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Structural & Thermal properties of PANI/ Fe_2O_3

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ABSTRACT : *Synthesis of Polyaniline/iron oxide composites (PANI/Fe_2O_3) have been implemented by oxidative polymerization of Polyaniline using various amounts (10, 20, 30, 40, 50 wt %) of the Fe_2O_3 particles using oxidant ammonium persulphate. The analysis of composites has been done by X-ray diffraction (XRD). Crystalline nature of the samples has been established by X-ray Diffractogram. Thermal stability has been calculated using TGA and exhibits an enhanced value of the thermal stability for PANI/Fe_2O_3 composites as compared to PANI.*

KEYWORDS - *Polyaniline, XRD, SEM, TGA.*

I. INTRODUCTION

Conducting polymers are magnificent, exclusive materials having prominent physical properties and substantial applications in science and technology. The unique properties of conducting polymers furnishes great horizon for their applications and also led to the evolution of new models to describe their observed properties, particularly various processes and mechanisms of charge transport [1]. Among different conducting polymers, polyaniline is the most substantially studied materials due to the better thermal and environmental stabilities and also it can be synthesized easily. However, when conducting polymers are synthesized in the composite form their structural, electrical, thermal as well as dielectric properties are altered from those of basic materials. Polyaniline and polypyrrole are becoming increasingly important for their technological importance due to their electrical, optical properties and their high air, chemical and electrical stability at ambient conditions and in field effect transistors [2–4]. Various applications of PANI have even attained significance role in the commercial industry like, electrodes of rechargeable batteries [5], artificial nerves and muscles [6], gas sensors [7], transducers for biosensor [8], diodes, solid electrolytic capacitor, and transistors [9, 10], biomedical applications [11] and anti-static electromagnetic shielding [12].

In composite form, the properties of PANI change significantly. The addition of inorganic particles to polymers allows the modification of polymer's physical properties as well as the implementation of new features in the polymer matrix. Although a number of studies on composites of PANI and transition metal oxides have been reported [13,14] and further researches are still going on at their various properties and applications, calculation of different parameters of PANI/Fe_2O_3 composites using TGA have not been described in the published papers till now. So in the present investigation, the synthesis of PANI/Fe_2O_3 composites with different doping concentrations has been implemented. The characterizations of all these samples have been performed using X-ray diffraction (XRD), Thermal analysis and SEM.

II. EXPERIMENTAL DETAILS

2.1 Synthesis of PANI and PANI/Fe_2O_3 composites

The chemicals of analytical grade (AR) were used to make all the solutions cooled in the refrigerator for 2-3 hours before mixing. PANI was synthesized by *in situ* polymerization, i.e. oxidizing 0.2 M aniline hydrochloride (Aldrich) using 0.25 M ammonium persulphate (Aldrich) in aqueous medium as an oxidant [14]. Iron oxide (0.1 M) with weight % (10, 20, 30, 40 and 50) has been added to the aniline hydrochloride solution with vigorous stirring, add 0·25M of ammonium persulphate as an oxidant slowly at 0–4 °C and left for 24 hours at rest in refrigerator to polymerize [15]. The precipitates were vacuum filtered and washed with 1M HCl and acetone till the filtrate turns colorless. At last the precipitate was dried firstly in air and then in a vacuum oven at 45^0C for one day. In this manner synthesis of PANI/Fe_2O_3 composites has been implemented and named as F1, F2, F3, F4 and F5.

2.2 Analytical techniques

The characterization technique like X-ray diffraction studies were performed on Rigaku Table-Top X-ray diffractometer with Cu Kα as source of radiation. TGA analysis has been accomplished by TA instrument (model no.SDT Q600) at heating rate of 10^0C/minute. SEM has been carried out for polyaniline/Fe_2O_3 composites, on Microtrac Semtrac Mini SM-300.

III. RESULTS AND DISCUSSION

3.1 XRD analysis

Figure 1 shows X-ray diffraction pattern of pure PANI, Fe_2O_3 and polyaniline/Fe_2O_3 composite with various wt% of Fe_2O_3 in polyaniline. It is observed from the fig. that the peak of Fe_2O_3 indicates the crystalline nature of the composites. XRD pattern of PANI has broad band at a value of 2θ about 25 degrees and iron oxide has sharp peak of maximum intensity at 33.21 degree corresponding to plane (121) along with certain other peaks of low intensity[16]. The observed 2θ values of the peaks are in accordance with the standard JCPDS values (JCPDS No. 85-0987). XRD patterns of the composite and Fe_2O_3 confirm that Fe_2O_3 with various wt% (10, 20, 30, 40, 50) preserve its structure when polymerized with PANI.

