

Synthesis, Characterization and Dielectric Property Study of Polypyrrole/Strontium Arsenate (Ceramic) Composites

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Abstract- In-situ polymerization of pyrrole (Py) was carried out with strontium arsenate (ceramic) in the presence of oxidizing agent ammonium persulphate to synthesize polypyrrole (PPy)/ strontium arsenate [Sr₃(AsO₄)₂] by chemical oxidation method. The PPy/Sr₃(AsO₄)₂ composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of Sr₃(AsO₄)₂ in Py. The surface morphologies of these composites were analyzed using Scanning Electron Microscopy (SEM) show that Sr₃(AsO₄)₂ particles were 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. Thermograph of thermal analysis (TG/DTA) were shown that, the PPy/Sr₃(AsO₄)₂ composites have stronger stability than PPy. The frequency dependent ϵ^1 , ϵ^{11} and tangent loss reveals that, concentration of the Sr₃(AsO₄)₂ in PPy is responsible for the variation in value of ϵ^1 and ϵ^{11} of the composites. The dimensions of Sr₃(AsO₄)₂ particles in the matrix have a greater influence on the ϵ^1 and ϵ^{11} .

Key words: Polypyrrole; Strontium arsenate; 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 polymers. 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].

II. EXPERIMENTAL DETAILS

A. 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 5 °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 0.3 M pyrrole solution, 0.36 g (wt. 10%) of Strontium arsenate [Sr₃(AsO₄)₂] 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/Sr₃(AsO₄)₂ (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 Sr₃(AsO₄)₂ [Sisco Research Lab Ltd.] powder [8] is taken and the above procedure is followed to get PPy/ Sr₃(AsO₄)₂ composites. The pure PPy and PPy/Sr₃(AsO₄)₂ 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 10¹ Hz to 10⁷ Hz.

B. Characterization

The SEM [6-12] images of the pure PPy, PPy/Sr₃(AsO₄)₂ (wt. 50%) composite and Sr₃(AsO₄)₂ 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 2 θ range 20°-80°. Thermal analysis studies/testing were done in the heat range from 40 °C to 740 °C at 10 °C/min for the pure PPy, PPy/Sr₃(AsO₄)₂ (wt. 50%)

composite and $Sr_3(AsO_4)_2$ using Thermal Analysis System (TG/DTA) (Perkin Elmer Diamond TG/DTA).

