Thermal study of polyaniline- Thiourea transition metal complex of cobalt (II) Composite

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ABSTRACT

In the present work doping of Polyaniline (PANI) has been done with a thiourea transition metal complex of cobalt (II) via in situ oxidative polymerization by ammonium persulphate. The dopant has been synthesized and characterized by using elemental analysis, FTIR ,XRD and thermogravimetric (TG) analysis. The composite based on the synthesized dopant has been subjected to FTIR, X-ray diffraction, TG and DSC techniques. Viscosity average molar mass of composite has been determined by viscosity method using Ostawald's viscometer and Mark-Hoewink Sakaruda polymer equation. XRD of composite shows crystalline structure. Various parameters like crystallite size, interplanar distance, micro strain and dislocation density have been calculated by using Bragg's and other related equations. Thermal analysis shows high thermal stability of dopant which in turn has improved the thermal stability of PANI composite; therefore, serve the potential of composite for high temperature application purposes.

Keywords: Polyaniline; Coordination complex; Thiourea; Composite; XRD; Thermal analysis

I INTRODUCTION

The synthesis of composites of conducting polymers has become a new area of research because of their technological importance. The composites of PANI have proven to possess a variety of unique properties such as mechanical, electrical and structure properties because of the synergistic effect owing to the intimate mixing between PANI and inorganic or organic components at a molecular level. PANI is known for its excellent thermal and environmental stability due to non degenerate ground state. Easy Synthesis, low cost of monomer, environmental stability, intrinsic redox tendencies, stability in aqueous solutions etc characteristic properties of PANI and its composites have lured the attention of scientists to explore their electrical, thermal, optical, magnetic and structural properties. [1, 2] Inspite of poor processibility due to insolubility and brittleness that limits its commercial applications, still PANI and its composites find applications as transducers of biosensor, electrodes of rechargeable batteries, artificial nerves and muscles, gas sensors, solid electrolytic capacitors, diodes and transistors, anti-static electromagnetic shielding, corrosion inhibitors and biomedical applications. [3, 4] PANI and its composites have been used in novel biosensors for environmental monitoring. [5] One more application that PANI explores is anion exchanging role with harmful chemicals present in water and waste water sources.[6] They are more unique among conducting polymers due to their more extended network of π bond system, reactive –NH groups of aniline

and unprecedented electrical conductivity in doped state.[3] Various fillers, binders and dopants viz. Mn_3O_4, SnO_2, V_2O_5, WO_3, Fe_3O_4, ZrO_2, Sb_2O_3, TeO_2, Al_2O_3, Y_2O_3, $MgCr_2O_4$, TiO_2, PF_6^-, BF_4^-, ClO_4^-, CNT's, TiO_2, $CaCO_3$ etc have been used as dopants in conjugated polymers and have been explored for various applications. [7, 8, 24, 25, 26] Conjugated polymers containing transition metal complexes are the most attractive systems under observation of material scientist. [9] These systems are attractive because the resulting material possesses many physical properties, taking the advantage of organic and inorganic parts of the composite. These properties arise because of the ability of transition metals to bind with anions, small molecules or ligands. [10] In some cases it has been observed that there exists a strong interaction between transition metal complexes and conducting polymer backbones which result in unique properties and applications. [11, 12]

As per literature survey little research has been carried out where transition metal complexes were used as dopants in conjugated polymers. This has remained as one motivation behind the selection of this work. Transition metal bis (salicyladeimine) compex, Ruthenium complexes with mixed ligands, photoadduct of potassium hexacyanoferrate(II) involving hexamine ligand, copper bisglycinate and many more transition metal compolexes have been used as dopants in polyaniline polymer.[13,14,15,16] It is observed that transition metal complexes find immense thermal stability and in the present work it is to be seen whether it will enhance the thermal stability of the composite or not.

Metal complexes of thiourea, commonly called semiorganics, include the advantage of both organic and inorganic part of the complex and are reported to possess antibacterial, antifungal, antithyroid and insecticidal properties [17, 18, 19]. The coordinating behavior of thiourea is interesting. Thiourea acts both as a monodentate as well as a bidentate ligand, thus coordinates either through sulphur of thiocarbonyl or through nitrogens of NH_2 to the metal ion. The choice of ligand is as a consequence of the capacity of various sites on ligand besides possessing multiple biological and pharmaceutical applications. [20, 21, 22, 23] Keeping the above points in view, synthesis of [Co $(NH_2CSNH_2)_2(NH_3)_2Cl_2$] has been carried out.

Owing to the aforementioned importance associated with dopant and Polyaniline, the present study is undertaken to investigate the successful doping of a thiourea complex of Co (II) into Polyaniline matrix using XRD, FTIR, TG and DSC analysis. The present study involves the discussion of XRD and thermal properties of composite.

II EXPERIMENTAL

Materials

Aniline was supplied by Loba Chemicals and was used after distillation. HCl, ammonium persulphate, Thiourea, $CoCl_2.6H_2O$ were also provided by Loba chemicals. All reagents used were of analytical reagent grade. All solutions were prepared in triply distilled water.

