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Synthesis, Characterization And DC Conductivity Studies Of Polypyrrole – BaTiO₃ Composites



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ABSTRACT

In-situ polymerization of pyrrole was carried out in the presence of BaTiO₃ (BT) to synthesize polypyrrole – BaTiO₃ composites (PPy/BT) by chemical oxidation method. The PPy/BT composites have been synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt % of BaTiO₃ in pyrrole. The polypyrrole – BaTiO₃ composites were characterized by employing X-ray diffractometry (XRD) and infrared spectroscopy (IR). The surface morphology of the composites was studied by scanning electron microscopy (SEM). The dc conductivity was studied in the temperature range from 40–200°C. The dimensions of BaTiO₃ particles in the matrix have a greater influence on the conductivity values. © 2006 Trade Science Inc. - INDIA

KEYWORDS

Polypyrrole;
BaTiO₃;
Conductivity;
Composites.

INTRODUCTION

In recent years electrical and optical properties of conducting polymers synthesized by electrochemical polymerization have been studied in great detail. Considerable attention has been paid to the polymers of five membered heterocycles such as polypyrrole, polythiophene and polyacetalene, since they can substitute for conductors and semiconduc-

tors in a wide variety of electric and electronic devices. The features of conducting polymers such as reversibility, availability in film form and good environmental stability enhance their potential use in practical applications. One of the most widely studied conducting polymers, polypyrrole (PPy), can be obtained chemically or electrochemically. The electrochemical polymerization of pyrrole has been extensively studied as it is easily obtained in the form

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of free standing films, and has good environmental stability and conductivity. It has been shown that polypyrrole (PPy) has many technological applications as secondary batteries^[1-3], electrochromic display devices^[4,5], light emitting diodes^[6,7], capacitors^[8,9], sensors^[10-12] and enzyme electrodes^[13-15].

The electrical transport in polymeric materials^[16-17] has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices. Similarly, conducting polymer composites have attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties^[18]. These materials are especially important owing to their bridging role between the world of conducting polymers 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 has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 Scm^{-1} .

