaVO₃ were recorded using Scanning Electron Microscope (Jeol 6390LV). The FTIR [6-7, 10-12] spectra 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 °C/min for pure PPy, PPy/NaVO₃ (wt. 50%) composite and NaVO₃ using Thermal Analysis System (TG/DTA) (Perkin Elmer Diamond TG/DTA).

Result and Discussion

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. Figure shown that, the NaVO₃ particles were embedded uniformly in PPy chain to form multiple phases, presumably because of weak inter-particle interactions. SEM micrograph of NaVO₃ in Figure 1.c shown semi crystalline nature [6-12].

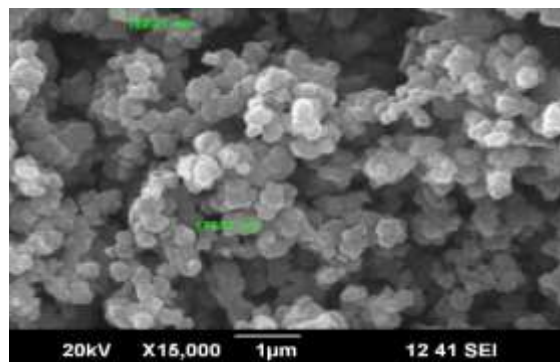


Figure 1.a SEM micrograph of the pure PPy

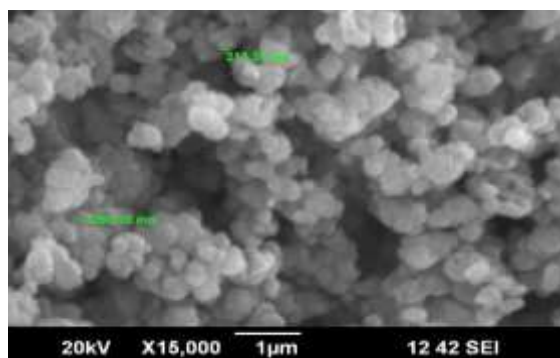


Figure 1.b SEM micrograph of the PPy/NaVO₃ (wt. 50%) composite

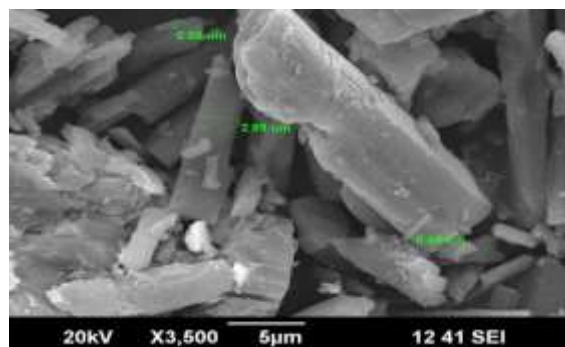


Figure 1.c SEM micrograph of the NaVO₃

FTIR Analysis

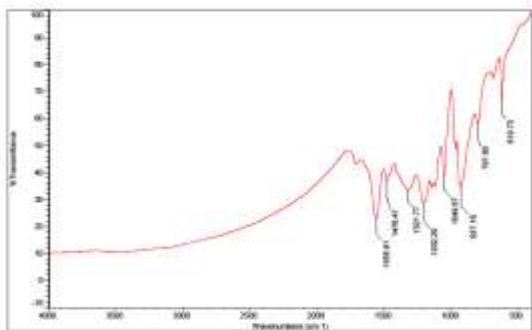


Figure 2.a FTIR spectrum of the pure PPY

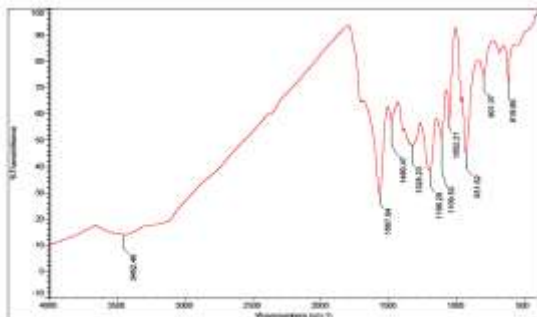


Figure 2.b FTIR spectrum of the PPy/NaVO₃ (wt. 50%) composite

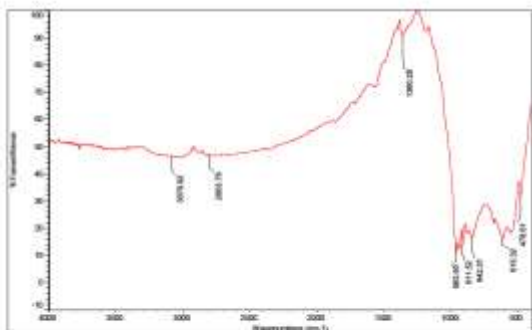


Figure 2.c FTIR spectrum of the NaVO₃

