THERMAL STUDIES OF POLYPYRROLE- NiZnFe$_2$O$_4$ NANOCOMPOSITES

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Abstract- **Thermal behavior and thermal stability of polypyrrole and Polypyrrole - NiZnFe$_2$O$_4$ (10% - 50%) nanocomposites prepared by in-situ polymerization method were studied by Thermogravimetric Analysis (TGA) and Differential thermal analysis (DTA) techniques. Thermo gravimetric analysis showed significant decrease in weight loss in nanocomposites compared to pure Ppy indicating decrease in thermal stability of the host matrix due to the incorporation of nano particles. All nanocomposites exhibit almost same thermal behavior as that of host polymer Ppy. Differential thermal analysis reveals the existence of a endothermic peak and an exothermic one corresponding to various physical and chemical changes taking place in pure polymer and composites subjected to heating.**

Index Terms- **Polypyrrole, nanocomposites, Nickel zinc iron oxide, TGA/DTA, Thermal properties, Thermal degradation**

I. INTRODUCTION

Polymer nanocomposites consisting of conducting polymers and metal nanoparticles have received considerable attention due to the potential possibilities to create suitable materials for electrocatalysis, chemical sensors, electronic devices, memory devices, lithium batteries, Energy storage, Microwave absorbers, electromagnetic shielding, etc; [1-2]Conducting polymers are the class of polymer that possess good tunable electrical conductivity. But they are chemically sensitive and have poor mechanical properties; on the other hand, nanomaterials possess good mechanical properties. Thus by reinforcing nanoparticles like oxides into conducting polymers nanocomposites can be formed which possess outstanding properties due to synergistic effects of the component materials. Polypyrrole (Ppy), a conducting polymer is a good host material due to its good thermal-stability, special transport properties, facile synthesis, tunable conductivity, good environmental stability and chemical stability[3]. Ppy is an important material in view of its large scale applications and addition of a small amount of dopant into Ppy matrix can tune its physical, chemical, electrical and thermal properties to a great extent. Nanomaterials are attractive dopants because of their high surface reactivity, which is attributed to high surface to volume ratio. The Thermo gravimetric Analyais (TGA) study on Ppy- NiZnFe$_2$O$_4$ nanocomposites showed that the barrier effect of nano NiZnFe$_2$O$_4$ on Ppy matrix increased the thermal resistance of Ppy. This paper reports the thermal behavior of Ppy- NiZnFe$_2$O$_4$ nanocomposites as a function of dopant concentration to understand the influence of nano NiznFe$_2$O$_4$ on Ppy matrix.

II. EXPERIMENTAL DETAILS:

Chemicals - The monomer pyrrole, , nanopowder Nickel zinc iron oxide, oxidising agent Ammonium persulphate were purchased from Sigma Aldrich. All chemicals were of analytical grade and used as received without any further treatment.

2.1.Synthesis of Polypyrrole

Ppy was synthesized by in-situ polymerization of monomer pyrrole in the presence of oxidising agent ammonium persulphate. 0.3M pyrrole taken in a round bottomed glass flask was placed in an ice tray mounted on a magnetic stirrer. 0.6M Ammonium persulphate was added drop wise using a burette to the above 0.3M pyrrole .The reaction was carried out for 5hours under continuous stirring maintaining temperature of 0 to 5 degree Celsius. The resulting precipitate was removed by filtration by suction. The

polypyrrole powder thus obtained was then dried in a hot air oven and subsequently in a muffle furnace at a temperature of 100 degree Celsius. The yield was 2.15 gm, taken as 100Wt% [4].

2.2. Synthesis of Ppy-NiZnFe$_2$O$_4$Nanocomposites.

Ppy /NiZnFe$_2$O$_4$ nanocomposites were synthesized by the same method. For 0.3M pyrrole solution, 0.215 gms (10 wt.%) of NiZnFe$_2$O$_4$ was added and mixed thoroughly in a round bottomed flask. O.6M ammonium persulphate was added drop-wise with the help of burette to the above solution and the entire procedure is repeated to get 10wt% composite. Similarly 0.430g, 0.6g, 0.860g, 1.075g of nanopowder is taken and the entire procedure is repeated to get 20, 30, 40 and 50 wt% Ppy/ NiZnFe$_2$O$_4$ nanocomposites. The immiscibility of heterophases of the polymer and NiZnFe$_2$O$_4$ constituents has been resolved by ultrasonicating the mixture, which has ensured the homogeneous dispersion of nanoparticles in the polymer matrix [5].