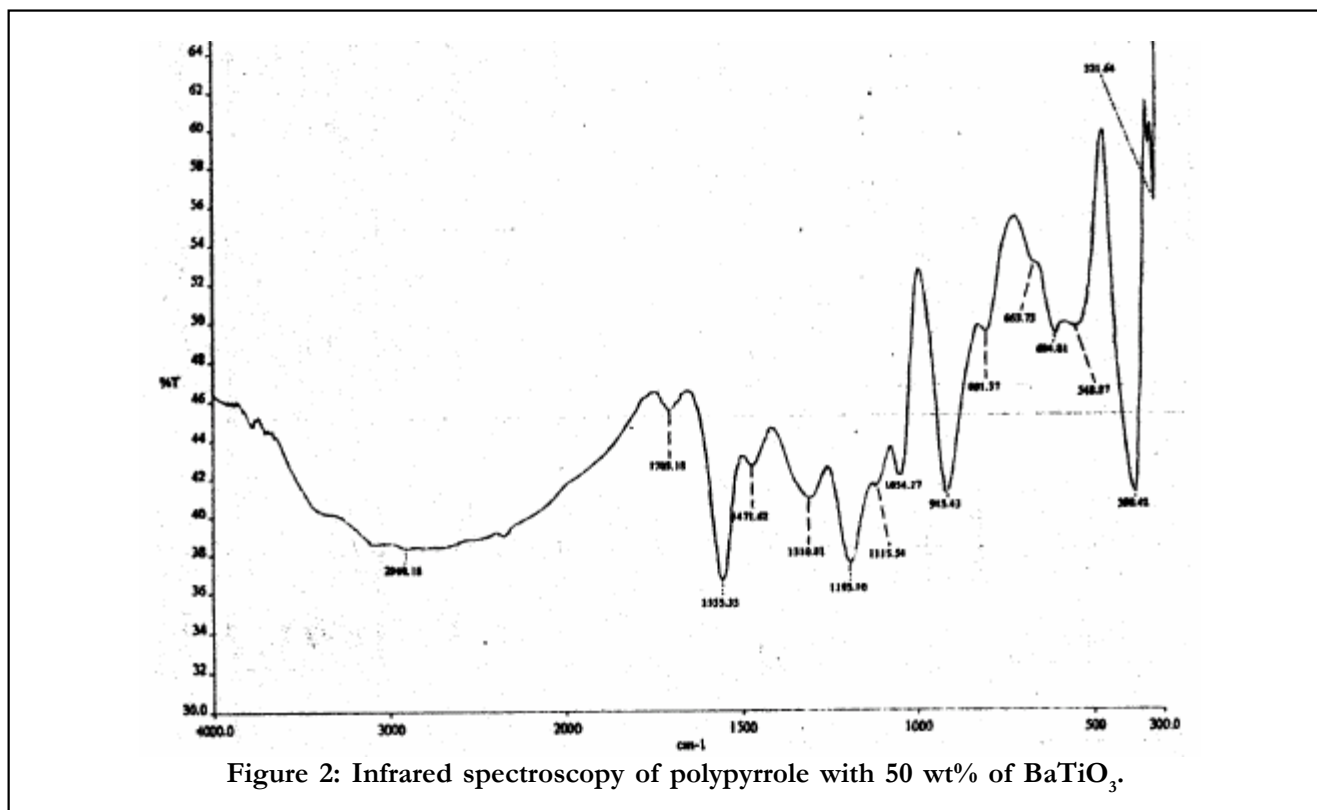
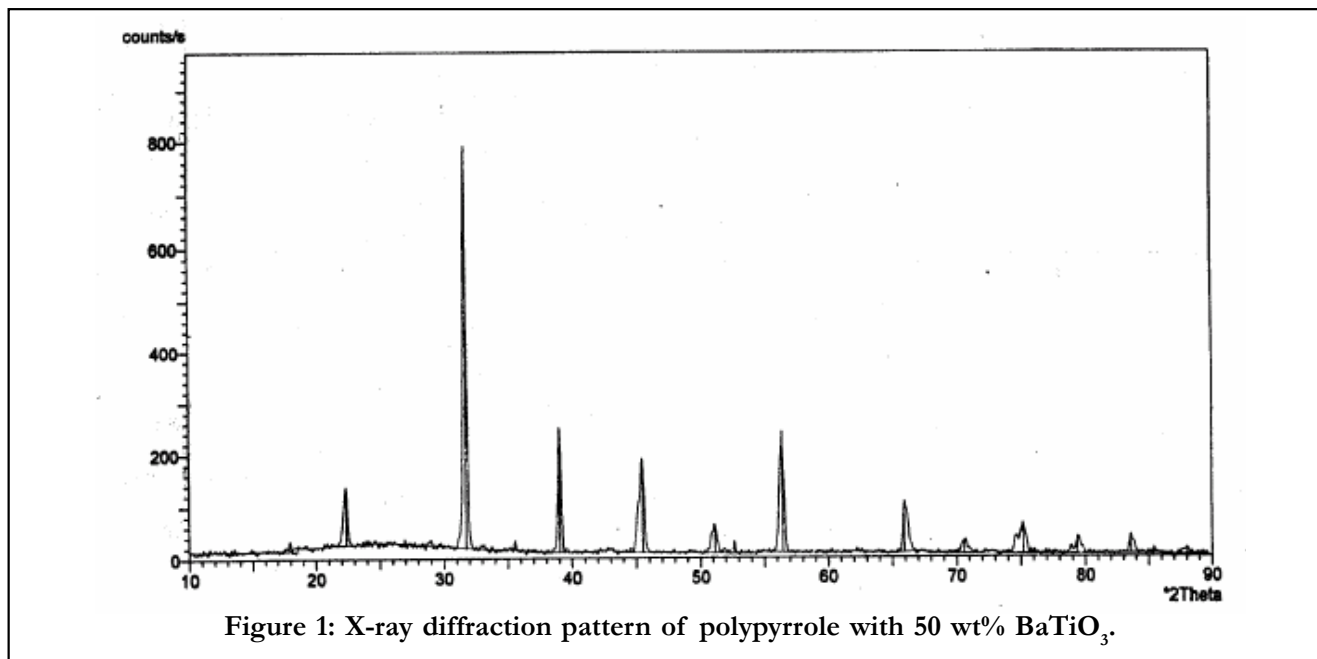
As was first reported by Italian chemists, pyrrole monomer is very readily polymerized to give a black conducting powder^[19]. This chemistry is particularly facile, taking place with a large number of oxidizing agents, and can even be observed taking place on the outside of bottles of pyrrole down which the monomer has been allowed to flow. The resulting conducting powders have been referred to as pyrrole black for many years. Oxidation of the powders with KMnO_4 has been shown to lead predominantly to the 2, 5-dicarboxylic acid, and this has been interpreted as evidence that the polymerization leads to an ∞, ∞' – bonded polymer^[19]. The polymerization can take place electrochemically^[20] as well as chemically. Chemically, pyrrole can be oxidatively polymerized in both solution and vapour phase^[20]. Though chemical oxidation usually leads to powders, films can be obtained by allowing the oxidation to take place at a solid or liquid surface^[20,21]; however, these chemically prepared films are of poor quality. In some

