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Thermo-Electric Power Study of Polypyrrole/Zirconium Oxide Composites

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Abstract

In-situ polymerization of pyrrole was carried out with zirconium oxide, in the presence of oxidizing agent ammonium persulphate, to synthesize polypyrrole/zirconium oxide composites, by chemical oxidation method. The polypyrrole/zirconium oxide composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of zirconium oxide in pyrrole. The powder X-ray diffraction spectrographs suggest that they exhibit semi-crystalline behavior. Fourier Transform Infra-Red Spectroscopy shows that, the stretching frequencies are shifted towards higher frequency side. The surface morphologies of these composites studied using Scanning Electron Microscopy indicate that zirconium oxide particles are embedded in the polypyrrole (PPy) chain, to form multiple phases. Thermographs of thermal analysis also imply that the polypyrrole/zirconium oxide composites have stronger stability than PPy. The observation of UV-VIS-NIR spectrum is proof of an interaction between polypyrrole/zirconium oxide. The PPy/ZrO₂ composites have exhibited semiconductor behavior for the thermo e. m. f. / See-beck voltage.

Keywords: Polypyrrole; Zirconium Oxide; Composite; Conductivity; Thermo-Electric Power.

Introduction

Polypyrrole (PPy) can be synthesized either chemically or electro-chemically. Polypyrrole is an intrinsic conducting polymer which can be made to have conductivity up to 1000 S cm⁻¹ rendering it versatile for applications in batteries, electronic devices, functional electrodes, electro-chromic devices, optical switching devices, sensors etc. [1–5].

Experimental

Synthesis

AR grade [SpectroChem Pvt. Ltd.] pyrrole [6] was purified by distillation under reduced pressure. 0.3 M pyrrole solution taken in a beaker 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 carried on for 5 hours under continuous stirring, maintaining a temperature of 0 °C to 5 °C. The precipitated polypyrrole was filtered, dried in a hot air oven and subsequently in a muffle furnace at 100 °C. The yield of the polypyrrole was 3.2 g (to be taken as 100 wt. %).

0.32 g (10 wt. %) of ZrO₂ was added to a 0.3 M pyrrole solution and mixed thoroughly. 0.06 M

ammonium persulphate was then continuously added drop-wise with the help of a burette to the above solution, to get PPy/ZrO₂ 10 wt.% composite. Similarly, for 20, 30, 40 and 50 wt. %, 0.64 g, .96 g, 1.28 g and 1.6 g of ZrO₂ [Sisco Research Lab Ltd.] powder [8] were taken and the above procedure repeated to get the PPy/ZrO₂ composites. Pure PPy and PPy/ZrO₂ powder were pressed in the form of pellets of 10 mm diameter using a hydraulic press [Shimadzu, Japan]. Conducting silver paste was applied to the pellets of synthesized composites to act as electrodes. The temperatures of hot and cold junctions and corresponding thermo e. m. f. were measured at different temperatures for the synthesized composites, in the temperature range from 473 K (200 °C) to 323 K (50 °C), with the help of a thermo-electric power setup (S E S Instruments Pvt. Ltd., Roorkee).

Characterization

The X-ray diffraction patterns of the PPy/ZrO₂ composites were recorded on X-ray Diffractometer (Bruker AXS D8 Advance) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range 20°–80°. The FTIR spectra of the PPy/ZrO₂ composites were recorded on IR Affinity-1 (Shimadzu, Japan)

spectrometer in KBr medium at room temperature and the SEM images studied using Scanning Electron Microscope (Jeol 6390 LV). Thermal analysis studies were done in the temperature range from 40 °C to 740 °C at a heating rate of 20 °C/min for the pure PPy, PPy/ZrO₂ composites and ZrO₂ using Thermal Analysis System (TG/DTA) (Perkin Elmer STA 6000 Diamond TG/DTA). The UV-VIS spectra for the pure PPy and PPy/ZrO₂ composite were recorded using UV-VIS-NIR Spectrophotometer (Varian Carry 6000).

