Synthesis, Characterization and D.C. Conductivity Studies of Polypyrrole/Tantalum Pentoxide Composites

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Abstract: **In-situ polymerization of pyrrole was carried out withtantalum pentoxidein the presence of oxidizing agent i.e. ammonium per sulphate to synthesize polypyrrole/tantalum pentoxidecomposites (PPy/Ta_2O_5) by chemical oxidation method. The PPy/ Ta_2O_5composites have been synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt. % of Ta_2O_5 in pyrrole. The PPy/Ta_2O_5 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 tantalum pentoxideparticles in the matrix have a greater influence on the conductivity values.**

Key words: Polypyrrole; Tantalum Pentoxide; Conductivity; Composites; Temperature; Current.

I. INTRODUCTION

Discovery and development of conducting polymers has opened up new frontiers in materials chemistry and physics. This new generation of polymers combines the mechanical properties and process ability of traditional polymers with electrical and optical properties unknown earlier. The enormous technological potential that, this rare combination offers, is beginning to be tapped [01].

One fundamental property which normally distinguishes polymers from metals is electrical conductivity. The value of electrical conductivity [02] for metals is very high and is generally of the order of 104 – 106 Scm^{-1}, 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 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 [03]. 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.

Polymers are generally considered to be electronic insulators. However, the first work describing the synthesis of a conducting polymer was reported as early as the mid-19th century by Henry Letheby. Although many other reports followed Letheby’s discovery, it is the work by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa[04] in the late 1970s on doped poly- acetylene that is considered by many to be the starting point for the research field of conducting polymers. This contribution resulted in their being awarded the Nobel Prize in Chemistry in 2000, which boosted activity in the field at the turn of the millennium.

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 [02] in the range of 1–100 Scm^{-1}. In this work, we have presented our results on PPy/Ta_2O_5 composites.

Tantalum[05] is a chemical element with the symbol Ta and atomic number 73. Tantalum pentoxide[06] is the inorganic compound with the formulaTa_2O_5. It is a white solid that is insoluble in all solvents, but is attacked by strong base and hydrofluoric acid. Orthorhombic and hexagonal phases are known. Ta_2O_5 has a high refractive index, low absorption (colorless), inert material, which makes it useful for coatings [07].

Tantalum pentoxide has found a variety of uses in electronicsdue to its high band gap of 3.7 eV [08]. It is used to make capacitors in automotive electronics, cell phones and pagers, electronic circuitry, thin-film components and high-speed tools. In the 1990s, interest grew in the use of tantalum oxide as a high-k dielectric for

DRAM capacitor applications [09]. It is used in on-chip MIM capacitors for RF CMOS integrated circuits. Tantalum pentoxide has been utilized in the fabrication of the glass of many photographic lenses due to its high index of refraction.

II. EXPERIMENTAL

A. Synthesis

The AR grade [SpectroChem Pvt. Ltd.] pyrrole [10] was purified by distillation under reduced pressure.The solution of 0.06 M [11] of ammonium per sulfate [$(NH_4)_2S_2O_8$] [Thermo Fisher Scientific] was adding dropwise continuously to 0.3 M of pure pyrroleand 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 Ta_2O_5[Sisco Research Lab Ltd]powder [12] viz., 10, 20, 30, 40 and 50 wt. % were taken and was added to polypyrrole. The PPy/Ta_2O_5 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. The composites were pressed in the form of pellets of 10 mm diameter by using hydraulic press.

B. Characterization

The X-ray diffraction patterns of PPy/Ta_2O_5composites were recorded on Philips X-ray Diffractometer [11]-[14], [17]-[18]using Cu k_∞ radiation (λ = 1.5418 Å) in the 2θ range 20°– 80°. So, we can obtain the information of structure of samples.

The FTIR [11]-[14], [17]-[18]spectra of the PPy/Ta_2O_5composites were recorded on IR Affinity-1 (Shimadzu, Japan) spectrometer in KBr medium at room temperature. We can obtain the information of functional groups of samples.

The SEM [11]-[14], [18] images of PPy/Ta_2O_5 composites were investigated using Scanning Electron Microscope. We can obtain the information of surface morphologies of samples.

C. D.C. Conductivity

The composites were made as pellets. The conducting silver paste is used as electrodes on both sides of pellets. The D.C. conductivities [13-15] of PPy/Ta_2O_5 composites have measured by applying constant voltage and measuring the current through the sample in the temperature range of 30°C – 200°C.