2.3 TGA/DTA Measurements.

Thermo gravimetric analysis measurements were carried out to investigate the thermal stability of PPy by employing Perkin Elmer thermal analyzer between 40°C to 730°C at a heating rate of 20°C/min in N$_2$ atmosphere.

III. RESULTS AND DISCUSSION

3.1 Thermogravimetry analysis (TGA)

The thermal stability of pure PPy and PPy/NiZnFe$_2$O$_4$ nanocomposites was investigated by TGA measurements. In thermogravimetric analysis, The variation of weight losses of the samples with increase in temperature are observed. Weight losses occur as a result of driving off volatiles and at higher temperatures, degradation products. The degradation mechanism isconsidered to be a combination of two or more process. One is the reaction of the host polymer with the dopant anion, and the other is the reaction of the polymer with oxygen or water. It is also possible that the dopant species itself might undergo thermal degradation and the products of this degradation could react with the polymer backbone [6]. Fig.1 shows the thermogravimetric profiles of

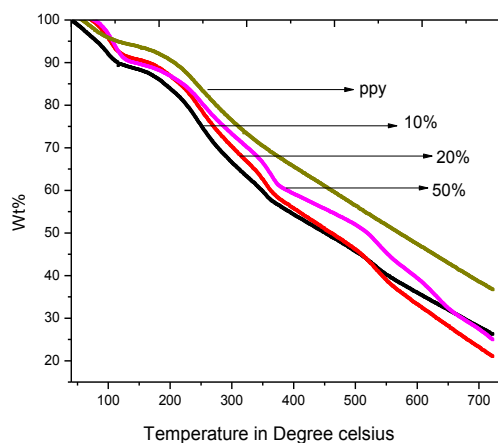nanocomposites with different particle loadings (10, 20 and 50 wt%).

Fig.1 Variation of residual weight (%) of composites with temperature

All the samples showed a three step weight loss as seen from Fig.1 and tabulated in Table 1. Variation of weight is almost linear and the maximum polymer decomposition temperature is there from 40 °C to 740°C for all. In the Figure1, two major weight loss stages for PPy were observed at 110 °C to 130°C and 723°C. The weight loss at temperatures lower than 120 ^{0} C is due to the removal of the physically adsorbed water. The melting of Ppy is around 200^{0}C and at higher temperatures the polymer undergoes a thermal decomposition. while the major loss at temperatures higher than 240^0 C is due to the decomposition of PPy.[7-8] The starting weight of 1.968 mg is reduced to 0.722mg at 723^{0}C

The thermal decomposition occurs at 2 different stages in pure Ppy and Ppy/ NiZnFe$_2$O$_4$ nanocomposites. Major weight loss was observed in the first decomposition stage in the range 113-208 degree Celsius with gradual weight loss of 9.5%. This was followed by a second decomposition in the temperature 208 -719 with weight loss of 64%. The differences in the residue reflect the different amounts of NiZnFe$_2$O$_4$ nanoparticles present. In addition, pure PPy formed with the aid of NiZnFe$_2$O$_4$ nanoparticles shows less stability than that formed without them. The thermal stability decreases slightly with nanoparticle loading, which is believed to be due to both the higher mobility of the polymer chains when the polymer chains are bound onto the