Results and discussion

XRD Analysis

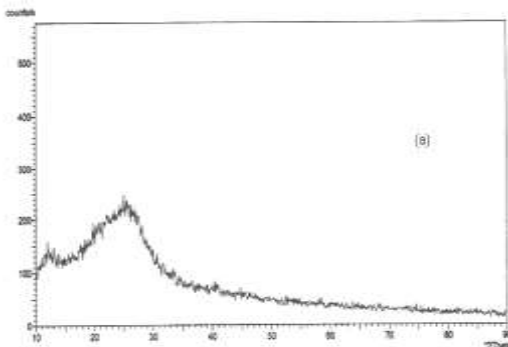


Figure 1.a X-Ray Diffraction pattern of pure PPy

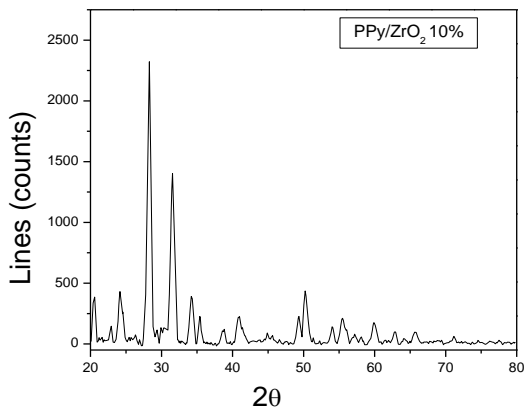


Figure 1.c X-Ray Diffraction pattern of PPy/ZrO₂ (10%) composite

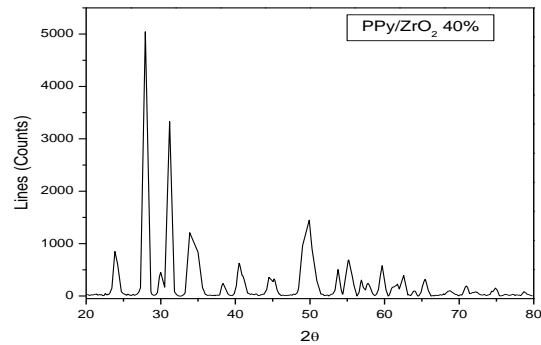


Figure 1.c X-Ray Diffraction pattern of PPy/ZrO₂ (40%) composite

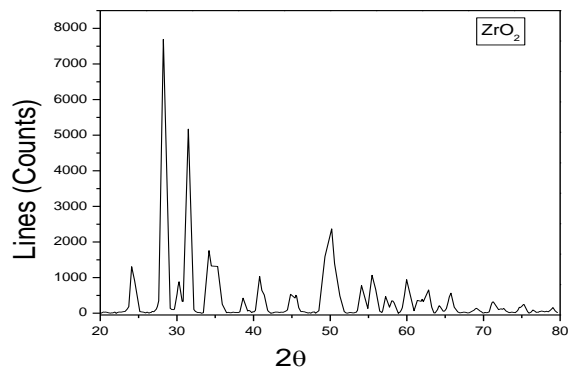


Figure 1.d X-Ray Diffraction pattern of ZrO₂

Figure 1.a represents X-ray diffraction pattern of pure PPy, which has a broad peak at about 2θ = 25°, a characteristic peak of amorphous polypyrrole. In the XRD pattern of PPy/ZrO₂ (10%) composite, characteristic peaks are indexed by lattice parameter values. Characteristic peaks are indexed by lattice parameter values. Main peaks are observed with 2θ at 22.28, 34.24, 38.72, 49.32, 54.05, 59.92 and 65.72 with respect to inter-planar spacing (d) 3.15, 2.61, 2.32, 2.21, 1.70, 1.54 and 1.42. In depth analysis of X-ray diffraction of PPy/ZrO₂ (10% and 40%) composite suggests that it exhibits semi-crystalline behavior. Figure 1.c represents the XRD pattern of ZrO₂ revealing the partial crystalline nature [8-10].