III. RESULTS AND DISCUSSION

A. FTIR Analysis:

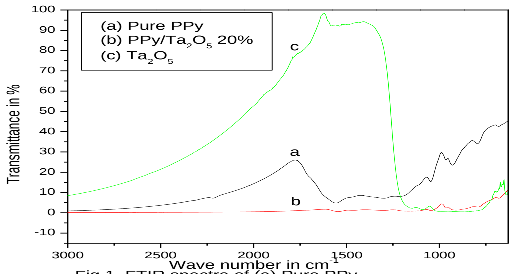
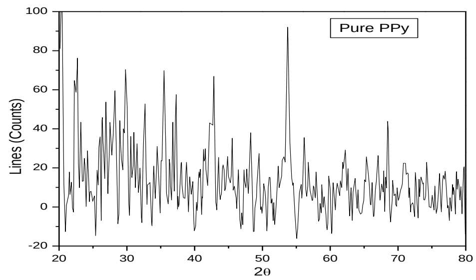


Fig.1. FTIR spectra of (a) Pure PPy, (b) PPy/$Ta_2O_5$20% and (c)Ta_2O_5

Fig.1 shows FTIR Spectra of PPy/ Ta_2O_5 (20 wt. %) Composite.The characteristic stretching frequencies are observed at 1546.91, 1467.83, 1300.02, 1045.42, 966.34, 912.33, 792.74, 680.87 and 617.22cm^{-1}. Fig.1 shows FTIR Spectra of (a). Pure PPy, (b). PPy/ Ta_2O_5 (20 wt. %) and (c). Ta_2O_5.They were shifted towards higher frequency side tillPPy/ Ta_2O_5 (20 wt. %)composites and from higher frequency, the characteristic stretching frequencies shifted towards lower frequency side tillPPy/Ta_2O_5 (50 wt. %) composite. This indicates that, there is homogeneous distribution of Ta_2O_5 particles in the polymeric chain due to the Vander-wall type of interaction between polymeric chain and Ta_2O_5 [13]-[14], [16]-[17].

B. XRD Analysis

Fig. 2a presents X-ray diffraction pattern of pure PPy, which has a broad peak at about 2 Theta= 22.694°, shows a characteristic peak of amorphous polypyrrole. Fig. 2b presents XRD pattern of PPy/Ta_2O_5 (20 wt. %) composite. Characteristic peaks are indexed by lattice parameter values. Main peaks are observed with 2 Theta at 22.649, 28.093, 36.490, 46.477, 49.554, 55.299, 58.264, 63.439 and 70.401 with respect to interplanar spacing (d) 3.92282, 3.17372, 2.46040, 1.96231, 1.83804, 1.65990, 1.58231, 1.46511 and 1.33631. Careful analysis of X-ray diffraction of PPy/Ta_2O_5 (20 wt. %) composite suggests that it exhibits semi-crystalline behavior. Fig. 2c presents XRD pattern of Ta_2O_5 revealing the partial amorphous nature [11]-[12], [14].



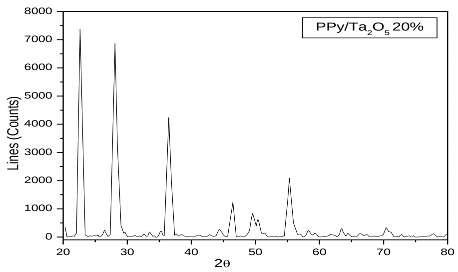


Fig.2b. XRD pattern of PPy/Ta_2O_5 20%

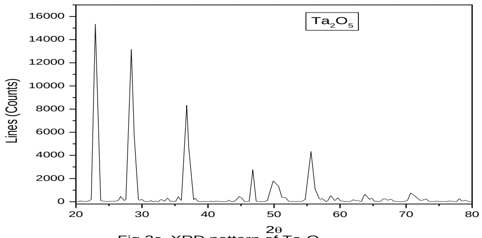
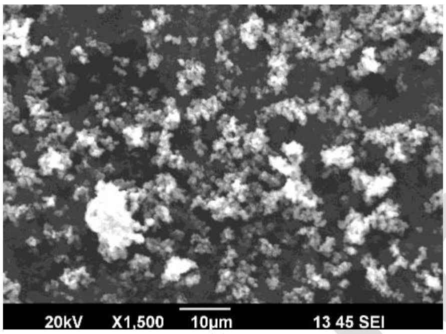
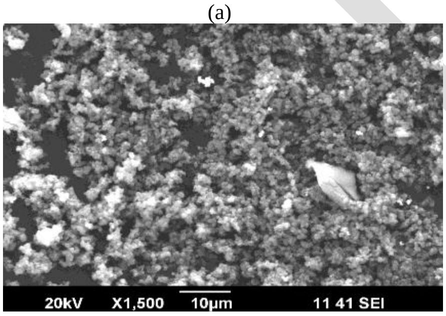