Synthesis of dopant [$Co(NH_2CSNH_2)_2(NH_3)_2Cl_2$]

Equimolar quantity of $CoCl_2 6H_2O$ and thiourea were mixed in hot aqueous solution with constant stirring. To this hot aqueous solution liquor ammonia was added drop wise and green colored precipitate was formed soon after its addition. The precipitate resulting from this solution was filtered and washed repeatedly with distilled water. The precipitate was collected and dried at about 40°C in an oven. The thermally synthesized complex was finally dried over fused $CaCl_2$.

Synthesis of Polyaniline (PANI)

Polyaniline was prepared by known methods of oxidation with ammonium persulphate $(NH_4)_2S_2O_8$. To precooled solution of 10 ml distilled aniline dissolved in 150 ml of distilled water with 10 ml concentrated HCl, 4.5g of $(NH_4)_2S_2O_8$ dissolved in 30 ml of water was added drop wise to the solution with constant stirring. The solutions were kept stirring for about two hours and were left for more than one hour. The precipitate resulting from this solution was filtered and washed repeatedly with distilled water. The precipitate was collected and dried in an oven at about 40 °C.

Synthesis of polyaniline/ [Co $(NH_2CSNH_2)_2(NH_3)_2Cl_2$] Composite

To precooled solutions of 10 ml distilled aniline dissolved in 150 ml of distilled water with 10 ml concentrated HCl, 1.5g of thermally synthesized complex of Co (II) with ammonia, chloride and thiourea as ligands was added into the solution with constant stirring. To this solution 4.5 g of $(NH_4)_2S_2O_8$ dissolved in 30 ml of water was added drop wise with constant stirring. The solution was kept stirring for about six hours and was left for more than one hour. The precipitate resulting from this solution was filtered and washed repeatedly with distilled water. The precipitate was collected and dried in an oven at about 40 °C.

Measurements

Elemental analysis was done on Elementar Analysensysteme Gmbh vario EL CHNS. Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer RX-1 FTIR spectrophotometer. The spectra were taken in KBr discs.. X-ray diffraction (XRD) was recorded on PW 3050 base diffractometer with Cu Ka radiations (1.54060 A°). Thermogravimetric analysis was carried on Universal TA instruments V4.5A in an argon atmosphere at a heating rate of 10 K min^{-1}. The temperature range was from ambient to 700^0C. An aluminium pan was used as a reference.

III RESULTS AND DISCUSSIONS

Elemental analysis

On the basis of elemental analysis of C, H, N and S, the molecular formula assigned to the complex is [Co(NH_2-CS-NH_2)$_2$(NH_3)$_2Cl_2$] for which the observed values of C, H, N and S are 8.01, 4.52, 27.02 and 21.12 against calculated values as 7.69, 4.49, 26.92 and 20.21 respectively.

Determination of viscosity average molecular weight of composite

It is a very convenient method to determine the molecular weight of polymers in solution. It has been observed that the presence of macromolecules raises the viscosity due to inhomogeneties introduced by macromolecules. For the determination of viscosity average molecular weight, we prepared solution of 0.002, 0.004, 0.006 and 0.008 concentration (g cm^{-3}) in 10 ml of 1-methy-2-pyrrolidone (NMP). The reduced viscosities of these samples were determined, using an oswald's viscometer. It is the reduced viscosity that depends upon the molecular weight of polymer. Average molecular weight of composite was determined using the following Mark-Kuhn-Houwink-Sakurada equation. [27]

$$[\eta] = K (M)^{\alpha} \qquad (1)$$

Where M is the average molecular weight, K and α are constants. In the present case K = 1.95×10^{-6} and α =1.36, [η] is intrinsic viscosity also called viscosity number or Staudinger index and is related to other quantities as [η] = Lim η_{sp} /C when C $\rightarrow$0, $\eta_{sp} = \eta_{rel} - 1$, and η_{rel} =t/t$_0$, where η_{red} is the reduced viscosity, η_{sp} is the specific viscosity, η_{rel} is the relative viscosity, t and t$_0$ are viscometer drain times of solution and solvent respectively [Table I]. η_{red} was then plotted verses the composite concentration for four concentrations and a linear exploitation to zero concentration produced the value of [η] = 41.25 (Figure 1). After putting the value of [η], K and α in the Mark-Houwink equation, the viscosity average molecular weight of the PANI composite comes out to be 243, 397.
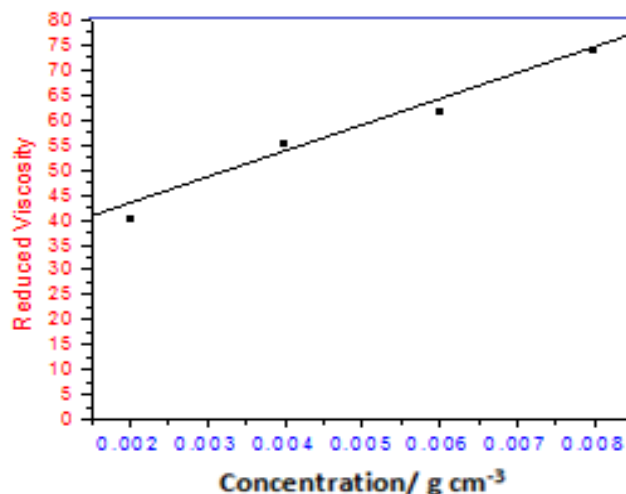

**Figure 1. Plot of reduced viscosity verses concentration**

Table I Parameters for calculating average molecular weight of PANI composite.

