

XRD Characterization and Thermal Study of Cobalt Complex Based Polypyrrole Composite

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ABSTRACT

In the present communication doping of Polypyrrole (Ppy) has been done with a multiligand urea complex of cobalt(II) via in situ oxidative polymerization using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as an oxidant. 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 and X-ray diffraction techniques. Surface morphology of Ppy and its composite with metal complex is investigated with scanning electron microscope (SEM). Thermal analysis has been done by using TG and DSC technique. The dopant has developed the crystallinity in amorphous Ppy and has increased its thermal stability. XRD results show crystalline nature of composite. Parameters like crystallite size, interplanar distance, micro strain and dislocation density have been calculated by using Bragg's and other related equations. Moreover lattice parameters a , b , c , α , β and γ have also been calculated for the dopant as well as the composite using powder X software. Thermogravimetric analysis reveals that the thermal stability of composite is better than polypyrrole.

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Introduction

Owing to their increased demand in the material sciences and tremendous applications in various fields, it has become imperative to study conducting and composite polymers. Research in the field of such polymers aims mainly at some suitable modifications of existing polymers so that their applicability can be improved, some of these modifications involve preparing hybrid materials in which organic materials and inorganic oxides or salts of different metals viz. Mn_3O_4 , SnO_2 , V_2O_5 , WO_3 , Sb_2O_3 , TeO_2 , Al_2O_3 , Y_2O_3 , Fe_3O_4 , ZrO_2 , MgCr_2O_4 , TiO_2 , PF_6^- , BF_4^- , ClO_4^- etc combine in some special fashion with the conducting polymers to give rise to the composites. In almost all the cases some specific nature of association between the two components has been observed.¹⁻⁷ Conjugated polymers containing transition metal complexes are the most attractive systems under observation of material scientist.⁸ 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.⁹ 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.¹⁰⁻¹² Little research is available in literature where transition metal complexes were used as fillers in conjugated polymers.^{13,14} Transition metal bis(salicylaldimine) has been used as a dopant in polythiophene polymer.

¹⁵Ruthenium complexes with mixed ligands were used as dopants in a series of novel conjugated polymers.¹⁶ Photoadduct of potassium hexacyanoferrate(II) involving hexamine ligand was used as a dopant in

polyaniline polymer and thermal study of composite was investigated.¹⁷ Some metal complex based composites were also used as fillers in the matrix of polypyrrole and the synthesized composites materials were explored for catalytic, electrical and dielectric properties.^{18,19}

Polypyrrole was the first of conducting polymers that shows relatively (1) high conductivity, (2) appreciable environmental stability and (3) easy synthesis.²⁰ Conducting polymers from five-membered heterocyclic compounds are very interesting. Ppy and polythiophenes are typical examples.²¹ Ppy can often be used as biosensors, gas sensors, wires, microactuators, antielectrostatic coatings, solid electrolytic capacitor, electrochromic windows and displays, and packaging, polymer batteries, electronic devices and functional membranes.²²⁻³⁰ Ppy is a good candidate for use in carbon composites. Ppy-based polymers can be used to load and release drugs and biomolecules.³¹ Ppy-based polymer blends can protect the corrosion of metals.³²

Coordination compounds of transition metal complexes with urea have found various applications in pharmaceuticals, catalysts, in extraction systems, water repellants, polymer dispersants, fertilizer pigments and packing material.³³ Some complexes have been found to have fungicidal activity and potentially useful in wood protection.³⁴

Urea has been of renewed interest in coordination compounds because it provides potential binding sites to metals. The coordinating behavior of urea is interesting. Urea acts both as a monodentate as well as a bidentate ligand, thus coordinates either through oxygen of carbonyl or through nitrogen's of NH_2 to the metal ion.^{35, 36} Keeping the above points in view, synthesis of $[\text{Co}(\text{NH}_2\text{-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$ has been taken into account. Owing to water solubility, easy preparation mode and wide biological-industrial applications

of cobalt-urea complex, here we report its thermal property and explore its doping tendency in the polypyrrole matrix.

In view of the aforementioned importance associated with the dopant and Ppy polymer, it is our endeavor to synthesize the composite. The composite synthesized is being evaluated thermally and its crystallinity is also being examined.

Experimental

Materials

Pyrrole was supplied by Loba Chemicals. Urea, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and FeCl_3 were also provided by Loba chemicals. All reagents used were of analytical reagent grade. All solutions were prepared in triply distilled water.