Fig.2a. XRD pattern of Ta_2O_5

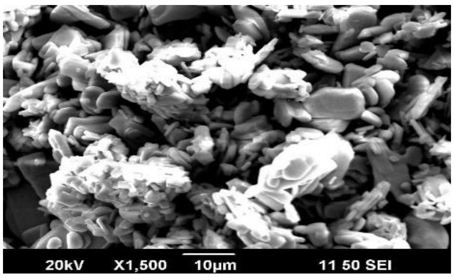
C. SEM Analysis:



(a)



(b)



(c)

Fig. 3. SEM Micrographs of (a). Pure PPy,
(b). PPy/Ta_2O_5 (20%) Composite and (c). Ta_2O_5

Fig. 3. (a), (b) and (c) shows SEM micrographs of Pure PPy, PPy/Ta_2O_5 (20 wt. %) composite and Ta_2O_5. A very high magnification of SEM images shows the presence of hemi spherical nature of polymer as clusters in the composite. Oxide particles are covered by spherical nature of polypyrrole to form multiparticle aggregates, presumably because of weak interparticle interactions[11]-[12], [14].

D. D.C. Conductivity Studies:

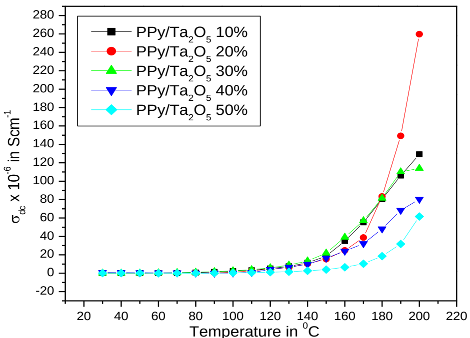


Fig.4. Variation of σ_{dc} as a function of temperature for PPy/Ta_2O_5 Composites

The variation of D.C. conductivities as a function of temperature for PPy/Ta_2O_5 composites as shown in Fig.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 259.753 x10^{-6} Scm^{-1} from wt. 10% to wt. 20% of Ta_2O_5 in polypyrrole. This may be due to the extended chain length of polypyrrole which facilitate the hopping of charge carriers when the content of Ta_2O_5 is increased up to 20%. The increase in conductivity for wt. 20% is due to the variation in distribution of Ta_2O_5 particles which may be supporting for more number of charge carriers to hop between favorable localized sites causing increase in conductivity. And conductivity of composites decreases from wt. 30% to wt. 50%. The decrease in conductivity from wt.30% to wt. 50% may be attributed to the trapping of charge carriers [11]-[12].

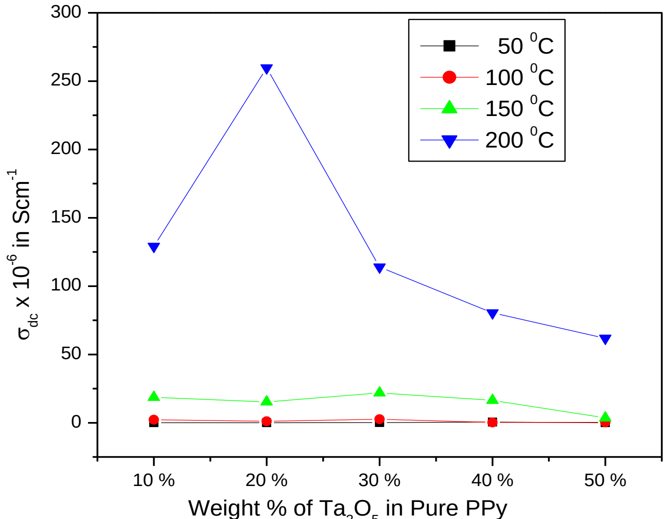


Fig.5. Variation of σ_{dc} as a function of the Wt. % of Ta_2O_5 in Pure PPy

The variation of the D.C. conductivities as a function of the weight percentage of Ta_2O_5in PPy at different temperatures as shown in Fig.5. In all the composites, the conductivity increases with respect to the temperature as compare to pure polypyyrole, forming multiple phases of conductivity. The values of the conductivity increases up to 20 wt. % Ta_2O_5 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 Ta_2O_5 is as high as 20%. This point is a percolation threshold and the composites obey percolation theory. Furthermore, a decrease in the conductivity can be observed after 20 wt. % and can be attributed to the distribution of Ta_2O_5 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 [11]-[12], [19]-[20].

CONCLUSION

Synthesis of polypyrrole/ tantalum pentoxidecomposites efforts has been made to tailor the transport properties. Detailed characterizations of the composites were carried out using SEM, XRD and FTIR techniques. The results of D.C. conductivities of polypyrrole/ tantalum pentoxidecomposites show a strong dependence on the weight percent of tantalum pentoxidein polypyrrole. Polypyrrole/ tantalum pentoxide composites may find applications in sensors.

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