Concentration/ g cm^{-3}	η_{rel}	η_{sp}	η_{red}
0.002	1.08	0.08	40.00
0.004	1.22	0.22	55.00
0.006	1.37	0.37	61.67
0.008	1.59	0.59	73.75

FTIR Analysis

The FTIR spectrum of dopant and PANI composite are shown in Figure 2(a) and Figure 2(b).

FTIR Characterization of dopant [Co (NH$_2$-CS-NH$_2$)$_2$(NH$_3$)$_2$Cl$_2$]: The peak appears at 841cm^{-1} is the stretching vibration of Co-N bond. The Co-S stretching vibration occurs at 508 cm^{-1} indicates the coordination of thiourea with the cobalt through sulphur. The stretching vibration of C=S in the free ligand is observed at 1598 cm^{-1}, shows a shift to 1618 cm^{-1} in the complex. NH$_3$ shows bending mode in the region of 1600-1660 cm^{-1}, thus the peak observed at 1664 cm^{-1} may be assigned to NH$_3$ molecule. The highly intense peak observed at 3551 cm^{-1} is due to stretching vibration of uncoordinated NH$_2$ groups of thiourea. The band observed at 2142 cm^{-1} is due to N=C=S stretching vibration of isothiocyanate group of thiourea. The band at 1112 cm^{-1} is due to N-CS-N bending vibration of thiourea. Co-Cl bond is verified by the appearance of some peaks at 620 cm^{-1} and 727 cm^{-1} against the known FTIR peaks of CoCl$_2$, observed at 593 cm^{-1} and 688 cm^{-1}. The peaks observed in the present work match well with the ones available in the literature. [18, 19, 20, 21, 22, 23] From the data of FTIR spectrum, following points have been abstracted. Thiourea acts as a monodentate ligand and coordination with the cobalt occurs via the sulphur of thiocarbonyl. One lone pair of electrons of sulphur is in conjugation with the lone pair of electrons available on nitrogens of thiourea. In the M-N stretching vibration, it is the nitrogen of ammonia that coordinates to the cobalt. The complex has been assigned octahedral geometry as shown in structure.
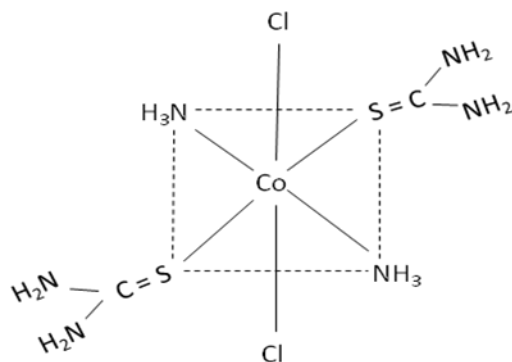
Diammine dichloro dithiourea Cobalt (II)