FTIR Analysis

The FTIR spectra of Pure PPy, PPy/ZrO₂ (10%), (PPy/ZrO₂ (40%) composites and ZrO₂ are shown in the Figure 2. The characteristic stretching frequencies at 1580, 1284, 1047, 966, 936, 800, 588

and 530 cm^{-1} may be attributed to the presence of C = N stretching, N – H bending deformation, C – N stretching and C – H bending deformations. In comparison with pure PPy and ZrO_2 , the stretching frequencies are shifted towards the higher frequency side. This indicates that there is homogeneous distribution of ZrO_2 particles in the polymeric chain, due to the Van der Waals interaction between polymeric chain and ZrO_2 [8-13].

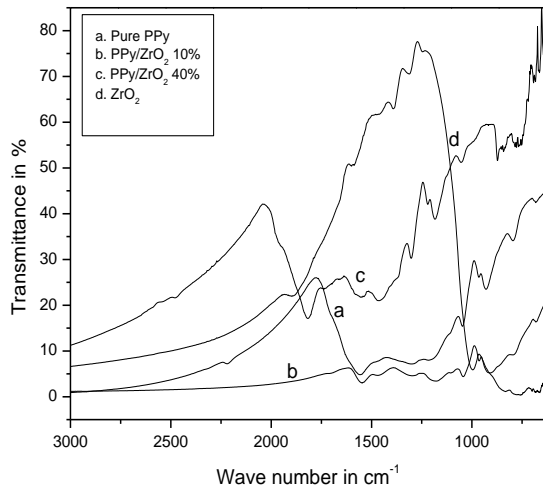


Figure 2 FTIR Spectra of a. pure PPy, b. PPy/ ZrO_2 (10%) composite, c. PPy/ ZrO_2 (40%) composite and d. ZrO_2

SEM Analysis

Figures 3.a, 3.b, 3.c and 3.d are SEM micrographs of Pure PPy, PPy/ ZrO_2 (10% and 40%) composites and ZrO_2 respectively. It is clearly seen from the SEM micrograph of polypyrrole that, it has clusters of spherical shaped particles. Elongated chain patterns of the polypyrrole particles are also observed. The chemically polymerized polypyrrole samples prepared with polypyrrole powder have a much larger specific surface than the electrochemically polymerized film. A granular morphology of the polypyrrole particle structures is measured from the SEM micrographs and is found to be about $1\ \mu\text{m}$ in diameter [11]. A very high magnification of the SEM image is indicative of hemispherical nature of polymer as clusters in the composites. ZrO_2 particles are embedded in PPy chain to form multiple phases, presumably because of weak inter-particle interactions [14-18].