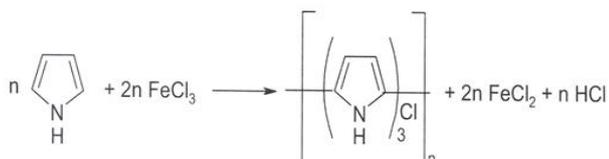
Synthesis of dopant $[\text{Co}(\text{NH}_2\text{-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$

1mole of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 1 mole of urea were mixed in 100 ml aqueous solution with constant stirring at 60 °C. 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 30°C in an oven. The thermally synthesized complex was finally dried over fused CaCl_2 .

Synthesis of pure Polypyrrole

1 ml of pyrrole was added via syringe to 100ml of a stirred aqueous solution containing 9.74g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at room temperature. The Fe^{3+} /pyrrole molar ratio was 2.5. Reaction was stirred for 24hr with a magnetic stirrer, which gives rise to the formation of a black precipitate. The resulting black precipitate was vacuum filtered. The precipitate was then washed with copious amounts of triply distilled water until the washings were clear. The Ppy so obtained was soft jet black powder, dried in a desiccator overnight and again dried in an oven at 25°C. The yield of the material was 1.91g.

The general reaction scheme for synthesis of Ppy is :



Synthesis of polypyrrole composite

Weighed accurately 9.74g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and made a total volume of 100 ml in a volumetric flask. Weighed 1.5g of thermally synthesized urea complex. Transferred 100 ml of ferric chloride solution to a conical flask and added 2ml of pyrrole via syringe. The weighed amount of dopant $[\text{Co}(\text{NH}_2\text{-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$ was also added to this mixture. The color of the solution abruptly changes from reddish yellow to greenish black. Stirred the reaction mixture by magnetic stirring for 24hr and the reaction mixture was filtered. A black colored precipitate was obtained. The precipitate was washed repeatedly with distilled water.

The material so obtained was first dried in desiccator overnight and then in oven at 25°C. The composite material was soft black powder with yield as 4.0g.

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 K_α radiations (1.54060 Å).

Surface morphology of the samples was studied on ZEISS EVO series scanning electron microscope model EVO50. Thermo gravimetric 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°C. An aluminum pan was used as a reference.

Results and Discussions

Elemental Analysis

On the basis of elemental analysis of C, H and N, the molecular formula assigned to the dopant is $[\text{Co}(\text{NH}_2\text{-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$ for which the observed values of C, H and N are 8.69, 5.21 and 30.29 against calculated values as 8.57, 5.02 and 30.00 respectively.

FTIR Analysis

The FTIR spectrum of dopant and Ppy composite are shown in Figures 1(a) and (b), respectively.

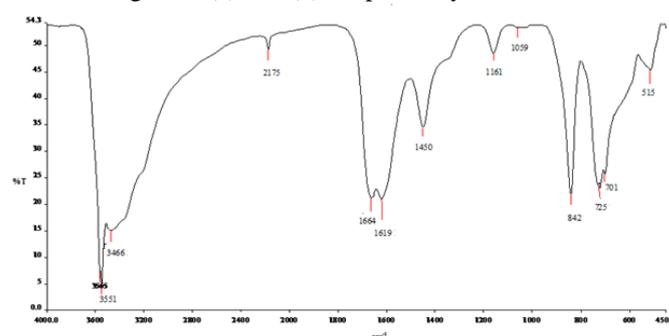


Fig1a. FTIR of dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$.

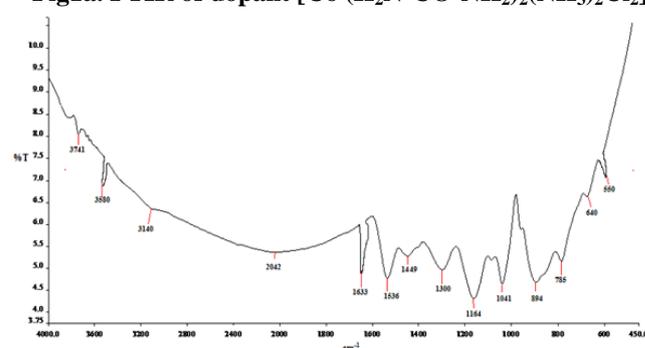


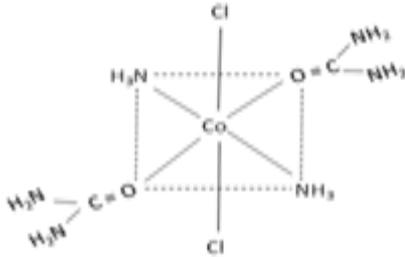
Fig 1b. FTIR of polypyrrole composite.

