Synthesis, Characterization and D.C. Conductivity 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 synthesize polypyrrole /zirconium oxide composites by chemical oxidation method. The PPy/ZrO_2 composites have been synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt % of ZrO_2 in pyrrole. The PPy/ZrO_2 composites were characterized by employing Powder X-ray Diffraction (XRD) Spectrometer and Fourier Transform Infra-Red Spectroscopy (FTIR). The surface morphologies of the composites were studied by Scanning Electron Microscopy (SEM). The D.C. conductivities were studied in the temperature range from 30°C – 200°C. The dimensions of zirconium oxide particles in the matrix have a greater influence on the conductivity values.
Key words: Polypyrrole; Zirconium Oxide; Composites; Conductivity; Temperature.
Abbreviations: D.C.; FTIR; Py; PPy; SEM; XRD; ZrO_2 .

INTRODUCTION

One fundamental property which normally distinguishes polymers from metals is electrical conductivity. The value of electrical conductivity for metals is very high and is generally of the order of 10^4–10^6 Scm^{-1} (Shirakawa H et al 1977) while for polymers which are generally insulators this value does not exceed 10^{-14} Scm^{-1}. Though the low electrical conductivity of polymers has found its immense use in the manufacture of insulators and dielectric substances, the question of producing polymers which exhibit a conductivity (György Inzelt 2011) similar to that of metals, has always engaged researchers. During the last two decades, the researchers, through the simple modification of ordinary organic conjugated polymers, have succeeded in preparing polymers with high electrical conductivity. Called electrically conducting polymers or synthetic metals (Kricheldorf H R 2005), these materials which combine the electrical properties of the metals with the advantages of polymers such as lighter weight, greater workability, resistance to corrosion and chemical attack and the lower cost have become extremely attractive and have infiltrated our day to day life with a wide range of products extending from most common consumer goods to highly specialized applications in space, aeronautics and electronics (Terje A Skotheim et al 2007). It is, therefore, no wonder that these polymers are being called as the materials of the 21st century.

A. J. Heeger, A.G. Mac Diarmid and H. Shirakawa (Nobel Prize winners in Chemistry of 2000) at the University of Pennsylvania in 1977, for the first time demonstrated that polyacetylene (PA), an intrinsically insulating polymer, becomes highly conducting on treatment with oxidizing (electron-accepting) or reducing (electron-donating) agents (S Ramakrishnan 1997).

Polypyrrole (PPy) is one of the most attractive polymers which has some special transport properties. These transport properties originates from the fact that, polypyrrole is an intrinsic conducting polymer and can be synthesized to have conductivities up to 1000 Scm^{-1}. Conducting polymers have approaches the conductivities of metals. Most practical polypyrroles have conductivities in the range of 1–100 Scm^{-1} (A K Bakhshi 1995).

In recent years much research was concerned with their composites with conventional polymers. This approach has been successful in producing electrical conductive composites with a wide range of interesting electrical properties. In this work, we have presented our results on synthesis, characterization and D.C. conductivity studies of PPy/ZrO_2 composites.

Experimental

Synthesis

In the chemical oxidation method, an oxidizing agent such as lead dioxide, quinones, ferric chloride or persulfates is added to the pyrrole and a dopant dissolved in a suitable solvent, resulting in the precipitation of doped PPy powder. In general, the electrical conductivities of chemically prepared PPy are a little lower than those of PPy films prepared electrochemically. Nevertheless, the chemical oxidation method is suitable for commercial mass production of PPy and may produce processible PPy since the method has much greater feasibility to control the molecular weight and structural feature. It is well known that various properties such as the electrical conductivity, stability and morphology of synthesized PPy strongly depend on various reaction conditions such as the kinds and concentrations of oxidant and dopant, polymerization temperature and time, stoichiometry, and solvent (Terje A Skotheim et al 2007).

The AR grade [Spectro Chem Pvt. Ltd.] pyrrole (Reza Ansari 2006) was purified by distillation under reduced pressure. To 0.3 M of pure pyrrole, the solution of 0.06 M (V K Gade et al 2007) of ammonium per sulfate [$(NH_4)_2S_2O_8$] [Thermo Fisher Scientific] was adding drop wise continuously and the reaction mixture was stirred continuously for 3 hours at temperature range from 0°C to 5°C to obtain polypyrrole. Different weight percents of ZrO_2 [Sisco Research Lab Ltd] powder (M.V.Murugendrappa et al 2007) (viz., 10, 20, 30, 40 and 50 wt. %) were taken and was added to polypyrrole. The PPy/ZrO_2 composites synthesized from chemical oxidation route. The resulting product was filtered and washed thoroughly and dried by using hot air oven and muffle furnace at 100°C.