Figures 2.a, 2.b and 2.c were shown the FTIR spectra of pure PPy, PPy/NaVO₃ (wt. 50%) composite and NaVO₃. 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/NaVO₃ (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 NaVO₃ 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 lower frequency side when pure PPy was compared with PPy/NaVO₃ (wt. 50%) composite. This indicates that, there is homogeneous distribution of the NaVO₃ particles in the polymeric chain due to the Van der Waals interaction between polypyrrole chain and NaVO₃ [6-7, 10-14].

XRD Analysis

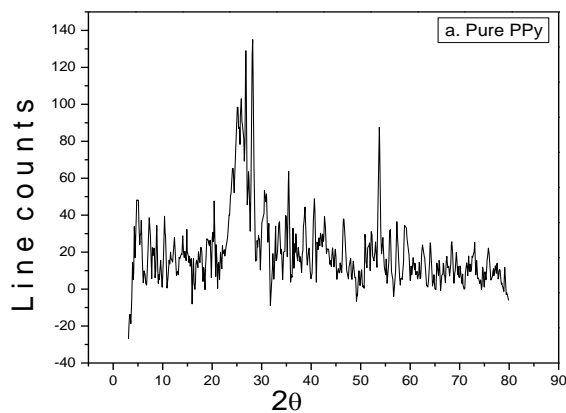


Figure 3.a XRD pattern of the pure PPY

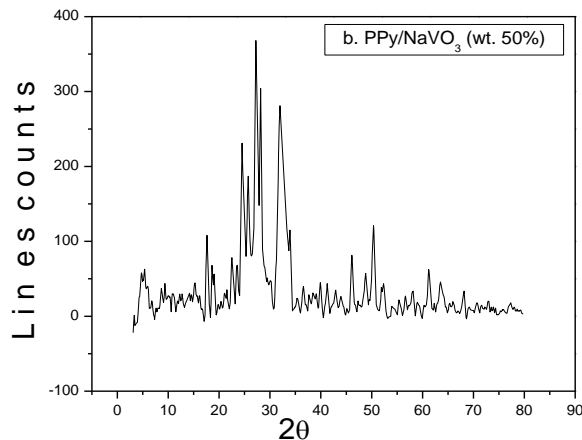


Figure 3.b XRD pattern of the PPy/NaVO₃ (wt. 50%) composite

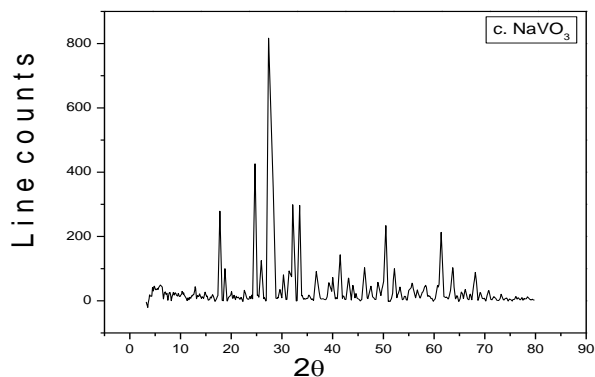


Figure 3.c XRD pattern of the NaVO₃

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/NaVO₃ (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 Å, 3.94 Å, 3.62 Å, 3.46 Å, 3.27 Å, 3.16 Å, 2.8 Å, 2.64 Å, 1.96 Å, 1.86 Å and 1.81 Å respectively. Careful analysis of the XRD of the PPy/NaVO₃ (50 wt. %) composite suggests that, it exhibits semi-crystalline behavior. The Figure 3.c represents the XRD pattern of the NaVO₃ revealing the semi-crystalline nature [6-11].