nanoparticles and stronger chemical interaction. The maximum weight loss is observed (80%) in the case of nanocomposites of 20%, For the remaining composites the Weight loss % lies between 66% to 75%. Greater weight loss at each stage and decrease in product residue indicates less stability of the composites. The weight loss is least in pure ppy compared to nanocomposites, which indicates that pure Ppy has more thermal stability compared to nanocomposites. [9-10].
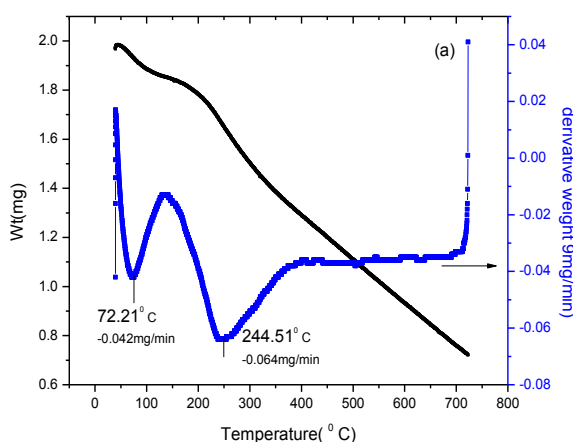
The first-order derivative of TGA curves as shown in figure 2. These TGA curves reveal the temperature at which the maximum decrease of mass occurs. The TGA data clearly shows that the side chains of Ppy decompose earlier than the main chains. For ppy the main endothermic peak is around 244.51°C at which 0.064mg/min is decomposed.
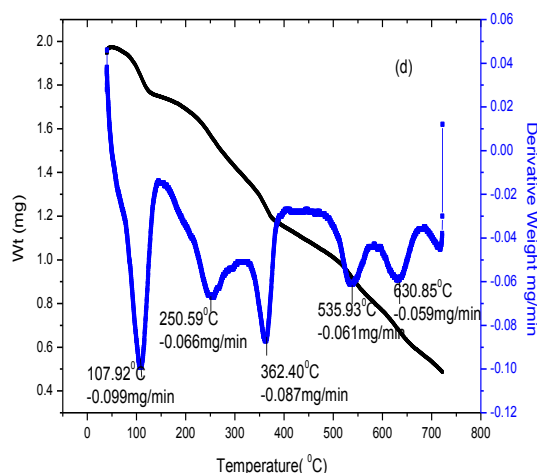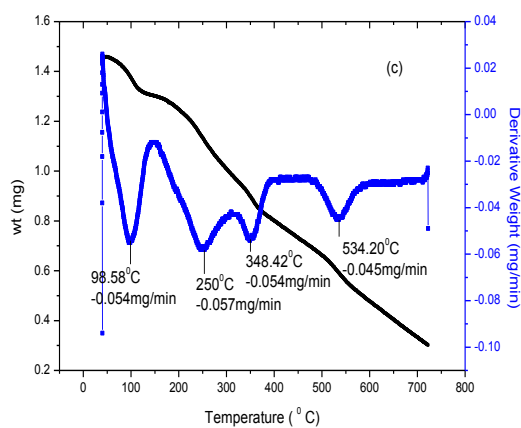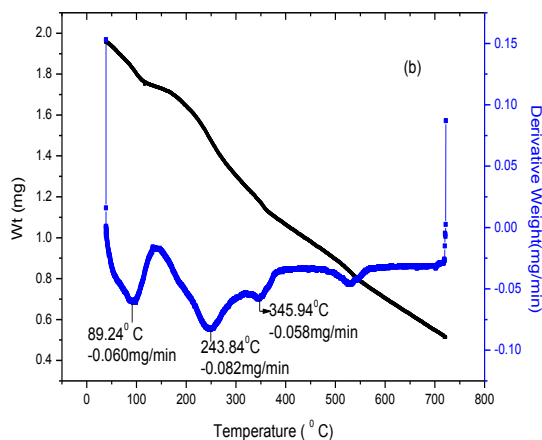

Fig.2. Derivative Weight thermogram of (a)Ppy (b)10% (C)20% d50% Ppy/NiZnFe2O4composites

For nanocomposites the main endothermic peaks lie in the range 243°C – 362°C. The maximum weight loss of the ppy-NiZnFe$_2$O$_4$ composites are shifted to higher temperature compared to pure Ppy and also increases systematically with the addition of NiZnFe$_2$O$_4$. The decrease in the weight loss with the addition of Nanoparticle NiZnFe2O4 may be due to the cross linking of Ppy matrix and NiZnFe$_2$O$_4$ leading to stronger intermolecular bonding. [11-12].

3.2 Differential Thermal Analysis

Thermal stability of pure Ppy and Ppy nano composites can also be analyzed from DTA technique. It is most commonly used to determine transition temperatures such as glass transitions, melting cross-linking reactions and decomposition. However, it measures only the total heat flow and the

sum of all thermal transitions in the sample. The DTA thermograms are shown in figure 3. The materials have been heated from 40 °C to 740 °C under a constant heating rate of 20 °C/min . A endothermic event and a exothermic one were observed in DTA curve of each sample. In pure Ppy, the endothermic peak at 121.32^0C is related to the removal of the   physically adsorbed water and the thermal phase transition of polymer matrix from glassy to rubbery state. The large exothermic peak at 406.92^oC indicates the beginning of degradation of the polymer. The endothermic peak observed in 110^oC-120^oC temperature range in case of nanocomposites   has been shifted to lower temperature compared to pure Ppy. This indicates the removal of physically adsorbed water and thermal phase transition taking place at an early stage in nanocomposites in comparison with Ppy [13-14]. The exothermic peak was observed in the temperature range of 396^oC- 412^oC in the composites indicating

(a)

(b)

