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Thermal Characterisation of PPy/$CeCl_3$ Composites Synthesized by Simple Chemical Oxidative Polymerization Method

KEYWORDS

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ABSTRACT *This paper describes the synthesis and characterization of polypyrrole (PPy) doped with Cerium Chloride (CeCl3). The synthesis method is based on chemical oxidative polymerization of pyrrole added with 0.01 and 0.2 M concentration of CeCl3 in the presence of ammonium peroxydisulphate as an oxidant. The thermal characterization of composites was carried out through TG and DT analysis and the results were compared with pure PPy. The TGA and DTA analysis of synthesized composite materials reveals that stability of materials is increased after doping with CeCl3.*

Introduction:

Polymer have traditionally been considered as good electrical insulators but from few decades researchers have shown that certain class of polymer which are conjugated having extended π-conjugation along the polymer back bone chain can be easily tailored in their structure and exhibit a further dramatic increase in the conductivity of such conjugated polymer [1]. Some of the conducting polymers such as Polyaniline, Polypyrrole and Polythiophene have emerged wide range of applications such as conducting films, Field Effect Transistors (FETs), Electroluminescent devices, Solar cells, Photochemical resists, Non linear optic devices, Chemical sensors, Electrochromic devices (ECD), Light Emitting Diodes (LED) and thus founds as a materials with immense potential in technological applications [2-4]. Another application for conducting polymers is controlled release devices. Principle used in this application is potential dependence ion transport. This potential dependence ion transport is an interesting way to deliver ionic drugs to certain biological systems. Thus there have been considerable interests to replace conventional Inorganic semiconductors by their organic counter parts [5].

Among these Polypyrrole is one of the most extensively studied materials due to its ease of synthesis, good environmental stability and versatile electrical properties. It has found a considerable application in electronics, technological, optical and biomedical fields [6]. So efforts to overcome these drawbacks have led to numerous studies on the synthesis of polypyrrole by electrochemical and chemical routes [7].

The early problems associated with the stability and solubility of this conducting polymer has largely been overcome by using chemical intuition and experimentation by using various dopants and formation of its composites with different materials have contributed to the modification on polypyrrole structure results into changes in the properties of polypyrrole [8]. Hence, it appeared sufficiently interesting to synthesize modified polypyrrole at different concentration of various dopants to investigate its properties and structure. In the present research contribution Polypyrrole has been synthesized by simple chemical oxidative polymerization methods and its thermal properties are studied by using TG and DT analysis.

Experimental:

The 0.1 M solution of AR grade pyrrole was contained in a beaker which was placed on a magnetic stirrer. 0.1 M ammonium peroxydisulphate (APS) solution was continuously added drop-wise with the help of a burette to the above 0.1 M pyrrole solution. The reaction was allowed for 6 hours under continuous stirring by maintaining a temperature of 0°C to 5°C. The precipitated polypyrrole was filtered and dried in hot air oven and subsequently in a muffle furnace at 100°C. For 0.1 M pyrrole solution, 0.1 M solution of $CeCl_3$ was added and mixed thoroughly, further 0.1 M ammonium persulphate was continuously added drop-wise with the help of a burette to the above solution to get PPy/0.1 M $LaCl_3$ composite. Similarly PPy/0.02 M $CeCl_3$ is also prepared by following the above procedure. The pure PPy and PPy/$LaCl_3$ thin films were prepared by bath deposition technique.

The synthesized composite materials were subjected to thermal studies through TG and DT analysis.

Results and Discussion:

As the conducting polymers are useful in number of electronic applications. It is necessary to study its themal properties. The effect of temperature on stability of polymer is studied by TGA/DTA analysis. TGA gives the information regarding to weight loss in material with increasing temperature and DTA is useful to determine glass transition temperature (T_g).

The TGA thermograms of PPy and PPy/$CeCl_3$ composites are given below in fig 1-3.

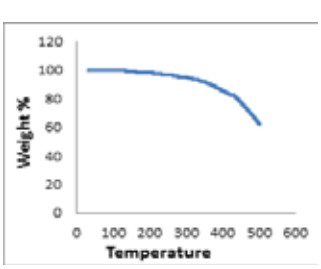

Fig 1:TGA curve of Polypyrrole

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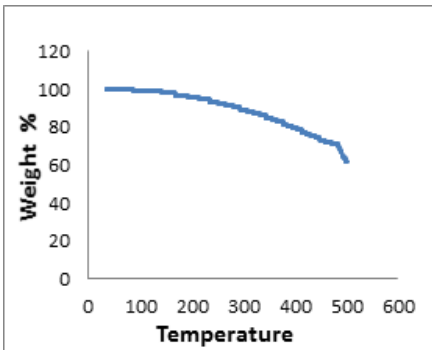