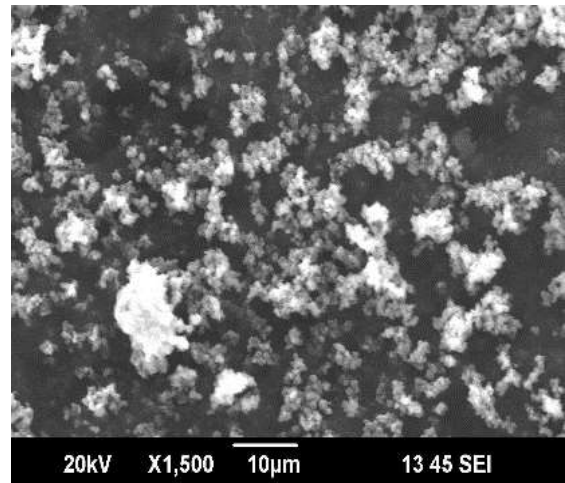


Figure 3.a SEM Micrograph of Pure PPy

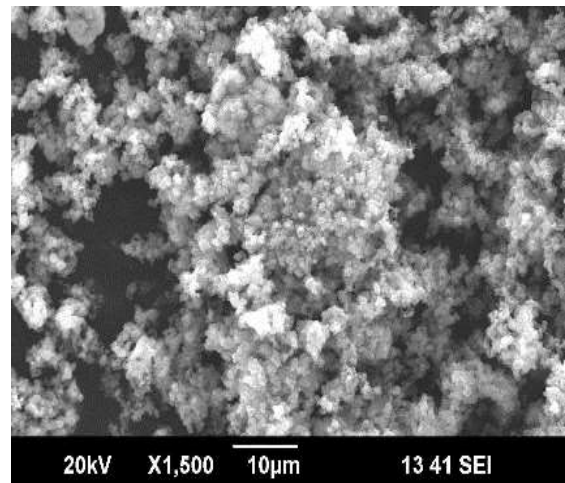


Figure 3.b SEM Micrograph of PPy/ ZrO_2 (wt. 10%) Composites

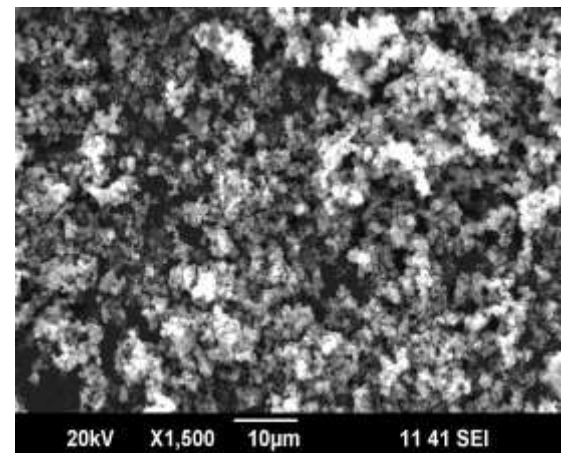


Figure 3.c SEM Micrograph of PPy/ ZrO_2 (wt. 40%) Composite

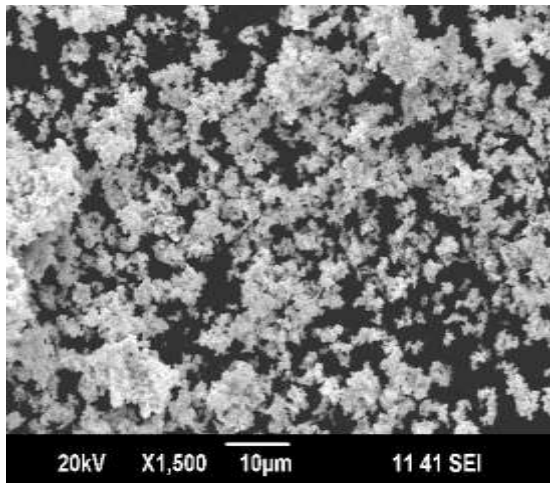


Figure 3.d SEM micrograph of ZrO₂

TG/DTA Analysis

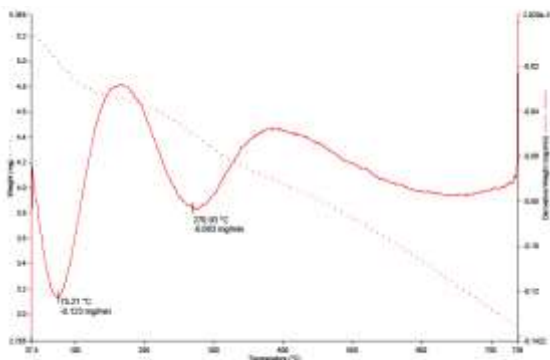


Figure 4.a TG/DTA thermograph of the pure PPy

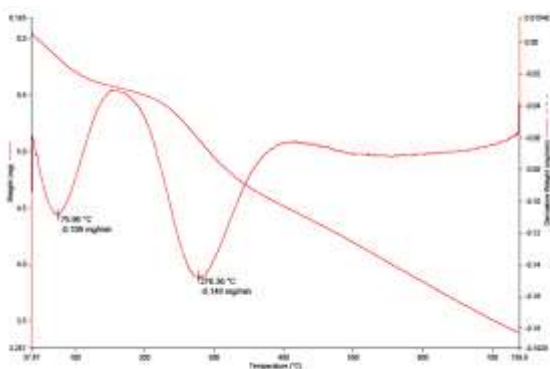


Figure 4.b TG/DTA thermograph of the PPy/ZrO₂ (wt. 40%) composite

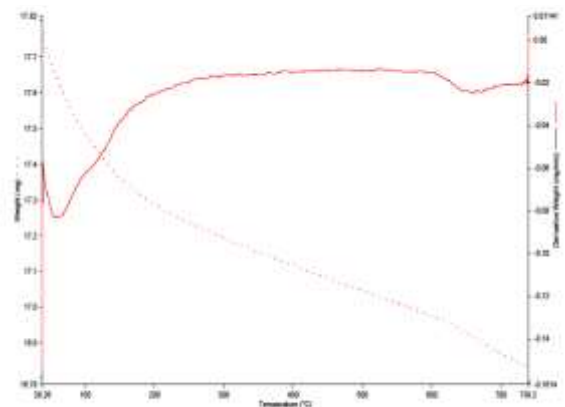


Figure 4.c TG/DTA thermograph of the ZrO₂

The most important and reliable factor in the study of heat stable polymers is the measurement / evaluation of thermal stability.

Derivative weight (mg/min) (RHS: Y-axis) versus temperature is shown in Figures 4.a - 4.c for the pure PPy, PPy/ZrO₂ (40%) composite and ZrO₂ respectively. For pure PPy, 0.123 mg/min is decomposed at 75.21 °C and 0.083 mg/min is decomposed at 270.93 °C with respect to total weight of the sample i.e. 5.265 mg. For PPy/ ZrO₂ (40%) composite, 0.109 mg/min is decomposed at 75.96 °C and 0.148 mg/min is decomposed at 276.36 °C with respect to total weight of the sample i.e. 6.086 mg. It is