(c)
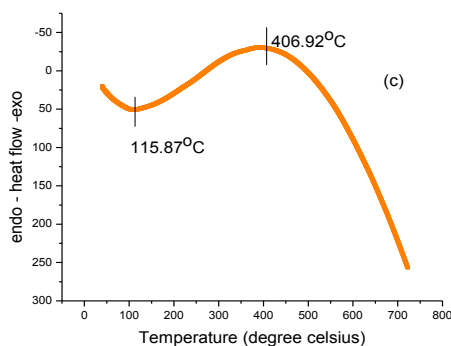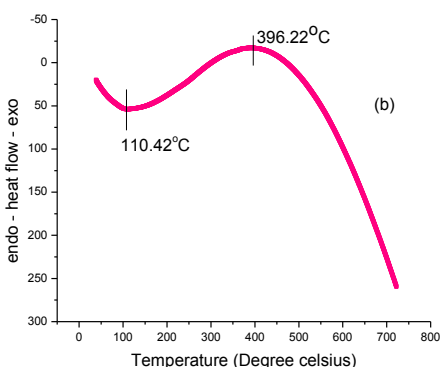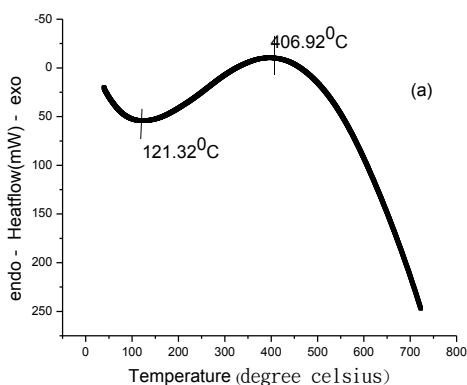
increase in the beginning of complete degradation temperature in compared to Ppy. The glass transition temperature and complete degradation temperature

(d)
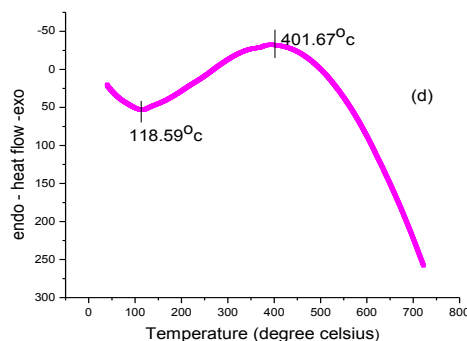
obtained from results of DTA thermograms are shown in the Table 2.

IV.   CONCLUSIONS

Ppy and Ppy-NiZnFe$_2$O$_4$ nanocomposites were synthesized by in-situ polymerization method and their thermal behavior was studied using TGA and DTA techniques. The melting point of all the samples was nearly the same indicating negligible effect of NiZnFe$_2$O$_4$ on it. The glass transition temperature decreases for Ppy/NiZnFe$_2$O$_4$ of 10, 20, 30 and 50% composites, and it is same as pure Ppy for composites of 40%. The final degradation temperature of the composite was noticed to be increased and final residual mass was found to be more compared to pure Ppy indicating the overall improvement in the thermal stability of composites. The maximum thermal stability has been observed in the 50% NiZnFe$_2$O$_4$ composites.

Table1. Thermogravimetric (TGA) data for pure Ppy and Ppy-NiZnFe$_2$O$_4$ composites

Sl. No	Sample	Temperature in 0 C		Weight loss %		Sample	Temperature in 0 C		Weight loss %
1	**Ppy**	I Stage	42-113	4.76	4	**30%**	I Stage	42-118	7.65
		II Stage	113-208	9.5			II Stage	118-219	15.1
		III Stage	208-719	64			III Stage	219-720	66
2	**10%**	I Stage	42-121	11	5	**40%**	I Stage	44-128	10.8
		II Stage	124-208	17			II Stage	128-238	19
		III Stage	208-722	73			III Stage	238-720	67
3	**20%**	I Stage	42-121	8	6	**50%**	I Stage	40-124	9
		II Stage	121-230	17			II Stage	124-230	16
		III Stage	230-720	80			III Stage	230-720	74.6

Table2. Glass transition temperature (T$_g$), and complete degradation temperature.(T$_d$)

Sample	Endothermic peak (Tg°C)	Exothermic peak (T$_d$)°C
Ppy	121.32^0 C	406.92^0 C
10%	110.42^0 C	396.22^{0}C
20%	115. 87^{0}C	406.92^0 C
30%	110.42^{0}C	412.37^0 C
40%	121.32^{0}C	406.92^0 C
50%	118.59^{0}C	401.67^{0}C

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