Preparation, Characterization and Current Studies 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 i.e. ammonium per sulphate to prepare polypyrrole/zirconium oxide composites by chemical oxidation method. The polypyrrole/zirconium oxide composites have been prepared with various compositions viz., 10, 20, 30, 40 and 50 wt. % of zirconium oxide in pyrrole. The polypyrrole/zirconium oxide composites were characterized by employing Powder X-ray Diffraction Spectrometer and Fourier Transform Infra-Red Spectroscopy. The surface morphologies of the composites were studied by Scanning Electron Microscopy. Current versus voltage at room temperature studies shows thatmetallic behavior of conducting polypyrrole and its composites. Current versus temperature at constant voltage studies shows the dimensions of zirconium oxide particles in the matrix have a greater influence on the current value.**

***Key words: Polypyrrole; Zirconium Oxide; Composites; Current; Voltage*.**

1. INTRODUCTION

Conducting polymer composites with some suitable compositions of one or more insulating materials lead to desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers [1] and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composite will affect the behavior in an electric field is a long-standing problem and of great importance. The discovery of doping in conducting polymer [2-6] has led to further dramatic increase in the conductivities of such conjugated polymers to values as high as 10^5 Scm^{-1}.

Authors were done synthesis of pure polypyrrole and its zirconium oxide composites by chemical polymerization method in the presence of oxidizing agent. Pure polypyrrole and its composites were analyzed by characterization like SEM, XRD and FTIR. And also current studies were done and reported.

Authors will be studied D.C., A.C. and thermal conductivities and dielectric properties in near future. Authors aim is to study the sensor response of pure polypyrrole and its composites. Now-a-days, different types of sensors have numerous applications in different fields. Thus, polypyrrole composites might find applications in sensors.

2. EXPERIMENTAL

A. Synthesis

The AR grade [Spectro Chem Pvt. Ltd.] pyrrole [7] was purified by distillation under reduced pressure. To prepare 0.3 M pyrrole, 20.8 ml of pure pyrrole was measured and mixed with 500ml water and solution was prepared. 0.3 M pyrrole solution in beaker was kept on the ice tray. Ice tray was kept on magnetic stirrer. To prepare 0.06 M [8] of ammonium persulfate [(NH4)2S2O8] [Thermo Fisher Scientific], 1.37 gm of ammonium persulfate mixed with 100ml water and solution was prepared. 0.06 M ammonium persulfate was adding drop-wise continuously with the help of burette and the reaction mixture was continuously stirred by using magnetic stirrer (REMI 5 ML, Techno Instruments Co., Max. RPM: 2500) which was used to mix the two solutions. The reaction mixture was continuously stirred for 3 hours at temperature range from 0°C to 5°C to obtain polypyrrole. The resulting precipitate was filtered and washed thoroughly and dried by using hot air oven and muffle furnace at 100°C. The yield of the polypyrrole was 3.2 gm. The polypyrrole powder was pressed in the form of pellets of 10 mm diameter by using hydraulic press.

Different weight percents 0.32gm, 0.64gm, 0.96gm, 1.28gm and 1.6 gm of ZrO_2 [Sisco Research Lab Ltd] powder [9] (viz., 10, 20, 30, 40 and 50 wt. %) were taken and was added to polypyrrole solution. Similar to polypyrrole preparation, PPy/ZrO_2composites were synthesized by chemical oxidation route.

B. Characterization

The X-ray diffraction [10-11, 13] patterns of PPy/ZrO_2 composites were recorded on X-ray

Diffractometer using Cu $k_\propto$ radiation (Bruker AXS D8 Advance) (λ = 1.5418 Å) in the 2θ range 20°–80°.

The FTIR spectra [09,11, 13] of the PPy/ZrO_2 composites were recorded on IR Affinity-1 (Shimadzu, Japan) spectrometer in KBr medium at room temperature.

The SEM (Jeol 6390LV) images of PPy/ZrO_2 composites were investigated using Scanning Electron Microscope[11-13]. The powder is pressed to form pellets of 10 mm diameter and thickness which varies from 1 to 3 mm by applying pressure of 10 to 12 tons by using hydraulic press [Shimazdu, Japan] with the help of die.