FTIR characterization of PANI composite: The characteristic stretching frequencies of PANI are observed at 1476 cm^{-1} for benzenoid ring stretching shows a shift to 1499 cm^{-1} in the composite, 1381 cm^{-1} for C-N stretching and C-C stretching shifts to 1446 cm^{-1} in the composite and 1580 cm^{-1} for quinoid ring stretching shows a shift to 1582 cm^{-1} in the composite. These stretching vibrations are shifted towards higher frequency side which may be attributed due to the van der waal's kind of interaction between dopant and PANI chain. [8] The benzenoid band is more intense than quinoid band in the FTIR spectrum of PANI composite indicating the partitial oxidation of PANI base. The peak at 1164 cm^{-1} in case of PANI because of a mode of N=Q=N, shifts to 1175 cm^{-1} shows the coordination at the site. The N-H stretching and C-H stretching in the composite are observed at 3854 cm^{-1} and 3231 cm^{-1} respectively. FTIR of PANI composite shows a peak at 505 cm^{-1} due to Co-S stretching vibration, 596 cm^{-1} and 694 cm^{-1} due to Co-Cl stretching vibration, a peak at 1073 cm^{-1} due to N-CS-N bending vibration and 811 cm^{-1} due to Co-N stretching vibration, thus all prominent peaks of dopant have been found in it. The peaks observed in the present work match well with the ones available in the literature. [8, 16, 24] From the above data and discussion, it proves the successful synthesis of PANI composite which is further supported by the results of XRD and TG analysis. By comparing the FTIR spectra of dopant and PANI composite, the stretching vibrations of dopant have shifted towards lower frequency side indicates the weak interaction of dopant and PANI chain. [8] This weak interaction may be due to the large size of sulphur and its inability to form hydrogen bond with protonated PANI base; can disfavor PANI chain formation and may hinder the efficient packing of PANI chains.
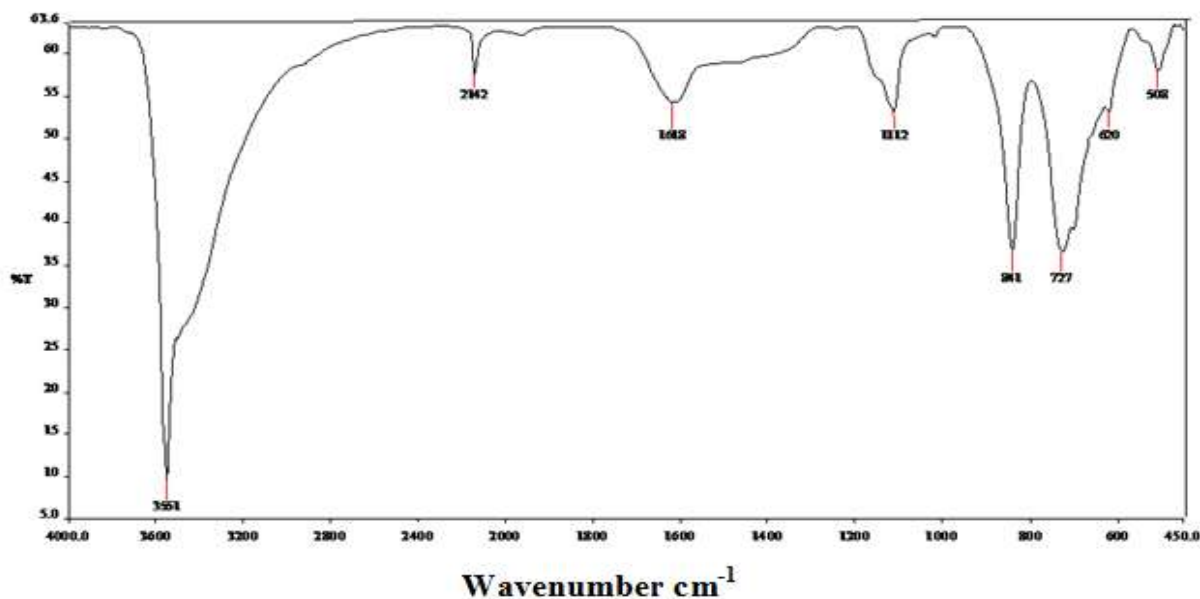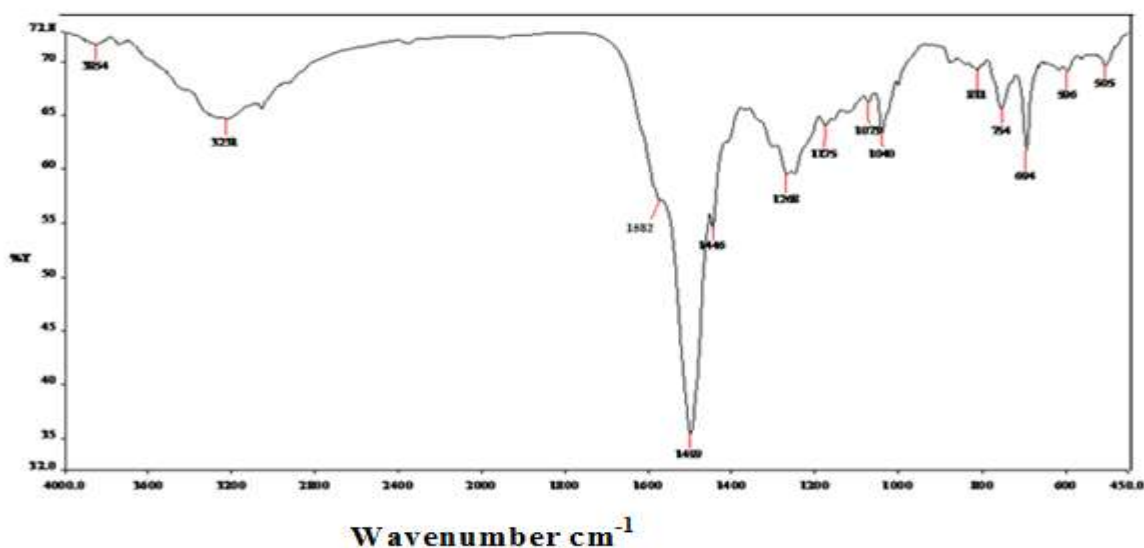

Figure 2(a). FTIR of dopant.