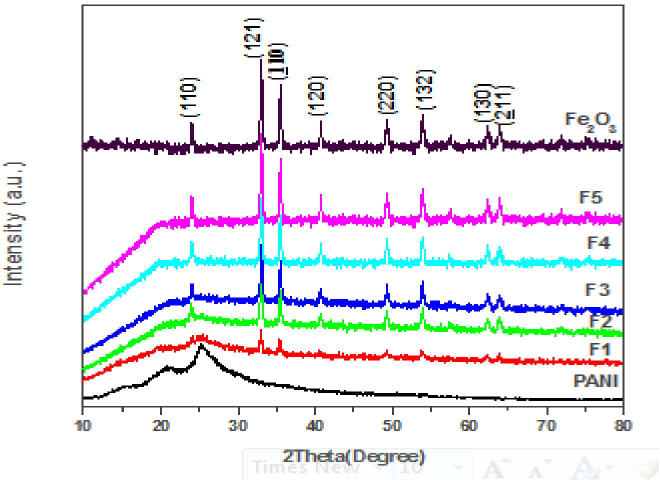

Fig. 1- XRD patterns of PANI and PANI/Fe_2O_3 composites and Fe_2O_3

The average crystallite size of PANI/ Fe_2O_3 composites and Fe_2O_3 can be obtained by Scherrer's formula [16]

$$D = \frac{K\lambda}{\beta} Cos\theta \qquad (1)$$

where D is crystallite size of particle, K is a constant called shape factor whose value is 0.89, λ is the X-ray wavelength of Cu K_α used in the present study, Cosθ is the cosine of the Bragg angle(θ) and β is the full width at half height of peak of diffraction in radians. On applying the Scherrer's formula to the characteristic (121 plane) peak of Fe_2O_3 and its composites with PANI, gives an average size of about 20 nm.

3.2 Thermo gravimetric analysis (TGA)

TGA analysis of PANI/Fe_2O_3 composites shows an initial weight loss at 100°C accounting to expulsion of water and dopant HCl molecules from polymer chains shown in figure 2. It further shows a second weight loss at 240–250°C owing to melting or volatilization of lower weight PANI. The third and final weight loss at higher temperature is due to thermal decomposition of PANI chains [17].

3.2.1 Activation energy

The activation energy of pure PANI and PANI/Fe_2O_3 composites has been deduced using the expression [14, 18]

$$'' \ln[\ln\left(\frac{\mathrm{wo}-\mathrm{w_f}}{\mathrm{w}-\mathrm{w_f}}\right)] = \frac{\mathrm{E_a}\theta}{RT_s^2} \qquad (2)$$

where w_0 is the initial weight, w is the remaining weight at temperature T, w_f is the final weight, E_a is the activation energy, R is gas constant and $\theta = T - T_s$ with T_s as the reference temperature corresponding to $\left(\frac{wo - w_f}{w - w_f}\right)$ = 1/e. From equation (2), the activation energy E_a can be calculated from the slope of the linear fitted line between ln [ln $\left(\frac{wo - w_f}{w - w_f}\right)$] and θ as illustrated in figure 3 for PANI and PANI/Fe_2O_3 composites.

*3.2.2 **Frequency factor***

The values of frequency factor for pure PANI and its composites with Fe_2O_3 have been determined by substituting the values of activation energy (E_a) in the expression [14, 19, 20]

$$A = \frac{\beta E_a}{R T_s^2} \exp\left(\frac{E_a}{R T_s}\right) \tag{3}$$

where A is the frequency factor and β is the constant rate of heating and other letters have their usual meaning.

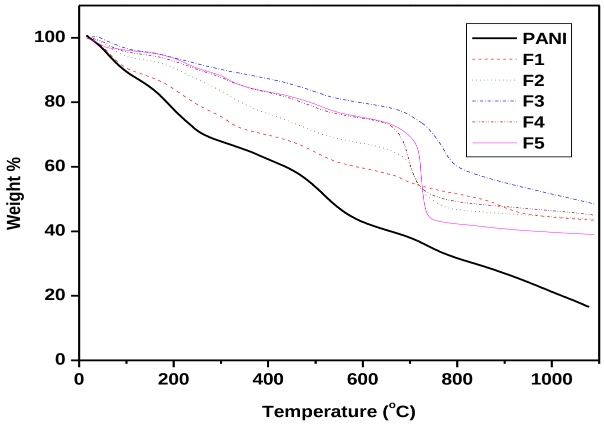

Figure 2- TGA thermogram of PANI and PANI/Fe_2O_3 composites

Table 1- Values of Various Kinetic Parameters for PANI and PANI/Fe_2O_3 Composites

Sample	E_a(KJ mol^{-1})	A (10^{10}) (s^{-1})	ΔS(J $mol^{-1}K^{-1}$)	ΔG(KJ mol^{-1})
PANI	123.30	0.40	-335.89	393.02
F1	204.130	0.206	-172.28	289.22
F2	209.069	0 .4005	-90.25	298.87
F3	467.848	9.190E+11	165.37	299.49
F4	661.959	4.837E+23	390.17	282.14
F5	1160.137	1.233E+49	876.43	285.46

3.2.3 *Entropy of activation (ΔS)*

Entropy of activation (ΔS) is calculated as [14, 19, 20]

$$\Delta S = 2.303\ R\log\left(\frac{Ah}{kT_s}\right) \tag{4}$$

where h is Planck's constant and k is Boltzmann constant and other letters have their usual meanings.