C. Current Study

The composites were made as pellets. The conducting silver paste is used as electrodes on both sides of pellets. The current values were noted down as varied values of voltage at room temperature and the current values were noted down as temperature values were decreasing from 200°C till 30°C.

3. RESULTS AND DISCUSSION

A. X-ray diffraction Study

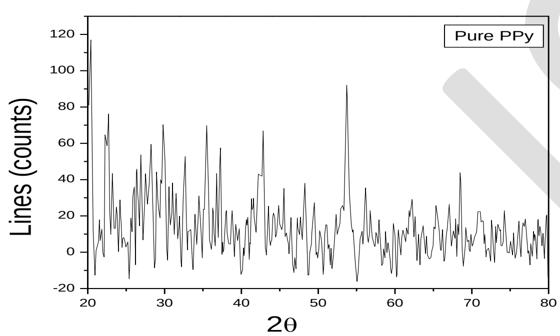

Figure 1.a X-Ray Diffraction pattern of Pure PPy

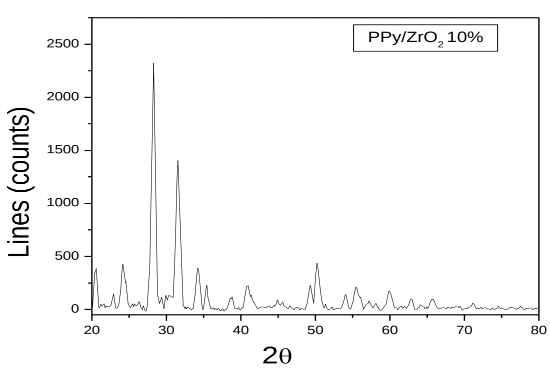

Figure 1.b X-Ray Diffraction pattern of PPy/ZrO_2(wt. 10%) Composite

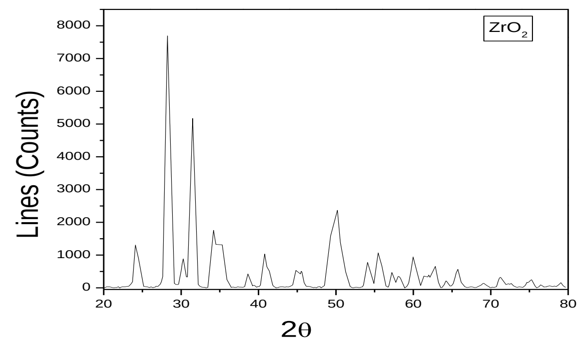

Figure 1.c X-Ray Diffraction pattern of ZrO_2

Figure 1.apresents X-ray diffraction pattern of pure PPy shows a characteristic peak of amorphous polypyrrole. Figure 1.b presents XRD pattern of PPy/ZrO_2(wt. 10%) composite. Characteristic peaks are indexed by lattice parameter values. Main peaks were observed with 2 Theta at 22.28, 34.24, 38.72, 49.32, 54.05, 59.92 and 65.72with respect to inter-planar spacing (d) 3.15, 2.61, 2.32, 2.21, 1.70, 1.54 and 1.42. Careful analysis of X-ray diffraction of PPy/ZrO_2(wt. 10%) composite suggests that it exhibits semi-crystalline behavior. Figure 1.c presents XRD pattern of ZrO_2revealing the partial amorphous nature [09, 11, 17].

B. Fourier Transform Infra-Red Spectroscopy study

FTIR spectrum of pure PPy shows an N–H stretching band from the pyrrole ring at nearly 3,428 cm^{-1}. The weak band at 2,850 cm^{-1} is due to C–H stretching. The other bands also show the characteristic PPy absorption at 1,600–1100 cm^{-1}. The peak at 1,690 cm^{-1} was assigned to the C=C ring stretch in pyrrole. The C–N ring stretching band of the pyrrole ring occurs at 1,467 cm^{-1}. The peak at 1,306 cm^{-1} was the C–H plane deformation of the pyrrole, and the peak at 1,180 cm^{-1} was due to C–C stretching [14-16].