found that, the weight loss caused by the volatilization of the small molecules in PPy/ZrO₂ (40%) composite at different temperatures is slow compared to that of pure PPy and indicates its higher stability; which clearly proves that ZrO₂ was inserted into the PPy to form the composite thereby increasing the thermal stability of the composite material [19-29].

Weight (mg/min) (LHS: Y-axis) versus temperature is shown in Figures 4.a - 4.c for the pure PPy, PPy/ZrO₂ (40%) composite and ZrO₂ respectively. As temperature increases, weight of the sample taken decreases linearly for the pure PPy, PPy/ZrO₂ (40%) composite and ZrO₂.

UV-VIS-NIR Absorption Analysis

Figure 5 (a & b) shows the UV-VIS-NIR spectra of the PPy and PPy/ZrO₂ (40%) composite. In the spectra of PPy/ZrO₂ (40%) composite, the B-band or Soret band, representing the π→π* transition appears at a modified peak position in the range about 280–320 nm (near UV region), depending on the concentration used. The absorption band in the

visible region for PPy representing the $\pi \rightarrow \pi^*$ transition has a doublet. The peaks around 900 nm and 1450 nm are created due to the electron transition from valence band to the bipolaron band. This observation is proof of an interaction between PPy and ZrO_2 [32-36].