3.2.4 *Free energy of change of decomposition (ΔG)*

Free energy of change of decomposition determines the spontaneity of the reaction [21]. The values of ΔG are calculated using the expression [14, 19, 20]

$$\Delta G = E_a - T_s\Delta S \tag{5}$$

Table 1 represents the values of activation energy, frequency factor, entropy of activation and free energy of change of decomposition. It shows that activation energy and thus thermal stability of all the composites are higher than that of pure PANI. This may be due to interaction between Iron oxide particles and PANI, making them useful as conducting polymers in high temperature applications. This finding agrees well with the results obtained by other researcher [14]. The values of frequency factor changes in accordance to change in values of activation energy. Further the negative value of entropy of activation for F1 and F2 indicates the more ordered structure of these composites [14, 15, 21]. The entropy of activation has positive values for F3, F4 and F5 corresponding to log A> 13.2 indicating presence of more disorderness in these composites [15, 22]. The Free energy of change of decomposition has positive values which support the non spontaneity of the degradation reaction [15]. Higher thermal stability of PANI/Fe_2O_3 composites make it useful as conducting polymer in high temperature applications [15].

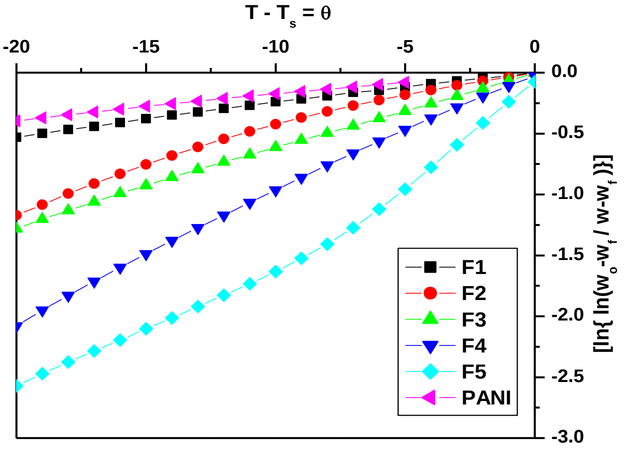

Fig. 3- Plot of $\ln[\ln\left(\frac{wo-w_f}{w-w_f}\right)]$ vs. θ for PANI and PANI/Fe_2O_3 composites

3.3 SEM

Figures 4 (a) and (b) show the SEM images of PANI and PANI/ Fe_2O_3 composite with 30 wt % of Fe_2O_3. A very high magnification of PANI/Fe_2O_3 composite with 30 wt % exhibits the presence of Fe_2O_3 in polyaniline which is homogeneously distributed throughout the polymer sample. The particle size comes out to be in few nanometers ranges. SEM micrograph clearly indicates highly branched chain structure (or branched morphology) of the composite F3.

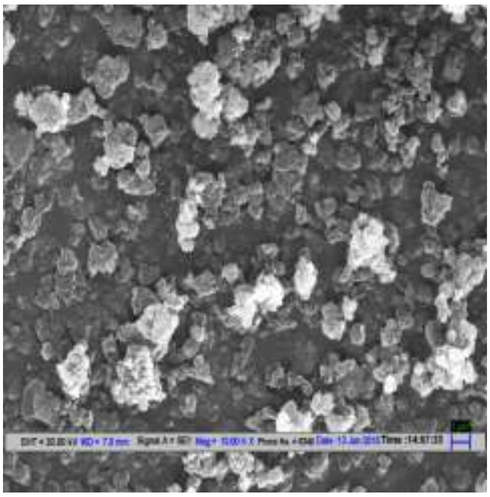

Fig. 4 (a) - SEM of PANI

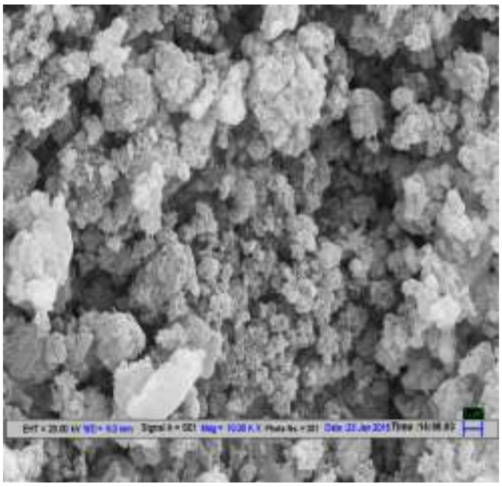

Fig. 4 (b)-PANI/ Fe_2O_3 composite (F3)

IV. CONCLUSION

PANI and PANI/Fe_2O_3 composites have been synthesized by oxidative polymerization of aniline hydrochloride doped with different wt% of Fe_2O_3 using ammonium persulphate as an oxidant. XRD confirms that Fe_2O_3 has retained its structure in composite form. PANI/ Fe_2O_3 composites are thermally more stable than PANI. The SEM study of PANI/Fe_2O_3 composites images revealed the cluster formation. Recent study shows that PANI/Fe_2O_3 composites may potentially be useful in high temperature applications.

V. ACKNOWLEDGEMENT

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