cases there is no evidence that these chemically prepared films have much in common with what is now meant by polypyrrole—indeed, they are not even conducting^[21].

Polypyrrole (PPy) is one of the most attractive polymers which has some special electrical properties. These properties originates from the fact that polypyrrole is an intrinsic conducting polymer and can be synthesized to have conductivities up to 1000 Scm^{-1} which approaches the conductivity of metals. Most practical polypyrroles have conductivities in the range of $1 - 100 \text{ Scm}^{-1}$. Ferroelectric materials can have unit cell structures with different degrees of complexity. When a –ve or +ve voltage is applied across opposite faces of a crystal, the small Ti^+ ions in the center of the cubic lattice are displaced up or down. While O^{2-} ions move down or up this polarization characterizes ferroelectric material. BaTiO₃ (BT) has the prototype cubic perovskite structure above 393 K. In this region the dielectric constant is given by Curie-Weiss law. In this work we presented our results on PPy/BT composites.

EXPERIMENTAL

The AR grade pyrrole was purified by distillation under reduced pressure. 0.03 M of distilled pyrrole was added to the solution of 0.06 M of ammonium per sulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ and the reaction mixture was stirred continuously at a constant temperature (5°C) to obtain polypyrrole. Different weight percents of BaTiO₃ powder (viz., 10, 20, 30, 40 and 50 wt%) synthesized from oxalate route was added to polypyrrole to obtain the composites. The resulting product was filtered and washed thoroughly with methanol (CH_3OH) and dried under vacuum at room temperature. The composites were pressed in the form of pellets of 1 cm diameter. The X-ray diffraction patterns of the samples were recorded on Philips X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range $20^\circ - 80^\circ$. The IR spectra of the samples were recorded on Perkin Elmer IR spectrometer (model 783) in KBr medium at room temperature. The SEM images of polypyrrole – BaTiO₃ composite (50 wt %) was investigated using Philips XL 30 ESEM Scanning Electron Microscope.



The dc conductivity of these composites was measured in the temperature range of 40 – 200 °C using laboratory made setup

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern of polypyrrole – BaTiO₃ composite with 50 wt % of BaTiO₃ in polypyrrole. The diffractogram shows a perfect crystalline phase due to the presence of