Figure 2(b). FTIR of Polyaniline composite

XRD Characterization

X-ray diffraction (XRD) was recorded on PW 3050 base diffractometer with Cu Kα radiations (1.54060 A°).The XRD data has been analyzed using Powder X software. [Figure 3(a), Figure 3(b) and Figure 3(c)] represents the XRD diffraction pattern of dopant, pure polyaniline and composite of PANI with the dopant respectively. Characteristic peaks are indexed by miller indices. Diffraction pattern of pure Polyaniline shows large amorphous material contents with a broad peak at $2\theta = 20^0$ as shown in Figure 3(b). The appearance of sharp peaks at 2θ values of 14.583°, 18.631°, 22.718°, 32.366°, 39.590°, 53.803° and 59.004° in dopant indicates that the molecule is crystalline. Sharp peaks in the composite have been observed at 2θ values of 12.555°, 17.445°, 20.701°, 26.615°, 35.243° and 40.110° besides some other peaks indicates degree of crystallinity. The sharp peaks due to $CoCl_2$, ammonia and thiourea in the dopant as well as in the composite match well with the JCPDS-International centre for diffraction data, file No 85-0446, 83-1438 and 83-2252. The dopant has retained the hexagonal structure of cobalt chloride. Various parameters like crystallite size (L), interplanar distance (d), micro strain (ε), dislocation density (ρ) and distortion parameters (g) were calculated for the dopant as well as the composite as shown in Table (II-V) using the following equations:

$L=K \lambda/bCos\theta$ (2)

$d= \lambda/2Sin\theta$ (3)

$\varepsilon=bCos\theta/4$ (4)

$\rho = 1/L^2$ (5)

$g = b/\tan\theta$ (6)

Where $\lambda = 1.54$Å is the wavelength of the Cu-Kα X-ray radiation used, b is the FWHM of the diffraction peak and θ is the Bragg angle (in degrees), k is the Scherrer's constant (usually taken as 0.89), L is crystallite size (A^0), d is the interplanar distance (A^0), ε is the micro strain, ρ is the dislocation density (calculated in 10^{15} m/m^3) and g is the distortion parameter. The lattice parameters have been calculated after refinement which are a=b= 4.9168 and c= 33.71 with α=β=90° and γ=120° for the dopant whereas for the composite, the lattice parameter values are a=4.9168, b=7.68 and c=13.56 with α=70°, β=90° and γ=110°. The value of d (calc.) spacing is in agreement with the experimental d-spacing.

It has been seen that pure PANI shows a typical noncrystalline pattern, while in the case of the PANI composite, the XRD pattern shows nearly semicrystalline structure. On analyzing the XRD data, dopant has increased the crystallite size of composite. Crystallite size of dopant is small and dislocation density is large at lower values of 2θ in case of dopant as shown in Table III. However the trend is random in case of composite, as evident from Table V, indicates the mixing nature of dopant and PANI matrix.
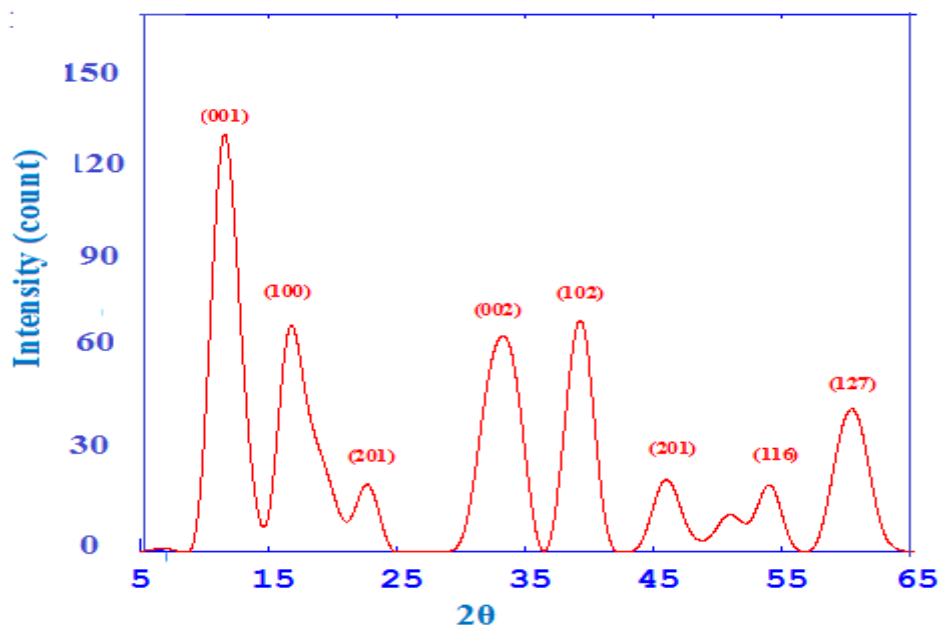

Figure 3(a). XRD of dopant.