TGA/DTA Analysis

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 thermo-gravimetric 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

$^\circ\text{C}/\text{min}$ 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 .

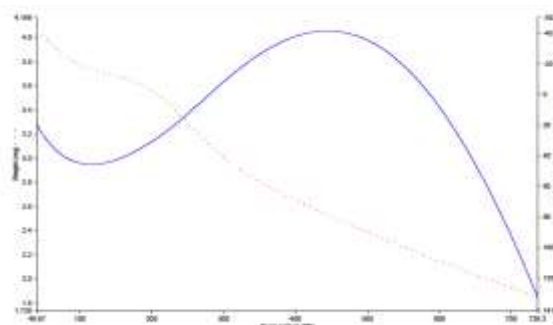


Figure 4.a Thermograph of the pure PPy

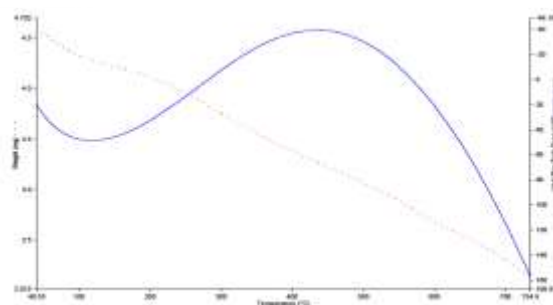


Figure 4.b Thermograph of PPy/NaVO₃ (wt. 50%) composite

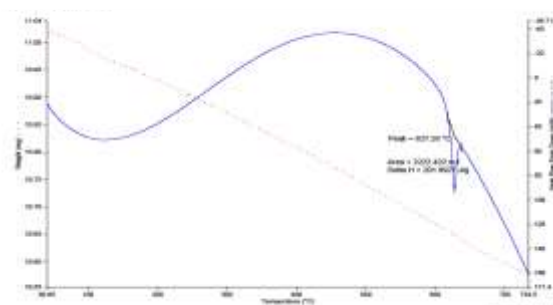


Figure 4.c Thermograph of the NaVO₃

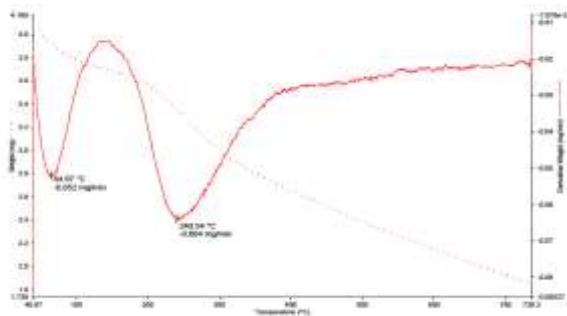


Figure 5.a Thermograph of the pure PPY

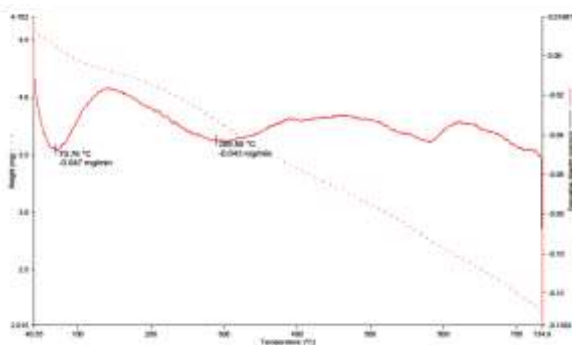


Figure 5.b Thermograph of the PPy/NaVO₃ (wt. 50%) composite

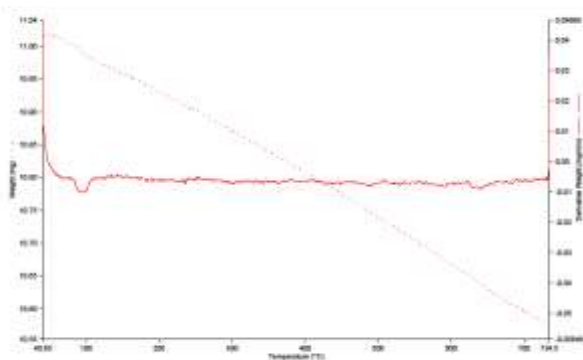


Figure 5.c Thermograph of the NaVO₃

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].

Dielectric Property Study

The variation of the dielectric relative permittivity (ϵ^1) as a function of frequency and variation of ϵ^1 as a function of wt. % of PPy/NaVO₃ composites for pure PPy and PPy/NaVO₃ composites decreases with the increasing of frequency were shown in the Figures 6.a and 6.b respectively. This may be attributed to the tendency of dipoles in polymeric samples to orient themselves in the direction of the applied field. However, the decreasing trend seems not too sharp as compared for lower frequency region at the high frequency range (10^4 Hz to 10^6 Hz). This trend is observed for all graphs for different concentration of dopants. It could be explained by dipoles orientation, which difficult to rotate at high frequency range. On