FTIR Characterization of dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$

The peak appears at 842 cm^{-1} is the stretching vibration of Co-N bond. The Co-O stretching vibration occurs at 515 cm^{-1} . The peak at 1619 cm^{-1} is the bending mode vibration of NH_3 molecule as ammonia shows a weak band in the region of 1600-1650 cm^{-1} . Urea shows two bands near 3400 cm^{-1} and 3500 cm^{-1} . These bands arise due to symmetrical and asymmetrical N-H stretching. The peaks observed at 3466 cm^{-1} , 3551 cm^{-1} and 3565 cm^{-1} are due to stretching vibrations of uncoordinated amide NH_2 groups. The band observed in 1059 cm^{-1} is due to NH_2 bending vibration.

In urea, the presence of nitrogen atom has – Inductive effect but a lone pair of electrons on N atom are involved in conjugation that tend to decrease C=O force constant. Thus the $\nu_{\text{C=O}}$ absorption occurs at lower wave number in urea. The stretching vibration of carbonyl group appears at 1649 cm^{-1} in the FTIR spectrum. The band observed at 2175 cm^{-1} is due to N=C=O stretching vibration of isocyanate of urea. The band at 1161 cm^{-1} is due to N-CO-N bending vibration of urea. Co-Cl bond is verified by the presence of some peaks at 701 cm^{-1} and 725 cm^{-1} which is further supported by TG analysis. The peaks reported in CoCl_2 IR spectrum are observed at 593 cm^{-1} , 688 cm^{-1} and 807 cm^{-1} . From the data

of FTIR spectrum, following points have been abstracted. Urea acts as a monodentate ligand and coordination with the cobalt occurs via the neutral oxygen of urea. One lone pair of electrons of oxygen is in conjugation with the lone pair of electrons available on nitrogen's of urea. In the M-N stretching vibration, it is the nitrogen of ammonia that coordinates to cobalt. The octahedral geometry has been assigned to the dopant as shown in structure below.



FTIR Characterization of polypyrrole composite

The characteristic peaks of stretching vibration of polypyrrole are observed at 1550 cm^{-1} and 1452 cm^{-1} for C=C and C-N of Ppy, shows a shift to 1536 cm^{-1} and 1449 cm^{-1} respectively in the Ppy composite and 1190 cm^{-1} for breathing vibration of the pyrrole ring has shown a shift to 1164 cm^{-1} in the composite. The bands of C-H and N-H in-plane deformation vibrations are located at 1037 has shifted to 1041 in the composite. The peak at 3110 cm^{-1} for aromatic C-H stretching is appearing at 3140 cm^{-1} in the composite, which may also because of aromatic N-H stretching. The peak at 1310 cm^{-1} due to mixed bending and stretching vibrations associated with C-N links is appearing at 1300 cm^{-1} in the composite. Encapsulation of dopant within the Ppy matrix is proved by the appearance of some peaks in the FTIR spectrum of composite which are in consonance with the FTIR of dopant. The stretching vibration of Co-O appeared at 515 cm^{-1} shows a shift to 550 cm^{-1} in the composite. The Co-N stretching vibration which appeared at 842 cm^{-1} shows a shift to 894 cm^{-1} in the composite. The peak at 1619 cm^{-1} appears at 1633 cm^{-1} in the composite is due to NH_3 bending vibration, which may be also due to librational modes of lattice water. The band observed at 2175 cm^{-1} due to N=C=O stretching vibration appears at 2042 cm^{-1} in the composite. The peaks observed at 3741 cm^{-1} and 3580 cm^{-1} in the composite is due to the N-H stretching vibrations of NH_2 of urea or may be due to lattice water. Lattice Water in the composite is further confirmed from thermograms. The peaks observed at 688 cm^{-1} and 725 cm^{-1} due to Co-Cl vibrations has been shifted to 640 cm^{-1} and 785 cm^{-1} in the composite. The peaks observed in the present work match well with the ones available in literature. By comparing FTIR spectra of dopant and Ppy composite, successful doping has been proved which is further reinforced with the results of XRD and TG analysis. The peaks observed in the IR spectrum of dopant has shown a shift towards higher frequency side in the composite indicates the stability of the composite which may be attributed due to the weak van der Waal's force of attraction between dopant and Ppy.^{37, 38}