Characterization

The X-ray diffraction (Yoshio Kobayashi et al 2009; C Basavaraja et al 2010; Anuar Kassim et al 2002) patterns of PPy/ ZrO_2 composites were recorded on Philips X-ray Diffractometer using Cu k_∞ radiation (λ = 1.5418 Å) in the 2θ range 20°–80°. The FTIR spectra (M.V.Murugendrappa et al 2007; C Basavaraja et al 2010; Anuar Kassim et al 2002) of the PPy/ZrO_2 composites were recorded on IR Affinity-1 (Shimadzu, Japan) spectrometer in KBr medium at room temperature. The SEM images of PPy/ZrO_2 composites were investigated using Scanning Electron Microscope (C Basavaraja et al 2010; Amparat Reung-U-Rai et al 2008; Anuar Kassim et al 2002).

D.C. Conductivity

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. The D.C. conductivity measurements on these composites were made using the conducting silver paste as electrodes on both sides of pellets. D.C. current in μA can be measured in the presence of D.C. power supply as temperature decreasing from 200°C to 30°C (M.V.Murugendrappa et al 2007; C Basavaraja et al 2010).

RESULTS AND DISCUSSION

XRD Analysis

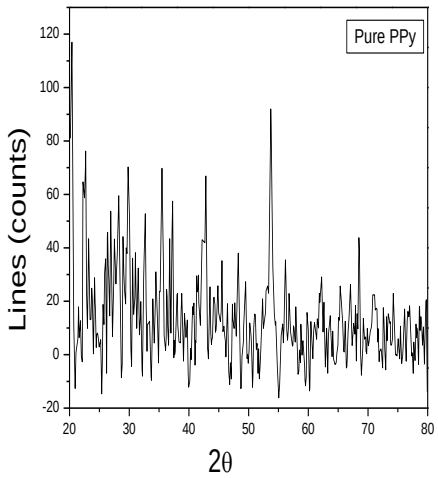

Figure 1a. X-Ray Diffraction pattern of Pure PPy

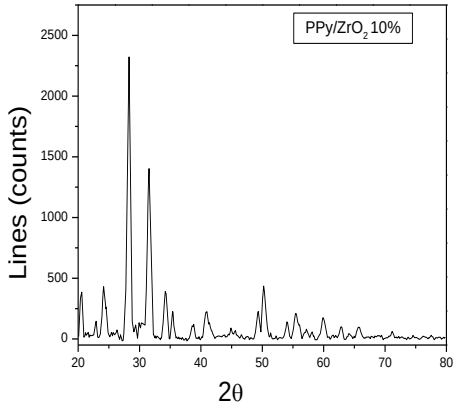

Figure 1b. X-Ray Diffraction pattern of PPy/ZrO_2 (wt. 10%) Composite

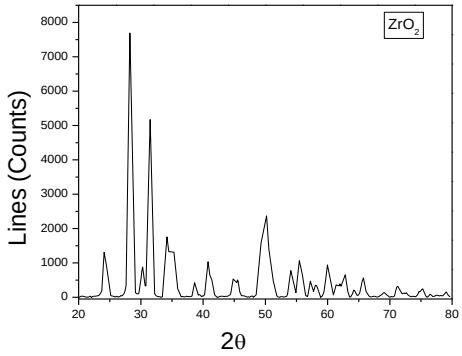

Figure 1c .X-Ray Diffraction pattern of ZrO_2

Figure 1a presents X-ray diffraction pattern of pure PPy, which has a broad peak at about 2 Theta= 28.28°, shows a characteristic peak of amorphous polypyrrole. Figure 1b 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 65.72 with 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 1c presents XRD pattern of ZrO_2 revealing the partial amorphous nature (M.V.Murugendrappa et al 2007; C Basavaraja et al 2010; Sakkopoulos S et al 2002).

FT-IR Analysis

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 (Chuan Y L 2004; Chuan Y L et al 2000; Patil S F 1992)

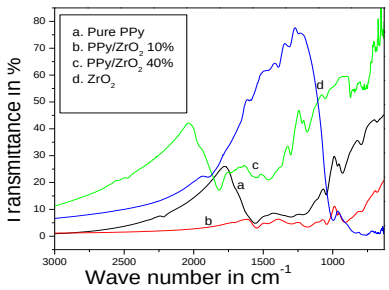

Figure 2. FTIR Spectra of (a). Pure PPy, (b). PPy/ZrO_2 (wt. 10%) (c). PPy/ZrO_2 (wt. 40%), Composite and (d). ZrO_2

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 (C Basavaraja et al 2010; Amparat Reung-U-Rai et al 2008;Anuar Kassim et al 2002). This shows that there is an interaction between the PPy components and its composites.