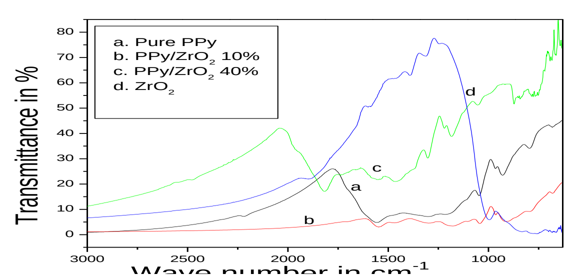

Figure 2 FTIR Spectra of a. Pure PPy, b. PPy/ZrO_2 (wt. 10%) c. PPy/ZrO_2 (wt. 40%), Composite and d. ZrO_2

The FTIR spectra of (a). Pure PPy, (b). PPy/ ZrO_2 (wt. 10%), (c). PPy/ZrO_2(wt. 40%) composites and (c). ZrO_2 is shown in Figure 2. The characteristic stretching frequencies for PPy/ZrO_2 (wt. 10%) are observed at 1580.06, 1284.59, 1047.36, 966.34, 936.48, 800.46, 588.29

and 530.42 cm^{-1}.They were shifted towards lower frequency side with respect to pure polypyrrole.The characteristic stretching frequencies shifted towards higher frequency side from PPy/ZrO_2(wt. 10%) composite to PPy/ZrO_2 (wt. 40%). They were again shifted towards lower frequency side for PPy/ZrO_2 (wt. 50%). This indicates that, there is homogeneous distribution of ZrO_2 particles in the polymeric chain due to the Vander-wall type of interaction between polymeric chain and ZrO_2[11-13]. This shows that there is an interaction between the PPy components and its composites.