III.RESULT AND DISCUSSION

A. SEM Analysis

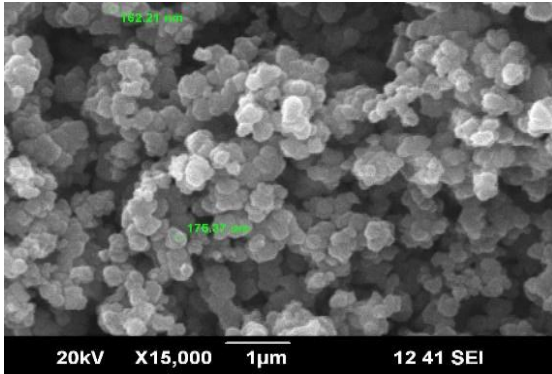


Figure 1.a SEM micrograph of the pure PPy

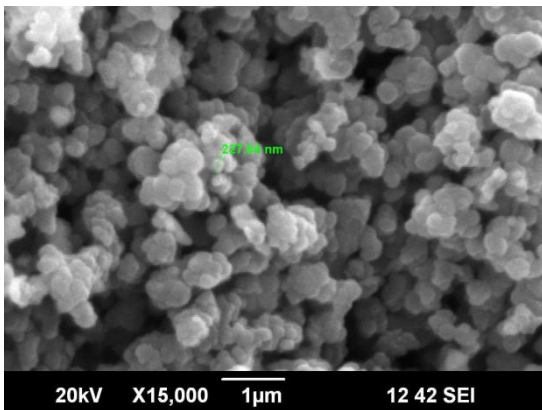


Figure 1.b SEM micrograph of the PPy/ $Sr_3(AsO_4)_2$ (wt. 50%) Composite

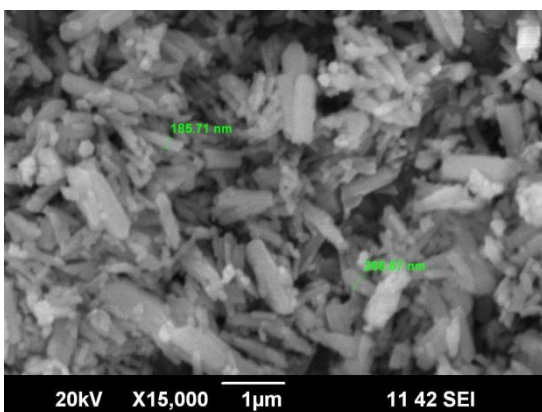


Figure 1.c SEM micrograph of the $Sr_3(AsO_4)_2$

Figure 1.a represents the SEM micrograph of pure PPy. The figure represents the size and spherical nature of PPy particles. The SEM micrograph is shown a characteristic peak of amorphous polypyrrole. 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/ $Sr_3(AsO_4)_2$ (wt. 50%) composite and shown semi-crystalline nature. Here, particle size was increased and measured as 227.84 nm. These show that, the $Sr_3(AsO_4)_2$ particles were embedded uniformly in PPy chain to form multiple phases, presumably because of weak inter-particle interactions. The SEM micrograph of $Sr_3(AsO_4)_2$ is shown in Figure 1.c and $Sr_3(AsO_4)_2$ has semi-crystalline nature [6-12].

B. FTIR Analysis

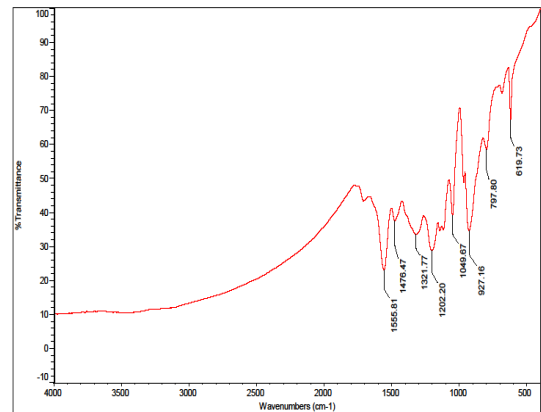


Figure 2.a FTIR spectrum of the pure PPy

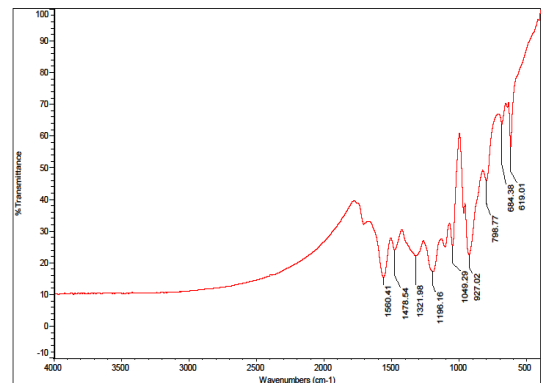


Figure 2.b FTIR spectrum of the PPy/ $Sr_3(AsO_4)_2$ (wt. 50%) composite

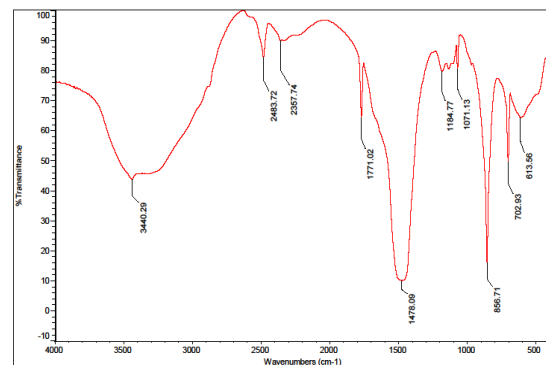


Figure 2.c FTIR spectrum of the $Sr_3(AsO_4)_2$

The Figures 2.a, 2.b and 2.c were shown the FTIR spectra of pure PPy, PPy/ $Sr_3(AsO_4)_2$ (wt. 50%) composite and $Sr_3(AsO_4)_2$. Characteristic frequencies

