THERMAL ANALYSIS AND DC CONDUCTIVITY OF POLYPYRROLE/YTTRIUM OXIDE COMPOSITES

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Abstract

Polypyrrole/Yttrium Oxide (PPy/Y_2O_2) Composites are synthesized by chemical method. Thermal stability of the above composites is characterized by TGA and DSC. Dc conductivity measurements of the composites are also carried out. The results are used to calculate the activation energy. Sensor activities of the composites are also discussed.

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1. INTRODUCTION

Organic and metallo-organic polymers gained importance because of their electrical, electronic, non-linear optical, electrochemical and photochemical applications (1-5). In order to make use of these polymer composites for specific applications, they are modified either by co-polymerization or by making blends with other polymers (6). Production of blends using organic and metallo-organic polymers is an attempt to derive new polymeric materials by combining the properties of the individual components of the blend (7). The use of blends/composites in various electric and electronic devices attracted attention because of their conducting nature, chemical stability and the economic viability. Among the many conducting polymers, PPy seems to be one of the best candidates for preparing conducting polymer composites since it is stable both thermally and environmentally (8). Conductivity of the polymer and polymer composites are explained by many literatures (9-11).

In this article, we present the study of thermal analysis of the PPy/Y_2O_2 composites. The Dc conductivity measurements of the composites are carried out by two probe method. Results are fitted with linear fit curve and activation energy is also calculated. Data is further tested by IV plots.

2. SYNTHESIS OF PPY/YTTRIUM OXIDE COMPOSITES

The synthesis of PPy/Yttrium oxide composites is similar to that of pure PPy, except that oxide is present during in situ synthesis. A 0.02 mole of pyrrole was added drop wise to 100 ml suspension containing 0.06 mole of $FeCl_3$ and varied amounts of Y_2O_3 (10%, 20%, 30%, 40% and 50%)powders with continuous stirring for 3 hrs. at 0 ^{0}C. The black precipitate of the PPy/Yttrium oxide composites formed was collected by filtration and thoroughly washed with distilled water, until the filtrate became colorless. Any unreacted pyrrole in the composite was removed by washing the precipitate with methanol and the composite was dried under vacuum at room temperature (24 ^{0}C).

The TGA of PPy, PPy/Yttrium oxide composites we recorded over a temperature range of 26 ^{0}C to 1200 ^{0}C in nitrogen atmosphere using a STA 409C thermal analyzer, to analyze the degradation pattern of polymer composites. Simultaneously, Differential Thermal Analysis (DTA) data was also recorded. Reference material used in the TGA/DTA is Alumina with heating rate of temperature is 5 ^{0}C/min.

Differential scanning calorimetric studies on PPy/Yttrium oxide composites were carried out using a METTLER thermal analyzer. DSC was recorded from 50 ^{0}C to 600 ^{0}C. The heating rate was kept constant at 10 ^{0}C per minute.

2.1 Effect of Temperature on Dc Conductivity:

2.1. Pellet Preparation

The powder of the PPy/Y_2O_2 composites are crushed and ground finally in the presence of acetone medium in agate, mortar. Finally ground powder is pressed to form, pellets of 0.1-0.25 cm. thickness and diameter of 10 mm or by applying a pressure of 90M Pa in a hydraulic press. The thickness of these pellets was measured using a micrometer screw-gauge.

2.1.2 Preparation of Electrodes on the Pellets

The pellets of Polypyrrole composites are coated with silver paste on either side of the surfaces. The copper electrodes are placed on each of the surface to obtain better electrical contacts.

2.1.3 Thermal Analysis:

The DTA and TGA traces of pure PPy and PPy/Y_2O_2 sample shows small exothermic dip at 69.9 ^{0}C which may be for the loss of dopant and an endothermic shoulder at 90.8 ^{0}C corresponding to the loss of water molecules. This is followed by the broad exothermic peak may be due to the degradation of the PPy chains.

Initially the steep trace TGA consists of two stages of weight loss, one from room temperature to 150 ^{0}C and another from 200 to 400 ^{0}C. Further as the degradation continues and complete at about 1100^{0}C. Steep trace of PPy indicates amorphous nature. The first stage weight loss may be due to water and the weight loss found to be 7.02%., the second stage weight loss may be due to the degradation of PPy-Cl chain, and the weight loss at this stage is-21.73%. The total weight loss at 1100 ^{0}C is about -95%.

This ensures the complete degradation of the polymer. The onset temperature (T_{onset}) and T_{max} for second step degradation is 310 ^{0}C and 400 ^{0}C, respectively. These are also confirmed from the DTG trace. Similarly on set temperature for the composites are shown in the table

Table 1: Indicate the onset temperature and weight loss from TGA for PPy and PPy/Y_2O_3 composites

Composites	Onset Temperature ^{0}C (from TGA)	Completed degradation Temperature ^{0}C	Total loss Occurred (from TGA)	Temperature At which Maximum Weight loss ^{0}C (From DTA)
PPy	69.9	1100	95%	704
PPY/20%Y_2O_3	70.2	1000	80%	846
PPy/50%Y_2O_3	74.9	920	53%	897

The DSC curve of PPy and PPy/Y_2O_3sample have a broad characteristic endothermic dip indicates the glass transition temperature of Polypyrrole at 97.32 ^{0}C. The nature of the curve indicates that the loss of water is overlapping with T_g of polymer (which is well matching with the reported value). Lack of any shoulder or melting peak beyond this region indicates amorphous nature with less orderness of the polymer molecules.