Figure 3(b) XRD of pure Polyaniline.
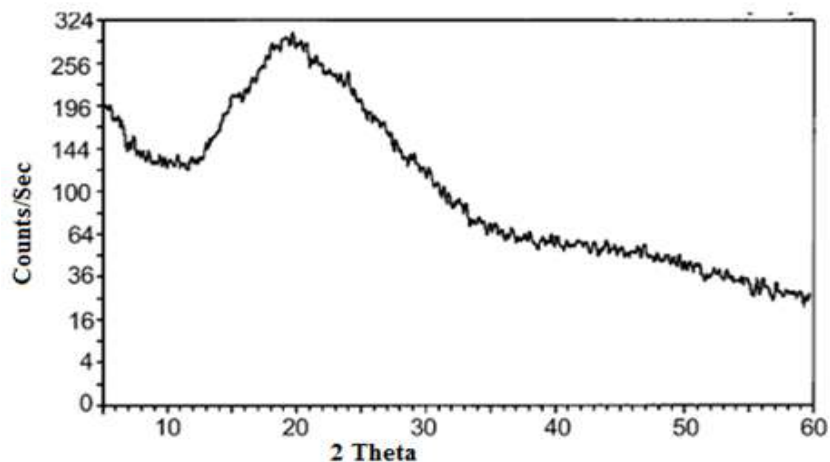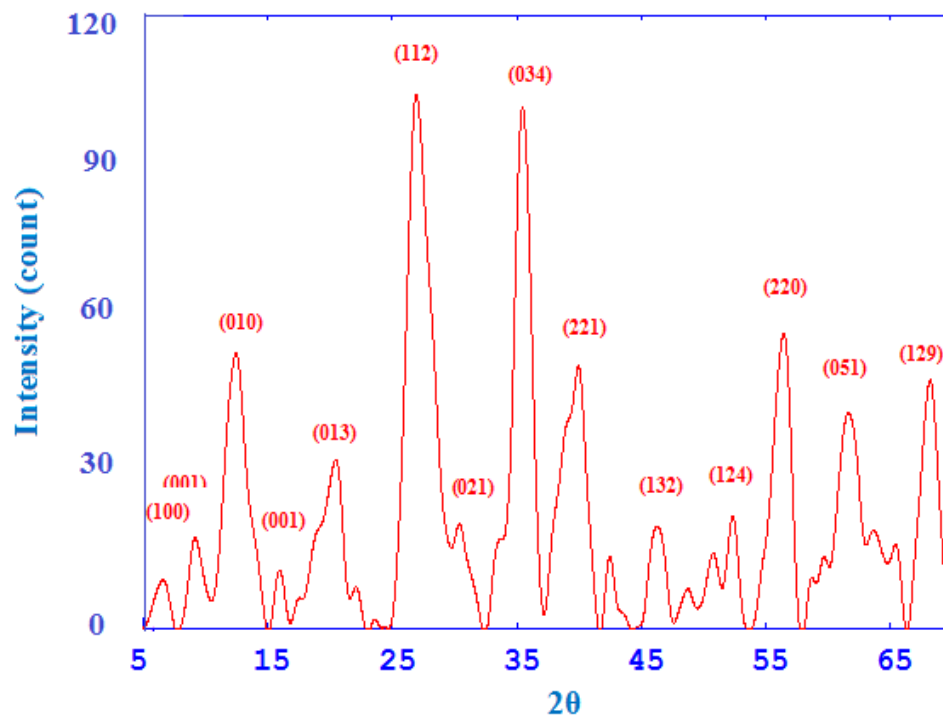

Figure 3(c). XRD of composite of Polyaniline.

Table II Evaluated parameters from XRD data for the dopant [Co (NH$_2$-CS-NH$_2$)$_2$(NH$_3$)$_2$Cl$_2$].

h	K	L	2θ (exp)	d (exp)	d (calc.)	Intensity
0	1	0	14.583	6.07152	6.06354	141.03
1	0	1	18.631	4.75861	4.74905	201.00

0	0	2	19.876	4.46495	4.46092	178.90
1	0	0	22.718	3.91184	3.91056	163.68
1	1	2	32.366	2.76239	2.75167	218.60
1	1	2	34.046	2.62969	2.62751	171.62
0	0	6	39.590	2.27370	2.27175	292.08
2	1	4	45.414	1.99527	1.99217	63.49
2	3	5	51.820	1.76314	1.76241	56.71
2	2	0	53.803	1.70215	1.70012	91.11
1	0	6	59.004	1.56387	1.55951	99.72

Table III Crystallite size (L), micro strain (ε), dislocation density (ρ) and distortion parameters (g) calculated from 2θ value for the dopant of [Co $(NH_2\text{-}CS\text{-}NH_2)_2(NH_3)_2Cl_2$].

2θ (exp)	L(A°)	ε	ρ (in 10^{15}m/m^3)	g
14.583	76.92	0.2582	16.90	8.1399
18.631	26.65	0.7449	140.84	18.412
19.876	32.44	0.6119	95.02	14.186
22.718	64.51	0.3078	24.02	6.273
32.366	198.87	0.0998	2.52	1.433
34.046	125.09	0.1587	6.39	2.170
39.590	230.16	0.0868	1.88	1.078
45.414	146.02	0.1359	4.69	1.405
51.820	151.19	0.1313	4.37	1.202
53.803	114.45	0.1735	7.63	1.534
59.004	174.71	0.1136	3.27	0.923

Table IV Evaluated parameters from XRD data of composite.