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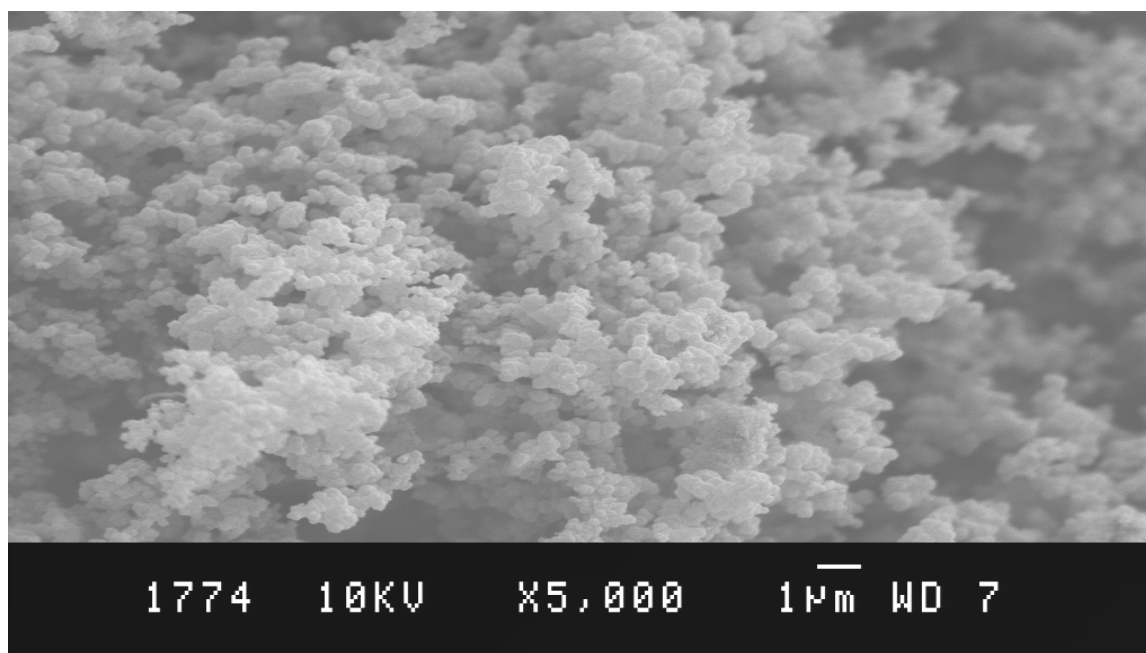


Figure 3: SEM micrograph of polypyrrole with 50 wt% BaTiO₃.

BaTiO₃. By comparing X-ray diffraction patterns of composites with that of BaTiO₃, the peaks at 31.72° has been assigned to (110) plane of perovskite structure and the one at 56.40° to the (222) plane of pyrochlore structure.

The IR spectrum of polypyrrole - BaTiO₃ composites is shown in figure 2. The characteristic stretching frequencies are observed at 1705, 1555, 1054, 915 and 548 cm⁻¹. They are shifted toward higher frequency side, which indicates that there is homogeneous distribution of BaTiO₃ particles in the polymeric chain due to the Vanderwall type of interaction between BaTiO₃ and polymeric chain.

Figure 3 shows a typical scanning electron micrograph of polypyrrole – BaTiO₃ composite having 50 wt % of BaTiO₃ in polypyrrole. It is observed that BaTiO₃ is homogeneously in the polymer matrix. It is also observed that the BaTiO₃ particles has needle like geometry. The dimensions of the needle like particles are found to be 650-820 nm in length and 160-180 nm in width. The presence of such sharp crystals has a strong influence on conductivity and dielectric behavior of the composites.

Figure 4 shows the variation of dc conductivity as a function of temperature for polypyrrole. The