XRD Analysis

Figure 2(a),(b) and (c) represents the XRD diffraction pattern of dopant, pure Ppy and Ppy composite, respectively. Characteristic peaks are indexed by miller indices. The broad peak at about $2\theta = 24^\circ$ is characteristic of amorphous polypyrrole.³⁹ This peak has been shifted to 24.921° in Ppy composite. The appearance of sharp peaks both in dopant as

well as in the composite indicates degree of crystallinity in the dopant which has remained dominant in the composite. The sharp peaks due to CoCl_2 , ammonia and urea 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 85-1179. 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 using the below mentioned equations and reported in Table 1-4.

$$L = K \lambda / b \cos \theta,$$

$$d = \lambda / 2 \sin \theta,$$

$$\epsilon = b \cos \theta / 4,$$

$$\rho = 1 / L^2 \text{ and}$$

$$g = b / \tan \theta$$

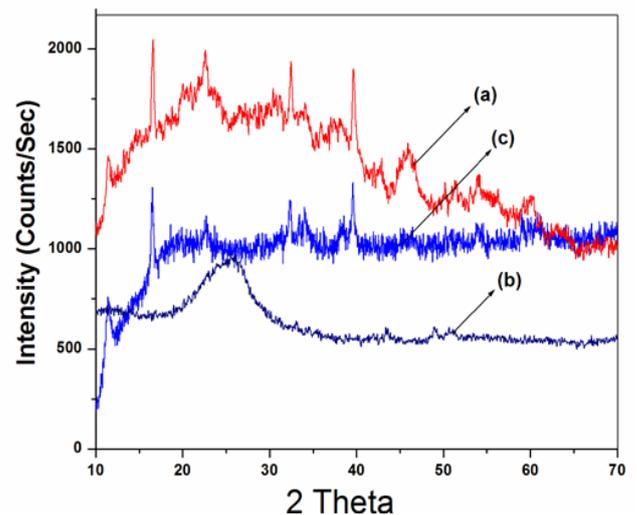


Fig 2. XRD of (a) dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$, (b) pure Polypyrrole and (c) Polypyrrole composite.

Where $\lambda = 1.54\text{ \AA}$ is the wavelength of the Cu- $\text{K}\alpha$ 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 (\AA), d is the interplanar distance (\AA), ϵ is the micro strain, ρ is the dislocation density and g is the distortion parameter. The lattice parameters have been calculated after refinement which are $a = b = 6.78$, and $c = 14.67$ with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ for the dopant whereas for the composite, the lattice parameter values are $a = b = 6.59$ and $c = 13.73$ with $\alpha = 90^\circ$, $\beta = 88^\circ$ and $\gamma = 118^\circ$. The value of d (calc.) spacing is in agreement with the experimental d-spacing. From XRD pattern and evaluated parameters successful synthesis of Ppy and its composite with dopant is proved. The structure of Ppy composite has improved from amorphous to crystalline.

Table 1. Evaluated parameters from XRD data of dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$.

h	K	l	2θ (exp)	d (exp)	d (calc.)	Intensity
0	0	1	13.23	6.687	6.683	1670
1	0	0	14.63	6.685	6.681	1770
2	0	1	22.62	3.926	3.919	1360
0	0	2	34.10	2.626	2.622	1790
1	0	2	38.22	2.353	2.352	1810
2	0	1	45.92	1.974	1.970	1258
1	1	6	56.29	1.633	1.633	1020
1	2	7	60.25	1.534	1.535	1590

Table 2. Crystallite size (L), micro strain (ϵ), dislocation density (ρ) and distortion parameters (g) calculated from 2θ value for the dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$.