h	K	L	2θ (exp)	d (exp)	d (calc.)	Intensity
1	0	0	6.424	13.74605	13.75172	20.14
0	0	1	9.108	9.70138	9.71542	19.19
0	1	0	12.555	7.04663	7.02650	42.25
0	0	1	17.455	5.40980	5.39812	29.58
0	1	3	20.701	4.28791	4.27891	28.06
1	1	2	26.615	3.34625	3.33545	82.16
0	2	1	30.296	2.94695	2.94860	32.65
0	3	4	35.243	2.54435	2.55011	71.35
2	2	1	40.110	2.24614	2.24864	38.27
1	3	2	46.215	1.96290	1.96015	31.77
1	2	4	49.558	1.83677	1.82951	18.97

2	2	0	56.603	1.62557	1.62492	51.37
2	0	4	58.653	1.57314	1.57400	20.73
0	5	1	62.406	1.48683	1.48691	28.35
1	2	9	68.263	1.35012	1.35012	18.78

Table V Crystallite size (_L_), micro strain (ε), dislocation density (_ρ_) and distortion parameters (_g_) calculated from 2θ value for the composite.

2θ (exp)	L(A°)	ε	ρ (in 10^{15}m/m³)	g
6.424	559.50	0.0355	3.19	2.534
9.108	350.43	0.0567	8.14	2.864
12.555	62.87	0.3158	25.29	11.596
17.455	317.40	0.0625	9.93	1.647
20.701	400.54	0.0495	6.23	1.102
26.615	29.55	0.0610	114.52	11.669
30.296	135.64	0.1464	5.43	2.241
35.243	56.60	0.3509	31.21	4.668
40.110	150.65	0.1318	4.41	1.543
46.215	383.84	0.0517	6.79	0.527
49.558	629.43	0.0315	2.52	0.301
56.603	64.76	0.3066	23.84	2.587
58.653	503.38	0.0393	3.95	0.316
62.406	241.66	0.0822	1.71	0.621
68.263	161.39	0.1231	3.83	0.878

Thermal Analysis

The TG/DSC of dopant, PANI and composite of PANI with synthesized dopant are shown in Figure 4(a), Figure 4(b) and Figure 4(c) respectively.

TG of dopant shows two transitions. First transition is initiating from ambient temperature to 241.29°C, with a weight loss of 48.92% against the calculated weight loss of 48.71% which is as a result of loss of two molecules of thiourea. The second thermal decomposition step initiates from 241.29°C and stops at 369.84°C, with a weight loss of 10.95% against the calculated weight loss of 10.89% accounts for the removal of two molecules of ammonia. The residue left behind at 370°C is 40.13% against the calculated value of 40.41% which is due to presence of $CoCl_2$ whose decomposition temperature is 1087°C. [28] Beyond 400°C, TG runs parallel to X-axis indicates stability of the dopant. DSC of dopant shows a small and a wide exothermic peak with transition temperatures of 226.83°C and 325.72°C. The heat flows during these transitions are 1.499W/g and 4.016 W/g respectively. These transitions are in tune with the TG data.

TG of PANI shows two transitions, the first one because of expulsion of certain amount of water. The temperature range of this transition is 18- 85^{0}C with a weight loss of 4.33%, which indicates that the moisture must be embedded in the outer layers of material. The second transition initiates from 278^{0}C and ends at 523^{0}C, with a weight loss of 89.82%, which is because of release of organic moieties like C, H and N. Thus the TG curve shows complete decomposition of PANI. DSC of PANI shows two transitions corresponding to two transitions of TG curve. Both these transitions are endothermic.

TG of PANI composite based on the synthesized dopant shows three transitions. The first transition is initiating from 16.07°C and stops at 126.00°C which is due to expulsion of moisture with a weight loss of 4.09%. The second decomposition starts from 126.00°C and stops at 276.12°C, which is as a result of loss of thiourea molecules of dopant. Third decomposition is initiating from 276.12°C and ends at 441.17°C which is because of loss of C, H and N of PANI part of composite and ammonia of dopant. The residue left behind is 23.21% at 411.17°C which is because of inorganic moiety $CoCl_2$ of dopant. TG curve runs parallel to x-axis beyond 411.17°C indicates stability of the composite. DSC of composite shows an exothermic peak at transition temperature of 439.62°C with a heat flow of 94.23 W/g.