SEM Analysis

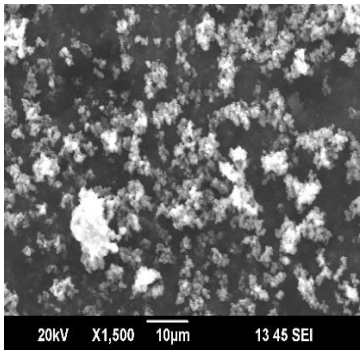

Figure 3a SEM Micrograph of Pure PPy

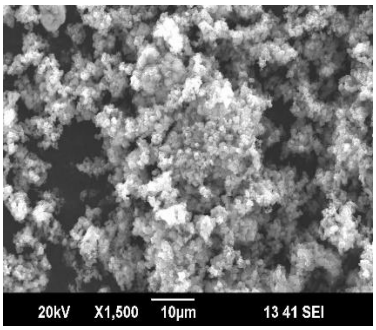

Figure 3b SEM Micrograph of PPy/ZrO_2 (wt. 10%) Composites

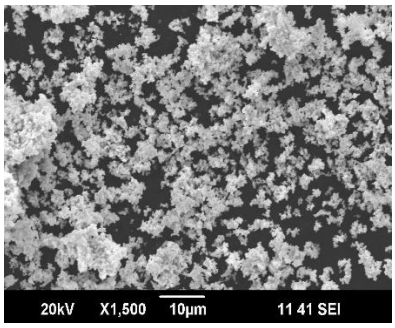

Figure 3c SEM Micrograph of ZrO_2

The morphology of PPy and its composites were studied, using scanning electron microscope. Figure 3a, 3b and 3c shows SEM micrographs of Pure PPy, PPy/ZrO_2 (wt. 10%) composite and ZrO_2. As shown in Figure 3a, 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

3b. 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 3c (M.V.Murugendrappa et al 2007; C Basavaraja et al 2010).

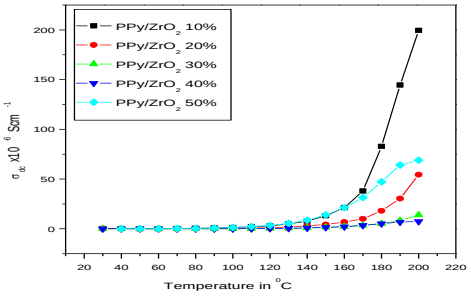

Figure 4

The variation of D.C. conductivities as a function of temperature for PPy/ZrO_2 composites as shown in Figure 4. The D.C. conductivity measurements on these composites were made using the conducting silver paste as electrodes on both sides. It is observed that, the conductivity increases with temperature showing multiple phases of conductivity. It can also be seen that, the values of conductivities increases up to 199.43 x 10^{-6} Scm^{-1} for ZrO_2 (wt. 10%) in polypyrrole. This may be due to the extended chain length of polypyrrole which facilitate the hopping of charge carriers when the content of ZrO_2 in polypyrrole. And then decreases up to 7.43 x 10^{-6} Scm^{-1} till PPy/ZrO_2 (wt. 40%) composites and increases again to 68.86 x 10^{-6} Scm^{-1} for PPy/ZrO_2 (wt. 50%) composite. The increase in conductivity for PPy/ZrO_2 (wt. 10%) composite 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. The decrease in conductivities may be attributed to the trapping of charge carriers (M.V.Murugendrappa et al 2007; T K Vishnuvardhan et al 2006; Papathanassiou A N et al 2002).

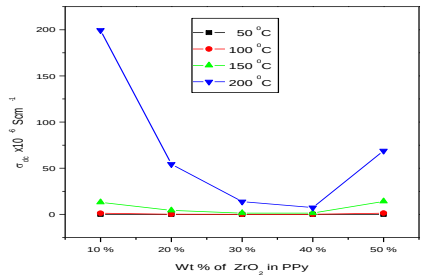

Figure 5

The variation of the D.C. conductivities as a function of the weight percentage of ZrO_2 in PPy at different temperatures as shown in Figure 5. In all the composites, the conductivity increases with respect to the temperature, forming multiple phases of conductivity. The values of the conductivity increases for ZrO_2 (wt. 10%) in PPy and decrease thereafter. This may be due to the extended chain length of PPy, which facilitates the hopping of charge carriers when the concentration of ZrO_2 is high. This point is a percolation threshold and the composites obey percolation theory. Furthermore, a decrease in the conductivity can be observed till PPy/ZrO_2 (wt. 40%) composites and can be attributed to the distribution of ZrO_2 particles of larger grain sizes, which are partially blocking the hopping of charge carriers. Charge trapping in PPy and blends is a general universal feature of these materials (M.V.Murugendrappa et al 2007; Papathanassiou A N et al 2002; Li Gang et al 2007; Sakkopoulos S et al 2002).

CONCLUSION

Synthesis of polypyrrole/zirconium oxide composites efforts have been made to tailor the transport properties. Detailed characterizations of the composites were carried out using XRD, FTIR and SEM techniques.

The results of D.C. conductivity shows a strong dependence on the weight percentage of ZrO_2 in PPy. Polypyrrole/zirconium oxide composites may find applications in sensors.

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