2θ (exp)	$L(\text{\AA})$	ϵ	$\rho \times 10^{17} \text{m}^{-3}$	g
13.23	26.49	0.749	1.425	26.065
14.63	27.11	0.732	1.360	23.042
22.62	62.05	0.320	2.597	6.527
34.10	64.29	0.309	2.419	4.215
38.22	39.33	0.505	6.464	6.156
45.92	41.27	0.482	5.871	4.970
56.29	29.88	0.665	1.120	5.637
60.25	76.39	0.260	1.713	2.072

Table 3. Evaluated parameters from XRD data of composite of Polyaniline with the dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$.

h	K	l	$2\theta(\text{exp})$	$D(\text{exp})$	$D(\text{calc.})$	Intensity
1	0	7	20.72	4.284	4.285	1342
2	1	5	24.92	3.570	3.567	1180
3	2	5	36.91	2.434	2.432	1879
2	0	13	39.65	2.271	2.270	1755
4	2	2	43.38	2.084	2.085	1128
4	2	5	45.16	2.006	2.006	1628
1	0	17	46.78	1.940	1.940	1377
4	1	10	48.15	1.888	1.888	1115
4	1	1	50.81	1.795	1.795	1095
3	3	1	55.99	1.641	1.641	776

Surface Morphology of Ppy and Ppy composite

Scanning electron microscope (SEM) images of Ppy and Ppy composite are shown in Fig. 3 (a) and (b), respectively. Pure Ppy shows lumps stacked together which indicates its layered structure. Composite of Ppy shows ice berg structures dispersed in its matrix, thereby supports the incorporation of metal complex in the Ppy matrix.

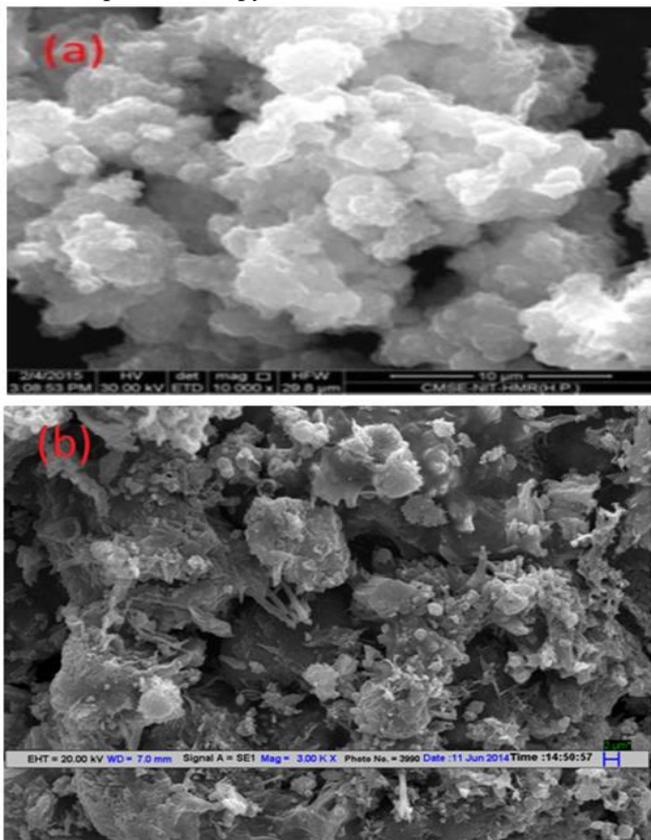


Fig 3. SEM image of (a) Pure Ppy and (b) Ppy composite.

Table 4. Crystallite size (L), micro strain (ϵ), dislocation density (ρ) and distortion parameters (g) calculated from 2θ value for the composite.

$2\theta(\text{exp})$	$L(\text{\AA})$	ϵ	$\rho \times 10^{17} \text{m}^{-3}$	g
20.72	42.12	0.471	5.636	20.996
24.92	49.65	0.400	4.056	14.839
36.91	122.71	0.647	6.641	2.046
39.65	209.53	0.095	2.278	1.118
43.38	137.64	0.144	5.278	3.124
45.16	274.41	0.290	1.328	0.754
46.78	458.41	0.043	4.759	0.437
48.14	196.21	0.101	2.597	1.986
50.81	141.56	0.140	4.990	1.308
55.99	49.05	0.405	6.103	6.899

Some particles are big enough in the Ppy composite which shows the agglomeration of particles. SEM of Ppy reflects amorphous nature while Ppy composite suggests semi-crystalline nature. In this way, SEM figures confirm successful composite formation.