On comparing thermograms of dopant, PANI and composite, it is evident that dopant and composite shows thermal stability beyond 500°C unlike pure PANI which shows complete decomposition at 523°C, hence proves that dopant has been inserted into the composite and has increased the thermal stability of the composite material. Moreover the nature of DSC transition of composite is different from pure PANI and dopant, thus showing the effect of dopant on composite. DSC of pure Polyaniline shows two endothermic peaks which are totally reversed with that observed in composite and dopant. This all proves the successful synthesis of Polyaniline composite.
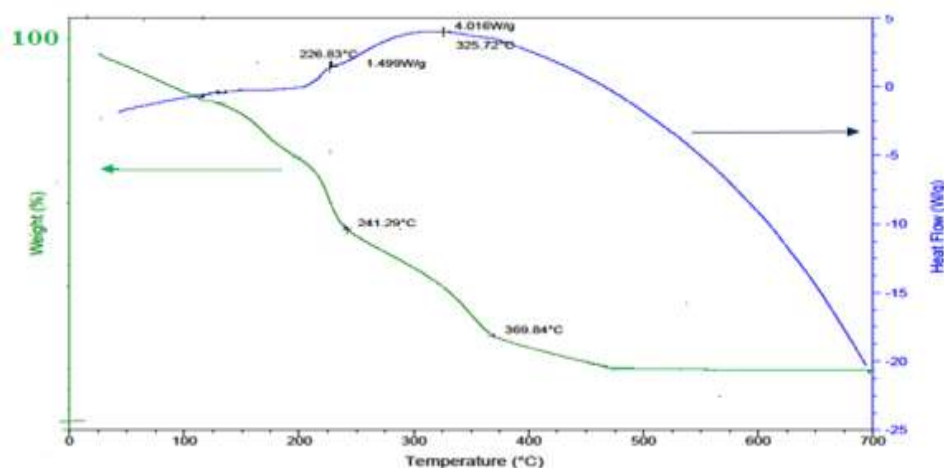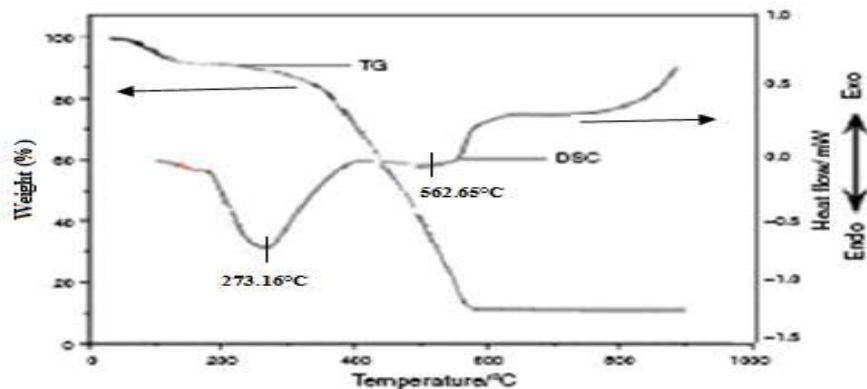

Figure 4(a). TG/DSC of dopant.
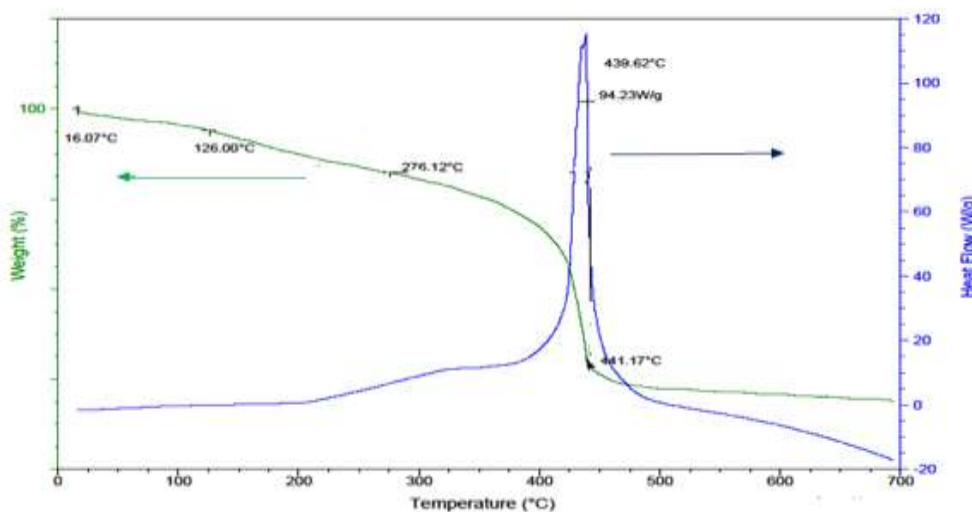
Figure 4(b). TG/DSC of polyaniline.

Figure 4(c). TG/DSC of Polyaniline composite.

IV CONCLUSIONS

Successful synthesis of composite of polyaniline based on the synthesized adduct [Co $(H_2N\text{-}CS\text{-}NH_2)_2(NH_3)_2Cl_2$] has been proved by FTIR, XRD and TG/DSC analysis. FTIR of dopant exhibits monodentate character of thiourea and its coordination with thiourea occurs via the sulphur of thiocarbonyl. Moreover octahedral geometry has been proposed for the dopant. FTIR spectral peaks of composite confirm the presence of dopant crystals. XRD reveals partitial crystalline nature of composite. Various crystallographic parameters including d-spacing, hkl values and distortion parameters of composite as well as dopant have been calculated using Bragg's and other mathematical

equations. TG and DSC analysis inferred that dopant has been inserted into PANI matrix and has increased the thermal stability of the composite material; hence the material can be used for high temperature application purposes.

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