were observed at 1555 cm^{-1} , 1476 cm^{-1} , 1321 cm^{-1} , 1202 cm^{-1} , 1049 cm^{-1} , 927 cm^{-1} , 797 cm^{-1} and 619 cm^{-1} for pure PPy. And characteristic frequencies were observed at 1560 cm^{-1} , 1478 cm^{-1} , 1321 cm^{-1} , 1196 cm^{-1} , 1049 cm^{-1} , 927 cm^{-1} , 798 cm^{-1} , 684 cm^{-1} & 619 cm^{-1} for PPy/ $\text{Sr}_3(\text{AsO}_4)_2$ (wt. 50%) composite and 3040, 2483, 2357, 1771, 1478 cm^{-1} , 1184 cm^{-1} , 1071 cm^{-1} , 856 cm^{-1} , 702 cm^{-1} & 613 cm^{-1} for $\text{Sr}_3(\text{AsO}_4)_2$ 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/ $\text{Sr}_3(\text{AsO}_4)_2$ (wt. 50%) composite. This indicates that, there is homogeneous distribution of $\text{Sr}_3(\text{AsO}_4)_2$ particles in the polymeric chain due to the Van der Walls interaction between polypyrrole chain and $\text{Sr}_3(\text{AsO}_4)_2$ [6-7, 10-14].

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/ $\text{Sr}_3(\text{AsO}_4)_2$ (wt. 50%) composite shown in the Figure 3.b. The characteristic peaks were indexed by lattice parameter values. The main peaks were observed with 2θ at 20.9°, 23.3°, 24.8°, 26.72°, 29.7°, 32.4°, 36°, 43.9°, 57.2° and 62.5° with respect to inter-planar spacing (d) 4.2 Å, 3.8 Å, 3.5 Å, 3.32 Å, 3 Å, 2.7 Å, 2.4 Å, 2 Å, 1.6 Å, and 1.4 Å respectively. Careful analysis of the XRD of the PPy/ $\text{Sr}_3(\text{AsO}_4)_2$ (wt. 50%) composite suggests that, it exhibits semi-crystalline behavior. The Figure 3.c represents the XRD pattern of the strontium arsenate [$\text{Sr}_3(\text{AsO}_4)_2$] revealing the semi-crystalline nature [6-11].

D.TG/DTA Analysis

C. XRD Analysis

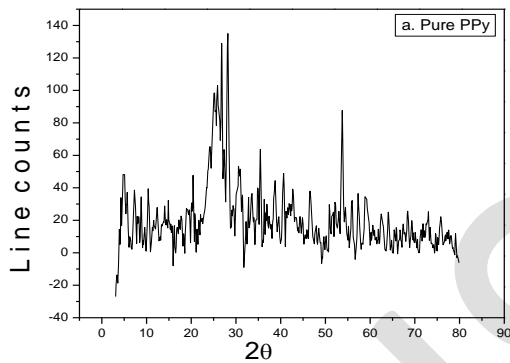


Figure 3.a XRD pattern of the pure PPy

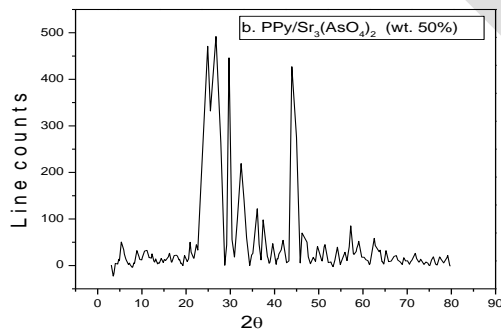


Figure 3.b XRD pattern of the PPy/ $\text{Sr}_3(\text{AsO}_4)_2$ (wt. 50%) composite