Fig 2: TGA curve of PPy/0.01 M $CeCl_3$

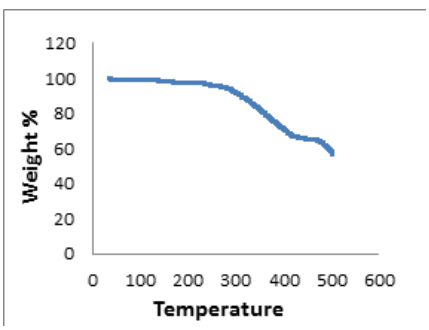

Fig 3: TGA curve of PPy/0.2 M $CeCl_3$

The thermal characteristic of PPy and PPy/$CeCl_3$ composite was studied by using thermogravimetric (TGA) technique (instrument DTG-60) by heating in the range 10°C/min from room temperature to 550°C in air. All the PPy and PPy/$CeCl_3$ were observed to exhibit three distinct weight losses as shown in fig1-3. The first stage of weight loss (~5%) at about 80-120°C is associated with the evaporation of solvents, moisture as well as unreacted monomers elimination. Heating of polymer at further high temperature (250-400°C), the weight loss of about 25-30 % occurs due to the loss of dopant component of the PPy. The drop in weight (~55-60%) observed at 400-500°C is due to the degradation of the PPy itself. PPy samples are thermally stable in the temperature range of 25-450°C and beyond this range; the decomposition route becomes very rapid. The residual weight of the PPy is about 40% in the oxygen atmosphere, which indicates that PPy does not completely decompose in O_2 even at high temperature.

The weight loss in each step and total weight loss for different weight % at different temperature for different composite materials of PPy composite is given in table 1.

Table 1: Weight Loss in each step for PPy/$CeCl_3$ composite

S.N.	Polymer Composite	Weight Loss (%)				
		Step I 50-120°C	Step II 250-400°C	Step III 400-500°C	Total wt loss (%)	Residue
1.	Pure PPy	0.38	12.57	47.65	60.6	39.4
2.	PPy/0.01M $CeCl_3$	1.08	19.36	36.56	57	43
3.	PPy/0.2M $CeCl_3$	1.972	27.33	41.972	71.274	28.726

Above table conveniently explains that first step of weight loss occurs in the temperature range 50-120°C and the weight loss at this range is quite low i.e., 0.38-2.0%. The second weight loss occurs in the range 250-400°C in which weight loss is nearly 12-27 % occurs, while third step weight loss is upto 35-50% in the temperature range 400-550°C. This indicates that loss of low fragment molecular weight takes place during heating. Above 550°C there is no weight loss is observed which indicates increase in thermal stability of the polymer composites.

DTA curves for PPy/$CeCl_3$ composites are explained in figures 4-6

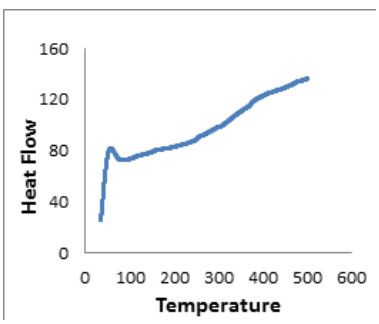

Fig 4: DTA curve of polypyrrole

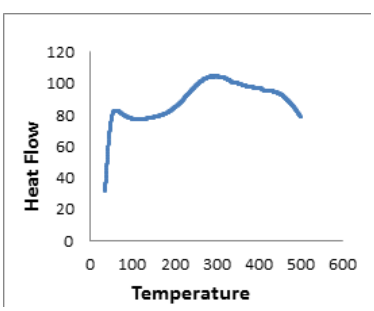

Fig 5: DTA curve of PPy/0.01 M $CeCl_3$

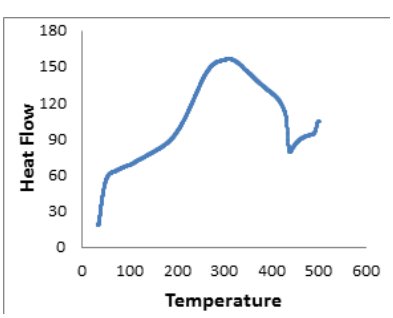

Fig 6: DTA curve of PPy/0.2 M $CeCl_3$ composites

Table 2: Thermodynamic Parameters from DTA curve of PPy/$CeCl_3$ composites

Polymer Composite	Glass transition Temp.(T) (° C)	Crystallization Exothermic Peak		
		Onset temperature (° C)	Peak temperature (°C)	End temperature (°C)
PPy	63.49	221.42	328.21	479.23
PPy/0.01 M $CeCl_3$	59.77	168.44	295.37	498.05
PPy/0.2M $CeCl_3$	51.34	158.02	300.07	460.85

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These DTA curve gives the glass transition temperature (T_g) which determines the softening of the polymer. The TG curve is analogous to DTA curves as the variation in TG curve will give the simultaneous variation in DTA curve.

The various parameters such as glass transition, onset and end temperatures from DTA curves are tabulated in table 2. It is observed that the glass transition temperature decreases with increasing content of $CeCl_3$. This means that the addition of $CeCl_3$ relives the structure of polymer composites and it becomes soft. The strong exothermic peak is observed above 300° C shows degradation started above this temperature.

Conclusion:

The above discussion reveals that efforts have been made to synthesize the polypyrrole/Cerium chloride composites to tailor the structural, morphological, and electrical properties of polypyrrole. Detailed thermal characterizations of the synthesized composites through TGA and DTA studies indicate the incorporation of dopant into the polymeric chain with increased stability.

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