C. Scanning Electron Microscope Study

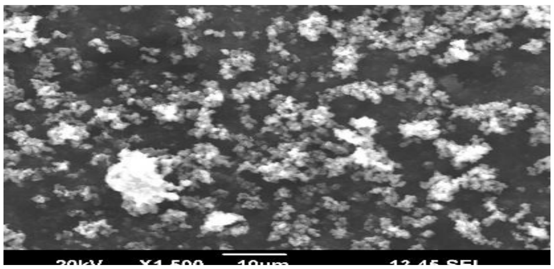

Figure 3.a SEM Micrograph of Pure PPy

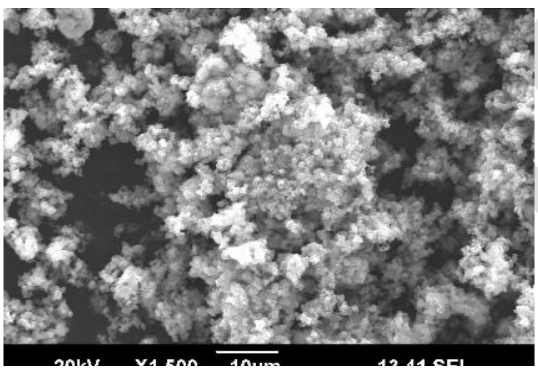

Figure 3.b SEM Micrograph of PPy/ZrO_2 (wt. 10%) Composites

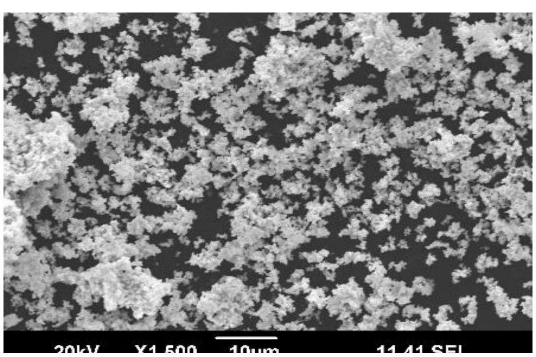

Figure 3c SEM Micrograph of ZrO_2

The morphology of PPy and its composites were studied, using scanning electron microscope. Figure 3.a, 3.b and 3.c shows SEM micrographs of Pure PPy, PPy/ZrO_2(wt. 10%) composite and ZrO_2. As shown in Figure 3.a,the bulk polymer tends to aggregate in large particles in the form of large globules. This is probably due to an increased inter-chain interaction compared to its stabilized particles in which the polymeric surfactant chains act as a limiting factor for such an interaction. The type of solution affects the homogeneity, particle size and size distribution, because oxidizing agent may influence the rate of polymerization. A very high magnification of SEM images shows the presence of hemi spherical nature of polymer as clusters in the composite as shown in Figure 3.b. Oxide particles are covered by spherical nature of polypyrrole to form multi-particle aggregates, presumably because of weak inter-particle interactions as shown in Figure 3.c [09, 11].

D. I-V Characteristics Studies

The plot of current versus voltage at room temperature for PPy/ZrO_2 composites as shown in Figure 4. As voltage increases, current increases for composites. PPy/ZrO_2 composites were shown metallic nature. Thus, different weight percentage of zirconium oxide is affected on the current. The increase in current is due to the variation in distribution of ZrO_2 particles which may be supporting for more number of charge carriers to hop between favorable localized sites causing increase in current [18].

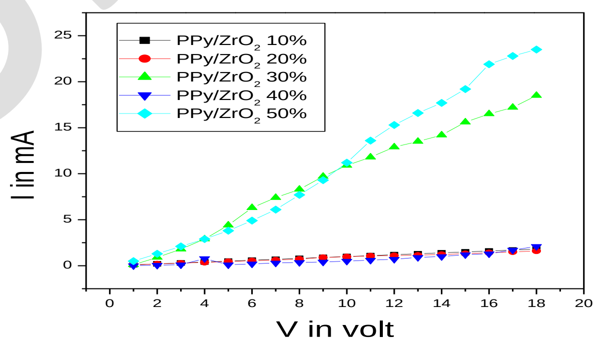

Figure 4 Current vs Voltage at RoomTemperature

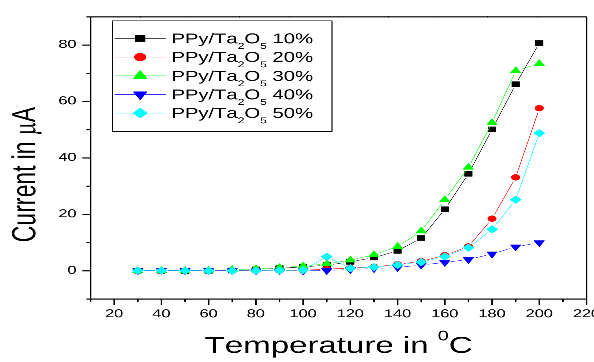

Figure 5 Current vs Temperature at Constant Voltage

The plot of current versus temperature at constant voltage is shown in Figure 5. As temperature decreases from 200°C, current is decreases almost linearly till 150°C. After this temperature, current is almost constant till the room temperature. This shows that the dimensions of zirconium oxideparticles in the matrix have a greater influence on the current value [18].

CONCLUSION

Synthesis of polypyrrole/zirconium oxidecomposites efforts have been mad to tailor the transport properties. Detailed characterizations of the composites were carried out usingXRD, FTIRand SEM techniques. As voltage increases current also increases showing the metallic behavior of conducting polypyrrole and its composites. As temperature decreases, current is decreases. Current values were different for Polypyrrole/zirconium oxide composites. This shows that the dimensions of zirconium oxide particles in the matrix have a greater influence on the current value. Polypyrrole/zirconium oxide composites may find applications in sensors.

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ACKNOWLEDGEMENT

The authors would like to acknowledge The Principal, Dr. T.S.Pranesha, (HOD, Dept. of Physics), BMSCE, Bangalore-560019 & The Management, Rajya Vokkaligara Sangha, The Principal and Colleagues, BIT, Bangalore-560004 for help to all works. SEM and XRD analysis of the samples were done at Sophisticated Analytical Instruments Facility (SAIF) of Cochin University of Science And Technology, Cochin, India.