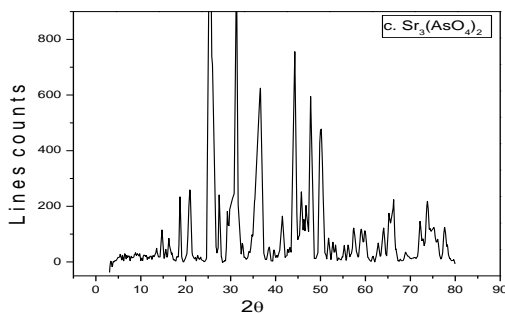


Figure 3.c XRD pattern of the $\text{Sr}_3(\text{AsO}_4)_2$

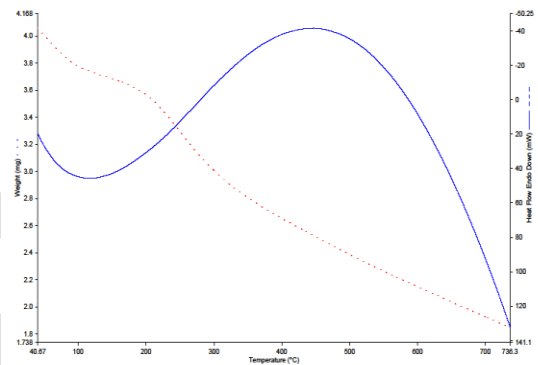


Figure 4.a TG/DTA thermograph of the pure PPy

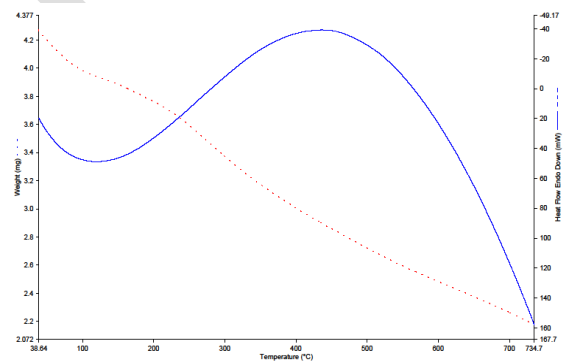


Figure 4.b TG/DTA thermograph of the PPy/ $\text{Sr}_3(\text{AsO}_4)_2$ (wt. 50%) composite