the other hand, the high value of ϵ^1 at low frequency might be due to the electrode effect and interfacial effect of the sample [24-26]. The variation of dielectric loss (ϵ^{11}) with frequency and variation of ϵ^{11} as a function of wt. % of PPy/NaVO₃ composites for the PPy and PPy/NaVO₃ composites decreases with the increasing of frequency were shown in the Figure 7.a and 7.b respectively. It is clear from the graph that, the dielectric loss decreases with frequency. The larger value of loss factor or dielectric loss at low frequency could be due to the mobile charges within the polymer backbone. The higher value of the dielectric loss for the higher concentration of dopant can be understood in terms of electrical conductivity, which is associated with the dielectric loss. On the other hand, the mobile charges i.e. polarons that belong to conducting PPy and free ions that come from ammonium persulphate increase at higher concentration of the dopant thus also influence lower value of ϵ^{11} at high frequency. Moreover, the NaVO₃ exhibits flexible polar side groups with polar bond as the bond rotating having intense dielectric α -transition. Thus, there is a change in the chemical composition of the polymer repeated unit due to the formation of hydrogen bonds with hydroxyl groups in

the polymerization process, which in turn makes the polymer chain flexible and hence, enhances the electrical conductivity [25-27].

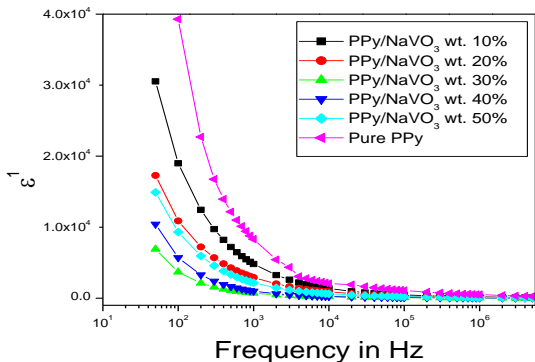


Figure 6.a Variation of ϵ^1 as a function of frequency for the PPy and PPy/NaVO₃ composites