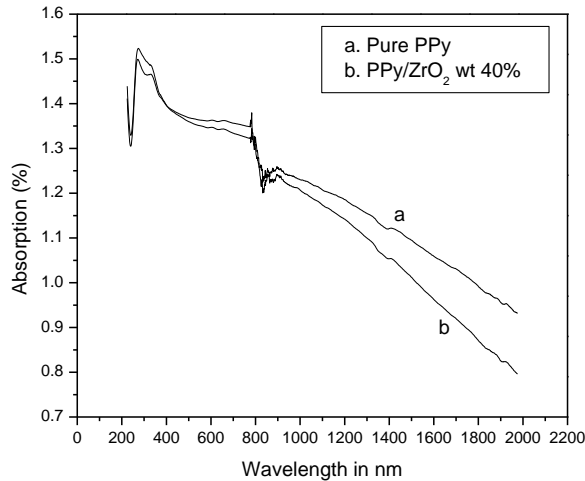


Figure 5 UV-VIS-NIR spectra of the PPy and PPy/ZrO₂ (40%) composite

Thermo-Electric Power Study

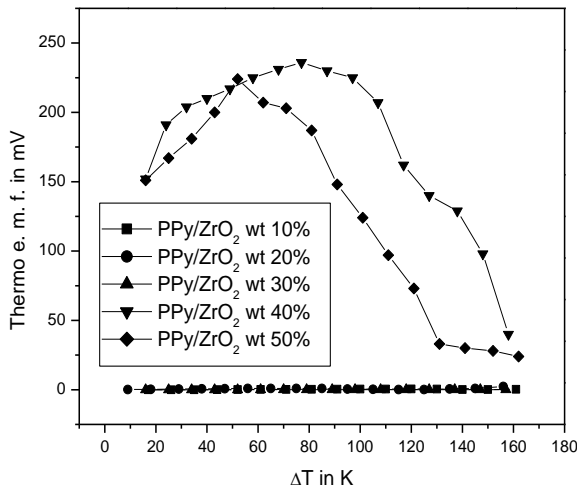


Figure 6.a Thermo e. m. f. as a function of temperature difference for PPy/ZrO₂ composites

The thermo e. m. f. as a function of temperature difference of cold and hot junction temperatures for PPy/ZrO₂ composites is as shown in Figure 6.a which reveals that the PPy/ZrO₂

composites have exhibited semiconductor behavior for the thermo e. m. f. / See-beck voltage [30].

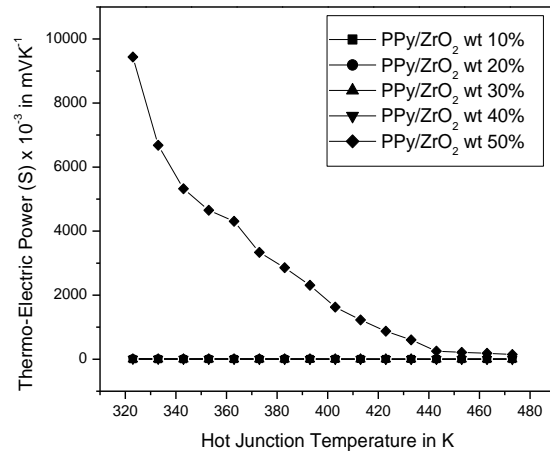


Figure 6.b Thermo-electric power as a function of hot junction temperature for PPy/ZrO₂ composites

The thermo-electric power as a function of hot junction temperature for PPy/ZrO₂ composites is shown in Figure 6.b. The thermo-electric power decreases as hot junction temperature increases for the PPy/ZrO₂ (50%) composite. It is constant as hot junction temperature increases for the PPy/ZrO₂ (10%, 20%, 30% and 40%) composites [37].

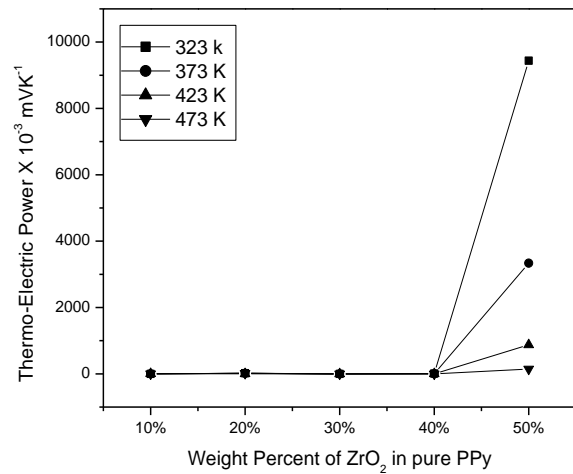


Figure 6.c Thermo-electric power as a function of weight percent of ZrO₂ in pure PPy