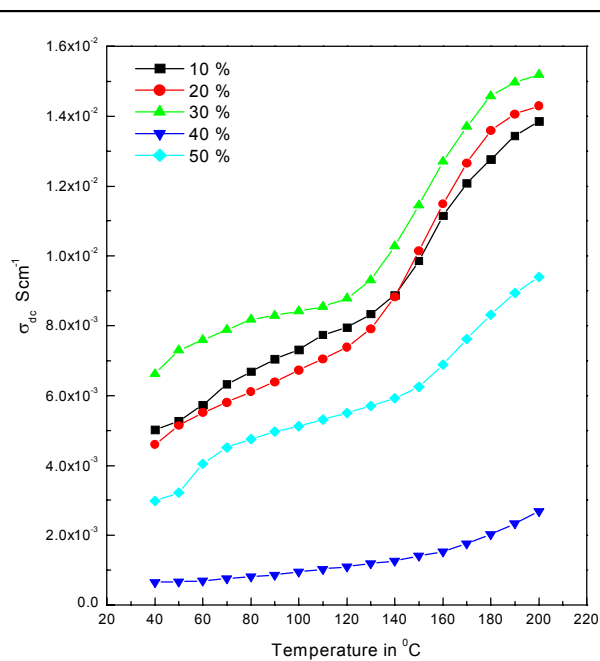


Figure 4: Variation of σ_{dc} as a function of temperature for Polypyrrole – BaTiO₃ composites

conductivity increases with increase in temperature. The dc conductivity of polypyrrole exhibit three phase in the temperature range 40°C to 200°C. In temperatures between 40-100°C, the conductivity values are almost constant and increases suddenly

in the temperature range 100-150°C. In stage III, between temperatures 150-200°C, a linear increment in the conductivity values is observed. Polymers can exist in different states depending upon the temperature. At low temperature they are hard, glassy materials. At a temperature referred as glass transition temperature T_g , they undergo transition to rubber like state. From X-ray diffraction pattern and SEM micrograph of polypyrrole employed in the present investigation shows semi crystalline behavior. Under such conditions a uniform crystallite is surrounded by amorphous regions. The crystalline contains some defects but by and large has a regular array of molecules. The localized states that forms extended band like structures may act in trapping the carriers from extended states of crystalline region. Lattice polarization around a charge in localized state may be responsible for multiple phases of conductivity in polypyrrole.

Figure 5 shows the variation of dc conductivity as a function of temperature for composites. 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 30 wt % of BaTiO₃ in polypyrrole and then decreases slightly for 40 wt % and increases there after. This may be due to the extended chain

length of polypyrrole which facilitate the hopping of charge carriers when the content of BaTiO₃ is increased to 30 %. The decrease in conductivity for 40 wt % may be attributed to the trapping of charge carriers. The later increase in conductivity for 50 % is due to the variation in distribution of BaTiO₃ particles which may be supporting for more number of charge carriers to hop between favorable localized sites causing increase in conductivity.

CONCLUSION

Efforts have been made to synthesize polypyrrole – BaTiO₃ composites to tailor make their electrical properties. Detailed characterization of the composites was carried out using XRD, SEM and IR techniques. The results of dc conductivity show a strong dependence on the weight percent of BaTiO₃ in polypyrrole.

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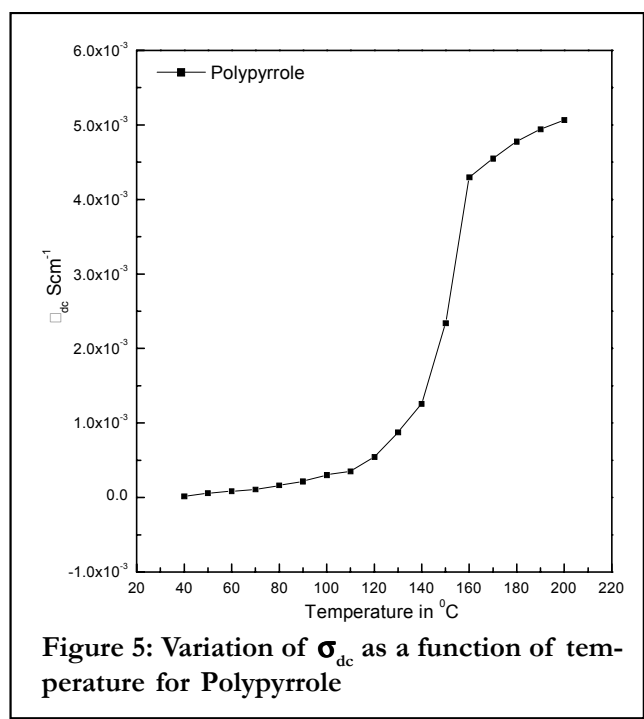


Figure 5: Variation of σ_{dc} as a function of temperature for Polypyrrole

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