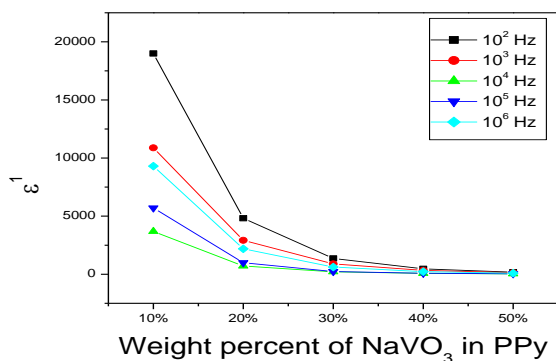


Figure 6.b Variation of ϵ^1 as a function of wt. % of PPy/NaVO₃ composites

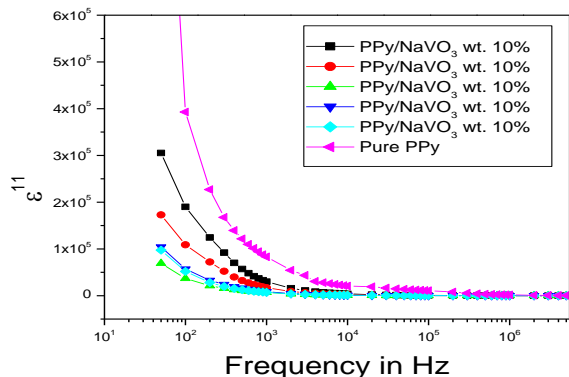


Figure 7.a Variation of ϵ^{11} as a function of frequency for PPy and PPy/NaVO₃ composites

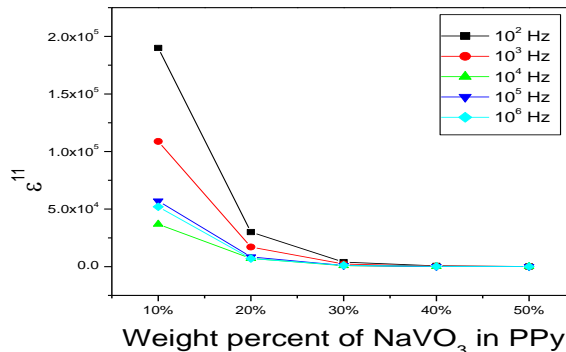


Figure 7.b Variation of ϵ^{11} as a function of wt. % of PPy/NaVO₃ composites

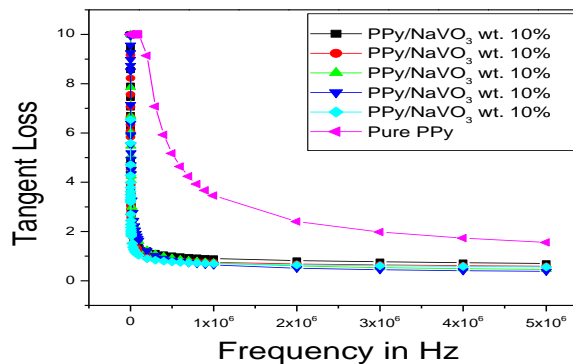


Figure 8 Variation of tangent loss as a function of frequency for the PPy and PPy/NaVO₃ composites

The Figure 8 is shown the variation of tangent loss as a function of frequency for the PPy and PPy/NaVO₃ composites. One can conclude that with the increasing amount of the dopant, the tangent loss (δ) is relatively reduced although it does not change for the whole samples as it is might be due to intrinsic behavior of the sample. These results confirm the explanation for the dielectric relative permittivity (ϵ^1) and dielectric loss (ϵ^{11}) characteristics as tangent loss (δ) decreases with the increasing composition of the dopant [20, 24-28].

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 dielectric relative permittivity (ϵ^1) and dielectric loss (ϵ^{11}) of PPy/NaVO₃ composites show a strong dependence on the weight percent of NaVO₃

in polypyrrole. PPy/NaVO₃ composites may find applications in sensors.

Acknowledgement

The authors would like to acknowledge The Principal, BMSCE, BMSET, Bangalore-560019 for their cooperation and help. The author¹ thank to wife and children for cooperation. FTIR, TGA, SEM and XRD analysis of the samples were carried out at Sophisticated Analytical Instruments Facility (SAIF) of Cochin University of Science And Technology, Cochin, India.