The DSC curve of PPy/50%Y_2O_3composite trace has a sharp dip at higher temperature, namely at 125.16 ^{0}C. This sharpness indicates the better crystalline. It also contains few more inflection points; one at 295.74 ^{0}C may be due to the melting of PPy chain, the other at 489.87 ^{0}C may be due to phase change of Y_2O_3.

2.2 Effect of Temperature on Conductivity Ppy/Y2o3 Composites

Figure 1 shows the temperature dependence of σ_{DC} for the PPy and PPy/Y_2O_3Samples. In this figure symbols indicate log values of experimental conductivities (for temperature range from 100-200 ^{0}C) for various composites. Solid lines indicate their fitting by linear fit equation by using the origin 6.0. The conductivity of all the composites shows that, as the temperature is increased conductivity increases. This figure also indicates that, conductivity increases as the percentage of oxide is increased and then for further increase in oxide content the conductivity decreases. Conductivity of polymer depends on the conjugation length. In the synthesis process, pyrrole monomer was first adsorbed on the surface of Y_2O_3Concentration, and as a result, the amount of pyrrole associated with each CeO_2 concentration, and as a result, the amount of pyrrole associated with each Y_2O_3 particle is diminished.

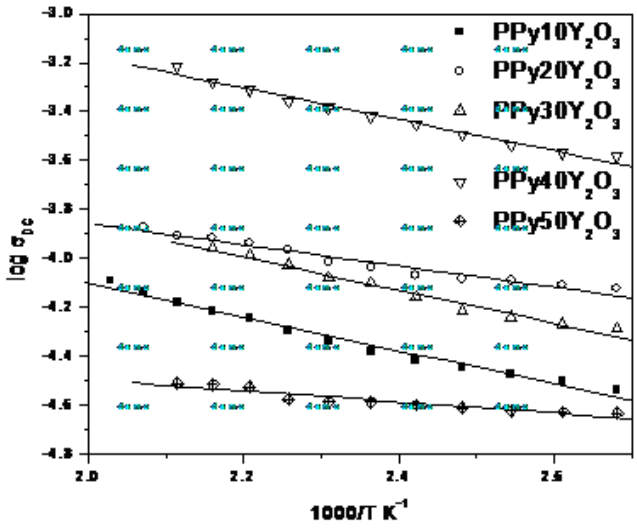

Figure 1: Arrhenius plot of conductivity of PPy/Y_2O_3samples

The temperature variation of conductivity of PPy composites is well described by Mott's variable range hopping formalism. This is applicable only in amorphous semiconductors. This is applicable only in amorphous semiconductors. Larger activation energy Implies higher potential barrier in the conduction process originating from the reduction of polymer chain length. Lower conductivity and higher activation energy are due to the poor contact between the polymer and oxide particles. Dispersion of oxide in the conducting polypyrrole due to percolation introduces more conducting paths resulting in higher conductivity. Loading in the polymer increases the conductivity is explained in literature (12)

Table 2: Indicates the activation energy of the conduction process for PPy/Y_2O_3 $_{samples}$. It indicates that as the oxide content Increases the activation energy goes on decreasing. But in case of PPy/40% Y_2O_3shows highest activation energy

Table 2: Activation energy for PPy/Y_2O_3composites

composites	Activation Energy me V
Pure PPy	302.85
PPy/10%CeO_2	203.98
PPy/20%CeO_2	194.98
PPy/30%CeO_2	149.51
PPy/40%CeO_2	94.08
PPy/50%CeO_2	393.23

Current Voltage plot of PPy CeO_2 composites:

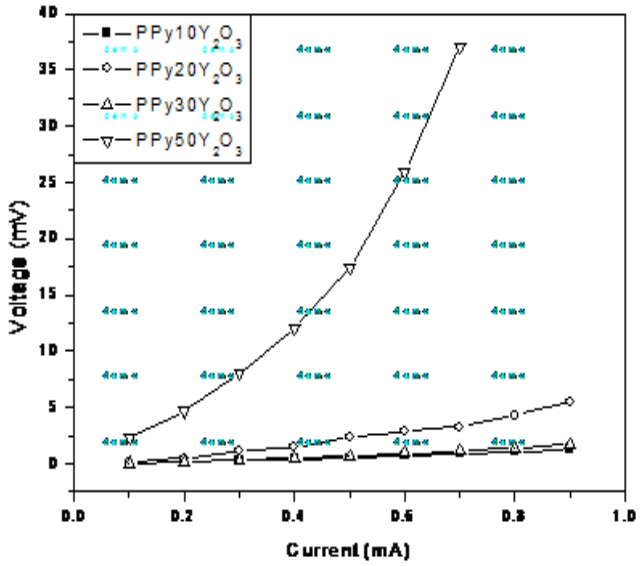

Figure 2: Representative Current -Voltage plots of PPY/Y_2O_3 samples

Figure 2 show the current voltage plots of the representative PPy/Y_2O_2 composites respectively. They show very good linearity in the range studied. Beyond this range thermal fluctuations due to significant joule heating take place and non linearity sets in.

CONCLUSIONS

PPy/Y_2O_3 composite shows the high thermal stability due to metal oxides. Activation energy of these compostes shows highest for ppy/50% Y_2O_3 due to more metal oxide particles increases the higher activation energy. It will be maximum upto critical percentages latter activation energy decreases. Current voltage characteristics of these polymer composites are also accounted. These electrical properties of polymer PPy/Y_2O_3 composites have strong applications in battery and sensor applications.

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