The thermo-electric power as a function of weight percent of ZrO₂ in pure PPy is shown in Figure 6.c reveals that, the PPy/ZrO₂ (10%, 20%, 30% and 40%) composites have constant thermo-electric power at all temperatures. 40 weight percent is the

percolation threshold for these composites. The thermo-electric power increases for 50 wt. % at the percolation threshold. The composites obey percolation theory. This can be attributed to the mobile charge carriers due to the distribution of ZrO₂ particles in the pure PPy.

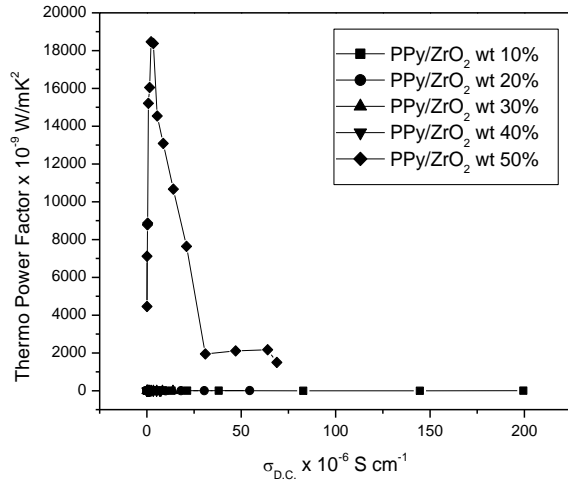


Figure 6.d Thermo power factor as a function of D.C. conductivity for PPy/ZrO₂ composites

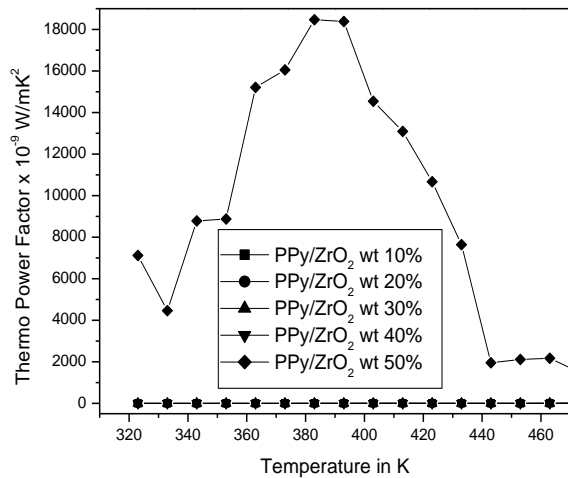


Figure 6.e Thermo power factor as a function of hot junction temperature for PPy/ZrO₂ composites

Thermo power factor as a function of D.C. conductivity for PPy/ZrO₂ composites is shown in Figure 6.d which reveals that the thermo power factor increases and thereafter decreases on increasing D.C. conductivity for the PPy/ZrO₂ (50%) composite.

The thermo power factor as a function of temperature for PPy/ZrO₂ composites is shown in Figure 6.e. The thermo power factor is constant as temperature increasing for the PPy/ZrO₂ (10%, 20%, 30% and 40%) composites, increases breaches a maximum value at 390 K and decreases for the PPy/ZrO₂ (50%) composite.

Conclusion

The polypyrrole/zirconium oxide composites were synthesized to tailor the transport properties. Detailed characterizations of the composites were carried out using SEM, XRD, FTIR, TG/DTA and UV-VIS-NIR techniques. The results of Seebeck coefficient and thermo-electric power factor values of polypyrrole/zirconium oxide composites have demonstrated a strong dependence on the weight percent of zirconium oxide in polypyrrole.

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