References

1. A Terje Skotheim and R John Reynolds, *Handbook of Conducting Polymers Third Edition Conjugated Polymers*, (CRC Press Inc., USA, 2006)
2. Mohd Hamzah Harun, Elias Saion, Anuar Kassim, Noorhana Yahya and Ekramul Mahmud, *JASA* 2, 63, (2007)
3. György Inzelt, *J. Solid State Electrochem.* 15, 1711 (2011)
4. R Struëmpfer and J Glatz-reichenbach, *J of Electro-ceramics*, 3:4, 329-346, 1999
5. A K Bhakshi, *Bull. Mater. Sci.*, Vol. 18, No. 5, September 1995, pp. 469-495
6. Reza Ansari, *E-Journal of Chemistry*, 3, 186, (2006)
7. V K Gade, D J Shirale, P D Gaikwad, K P Kakde, P A Savale, H J Kharat, B H Pawar and M D Shirsat, *Int. J. Electrochem. Sci.*, 270 (2007)
8. M V Murugendrappa and M V N Ambika Prasad, *J. App. Poly. Sci.*, 103, 2797 (2007)
9. T K Vishnuvardhan, V R Kulkarni, C Basavaraja and S C Raghavendra, *Bull. Mater. Sci.*, 29(1), 77, (2006)
10. M V Murugendrappa, Syed Khasim and M V N Ambika Prasad, *Bull. Mater. Sci.*, 28(6), 565 (2005)
11. Himanshu Narayan, Angela M Montano, Monica L Hernandez, July A Hernandez, Claudia P Gonzalez and Cesar A Ortiz, *J. Mater. Environ. Sci.*, 3(1), 137 (2012)
12. Qunwei Tang, Xiaoming Sun, Qinghua Li, Jianming Lin and Jihuai Wu, *J. Mater. Sci.*, 44, 849 (2009)
13. Qingzhi Luo, Xueyan Li, Desong Wang, Yanhong Wang and Jing An, *J. Mater. Sci.* 46, 1646, (2011)
14. Lunhong Ai and J. Jiang, *J. Mater. Sci.: Mater. Electron.*, 21, 410 (2010)
15. S Hossein Hosseini and A Ali Entezami, *Iranian Polymer Journal*, 14(3), 201 (2005)
16. Nakamura O, Ogino I and Kodama T, *Solid State Ionics*, 3-4, 347 (1981)
17. Doyle CD, *Anal Chem*, 3, 77 (1961)
18. Juan C Apesteguy and Silvia E Jacobo, *J. Mater. Sci.*, 42, 7062 (2007)
19. Mohammad Sideeq Rather, Kowsar Majid, Ravinder Kumar Wanchoo and Madan Lal Singla, *J. Therm. Anal Calorim.*, 112, 893 (2013)
20. S Anoop Kumar, Avanish Pratap Singh, Parveen Saini, Fehmeeda Khatoon and S Dhawan, *J. Mater. Sci.*, 47, 2461 (2012)
21. Nikola Perinka, Marketa Drzkova, Milena Hajna and Bohumil Jasurek, *J. Therm. Anal Calorim.*, 116, 589 (2014)
22. Zihang Huang, Shaoxu Wang, Hui Li, Shihui Zhang and Zhicheng Tan, *J. Therm. Anal Calorim.*, 115, 259 (2014)
23. Samrana Kazim, Shahzada Ahmad, Jiri Pflieger, Josef Plestil and Yogesh M Joshi, *J. Mater. Sci.*, 47, 420 (2012)
24. Dutta P, Biswas S and De S K, *Materials Research Bulletin*, 37 (2002)
25. Mohd Hamzah Harun, Elias Saion, Anuar Kassim, Ekramul Mahmud, Muhd Yousuf Hussain, and Iskandar Shahrim Mustafa, *J. For The Advancement OF Science & Arts*, 1(1), 9 (2009)
26. Havriliak S and S Negami, *Polymer*, 8, 161 (1967)
27. Singh K P and Gupta P N, *European Polymer Journal*, 34, 1023 (1998)
28. M L Singla, Rajeev Sehrawat, Nidhi Rana and Kulvir Singh, *J. Nanopart Res.*, 13, 2109 (2011)