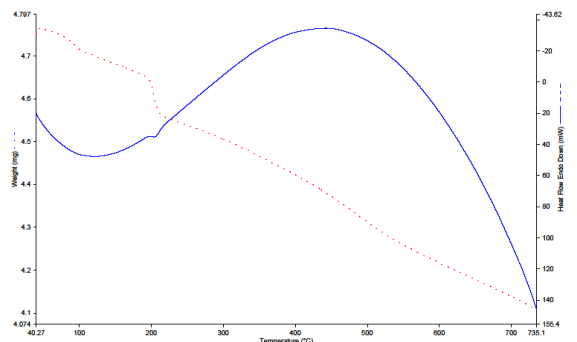


Figure 4.c TG/DTA thermograph of the $\text{Sr}_3(\text{AsO}_4)_2$

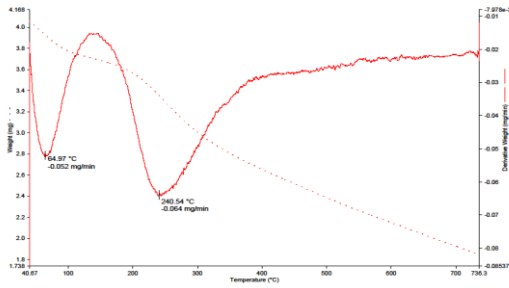


Figure 5.a TG/DTA thermograph of the pure PPy

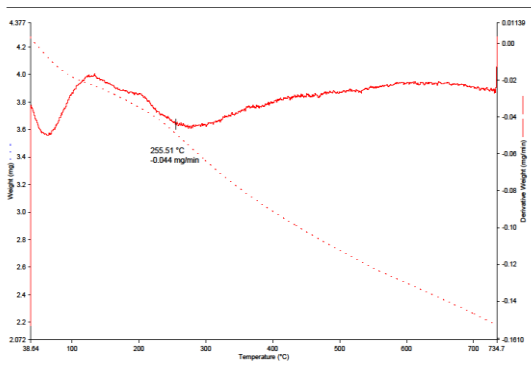


Figure 5.b TG/DTA thermograph of the PPy/Sr₃(AsO₄)₂ (wt. 50%) composite

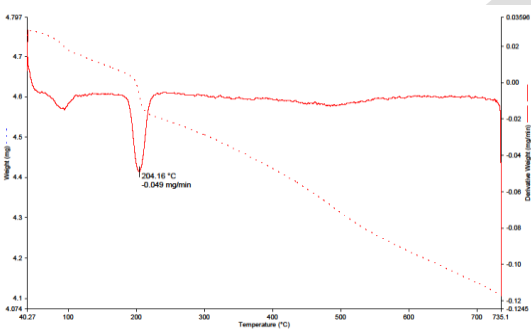


Figure 5.c TG/DTA thermograph of the Sr₃(AsO₄)₂

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/Sr₃(AsO₄)₂ (wt. 50%) composite and Sr₃(AsO₄)₂ are shown in Figures 4.a-4.c respectively. The samples were heated from 40 °C to 740 °C under a constant heating rate of 10 °C/min and in the inert atmosphere of nitrogen gas. The residual weights (γ_c) of the pure PPy, PPy/Sr₃(AsO₄)₂ (wt. 50%) composite and Sr₃(AsO₄)₂ were reported at 736.3 °C, 734.7 °C and 735.1 °C respectively. Variation of weight loss 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/Sr₃(AsO₄)₂ were observed at 120 °C to 140 °C, 200 °C and 734.8 °C. And in the Figure 4.c, three major weight loss stages for PPy/Sr₃(AsO₄)₂ were observed at 120 °C to 140 °C, 625.26 °C and 734.5 °C.

Derivative weight (mg/min) versus temperature is shown in Figures 5.a-5.c for the pure PPy, PPy/Sr₃(AsO₄)₂ (wt. 50%) composite and Sr₃(AsO₄)₂ 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/Sr₃(AsO₄)₂ (wt. 50%) composite, 0.044 mg/min is decomposed at 255.51 °C mg/min with respect to total weight of the sample i.e. 4.272 mg. It is found that, the weight loss caused by the volatilization of the small molecules in PPy/Sr₃(AsO₄)₂ (wt. 50%) composite at different temperatures is slow compared to that of pure PPy and indicates its higher stability, which clearly proves that Sr₃(AsO₄)₂ was inserted into the PPy to form composite and has increased the thermal stability of the composite material [15-23].

E. Dielectric Property Study

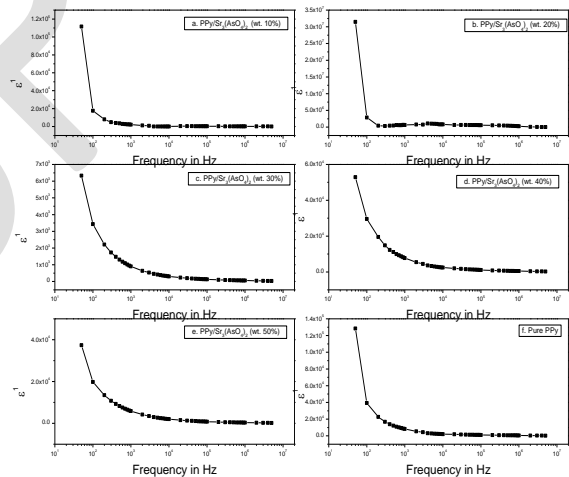


Figure 6.a Variation of ϵ' as a function of frequency for the PPy and PPy/Sr₃(AsO₄)₂ composites

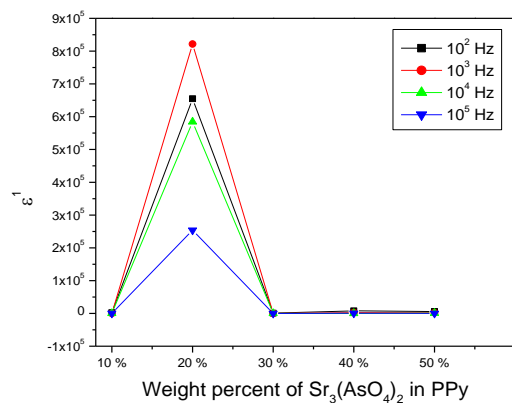


Figure 6.b Variation of ϵ' as a function of wt. % of PPy/ Sr₃(AsO₄)₂ composites

The variation of the dielectric relative permittivity (ϵ^1) as a function of frequency for the pure PPy and PPy/Sr₃(AsO₄)₂ composites decreases with the increasing of frequency were shown in the Figures 6.a. 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 higher frequency region at the high frequency range (10⁴ Hz to 10⁶ 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].

Variation of the dielectric relative permittivity (ϵ^1) is as a function of the wt. % of Sr₃(AsO₄)₂ in the pure PPy at different frequencies is shown in Figure 6.b. The value of the conductivity was increase up to 20 wt. % of Sr₃(AsO₄)₂ in PPy. This weight percent is the percolation threshold for these composites. The composites obey percolation theory. This can be attributed due to the distribution of Sr₃(AsO₄)₂ particles in PPy due to hopping of the charge carriers [9-10, 24-26].

Variation of dielectric loss (ϵ^{11}) with frequency for the PPy and PPy/Sr₃(AsO₄)₂ (wt. 20%) composite decreases with the increasing of the frequency is shown in the Figure 7.a and 7.b respectively. It is clear from the graph that, the dielectric loss decreases with the 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 Sr₃(AsO₄)₂ (wt. 20%) 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].

The Figure 8 is shown the variation of tangent loss as a function of the frequency for the PPy and PPy/Sr₃(AsO₄)₂ 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 the frequency [20, 24-28].

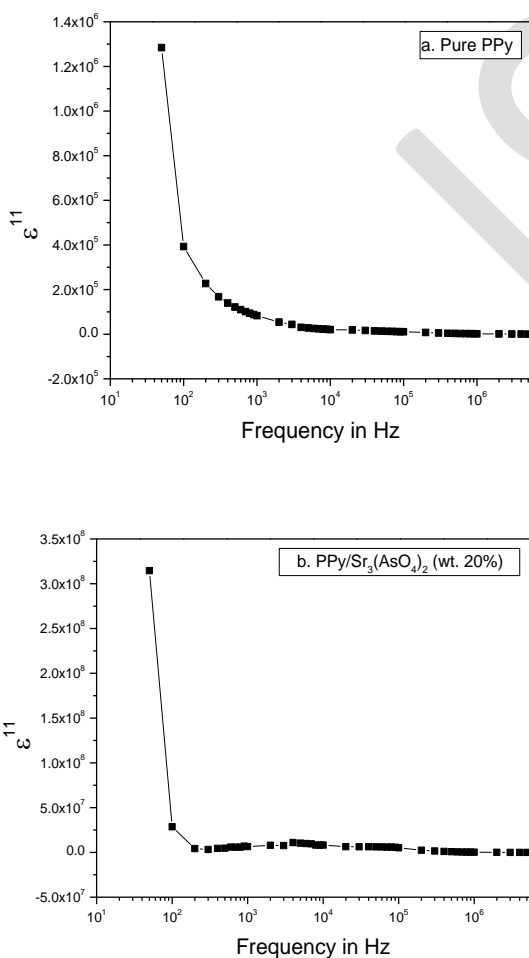


Figure 7.a and 7.b Variation of ϵ^{11} is as a function of frequency for the PPy and PPy/Sr₃(AsO₄)₂ (wt. 20%) composite

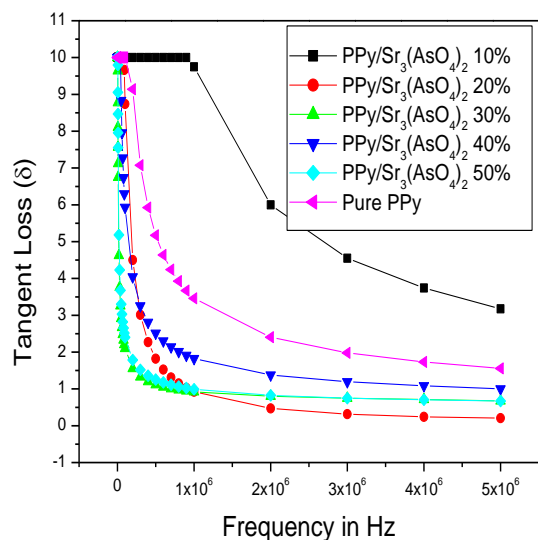


Figure 8 Variation of tangent loss is as a function of frequency for the PPy and PPy/Sr₃(AsO₄)₂ composites

CONCLUSION

The PPy/Sr₃(AsO₄)₂ 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') and dielectric loss (ϵ'') of PPy/Sr₃(AsO₄)₂ composites show a strong dependence on the weight percent of Sr₃(AsO₄)₂ in polypyrrole. PPy/Sr₃(AsO₄)₂ composites may find applications in sensors.

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REFERENCES

- [1] [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 Struèmpel and J Glatz-reichenbach, *J. of Electro-ceramics*, 3(4), 329 (1999)
- [5] A K Bhakshi, *Bull. Mater. Sci.*, 18(5), 469 (1995)
- [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] .Haviliak 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)