TG/DSC of dopant, pure Ppy and composite

The TG/DSC of dopant, Ppy and composite of Ppy with synthesized dopant are shown in Figure 4(a), (b) and (c), respectively. TG of dopant shows two transitions. First transition is initiating from ambient temperature to 241°C , with a weight loss of 43.12% against the calculated weight loss of 42.83% which is as a result of loss of two molecules of urea. The second thermal decomposition step initiates from 241°C and stops at 370°C , with a weight loss of 12.95% against the calculated weight loss of 12.14% accounts for the removal of two molecules of ammonia. Urea besides an organic moiety, is coordinated to cobalt atom via oxygen of carbonyl therefore chances of removal of urea becomes more as compare to ammonia.

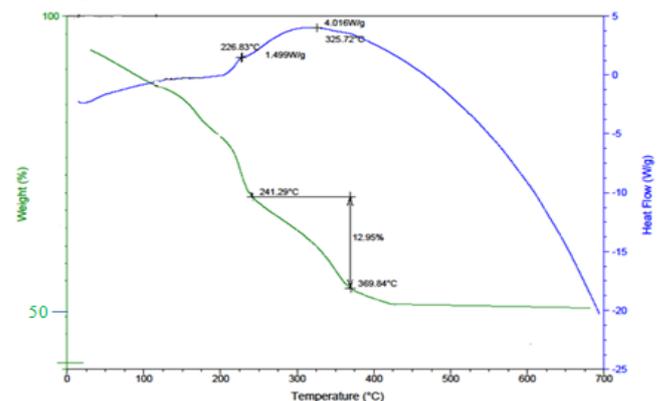


Fig 4a. TG/DSC of dopant $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$.

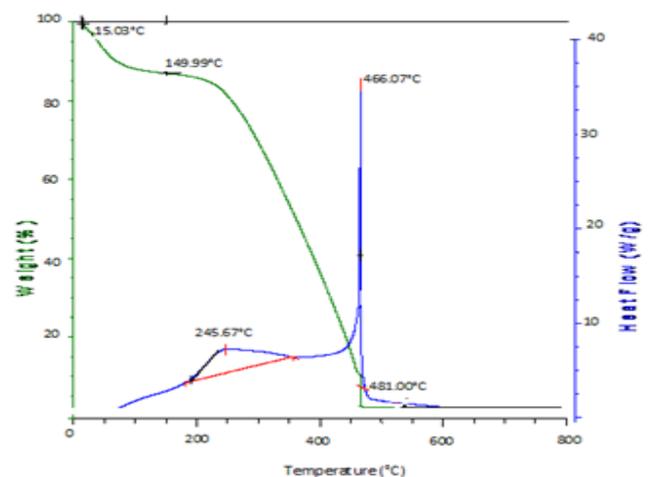


Fig4b. TG/DSC of pure polypyrrole.

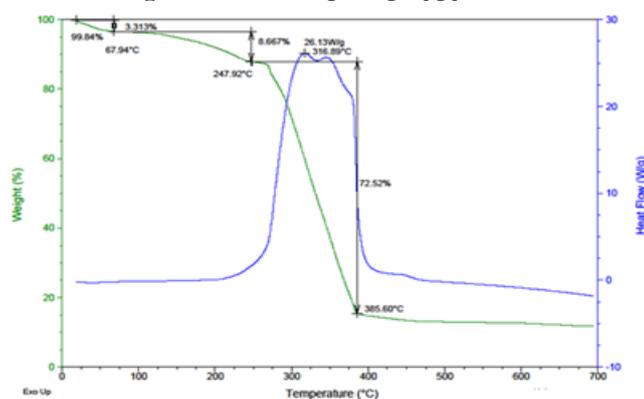


Fig4c. TG/DSC of polypyrrole composite.

The residue left behind at 370°C is 43.93% against the calculated weight value of 45% which is due to presence of CoCl_2 whose decomposition temperature is 1087°C.⁴⁰ 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 227°C and 326°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 pure polypyrrole shows two transitions. One transition is initiating from 15°C and ends at 150°C, with a weight loss of 13.03% which is as a result of loss of moisture. The second thermal decomposition starts from 150°C and stops at 481°C, with a weight loss of 84.76% accounts for the removal of organic matter C, N and H of Ppy. In this way complete decomposition of polypyrrole takes place upto temperature 480°C. DSC of Ppy shows two transitions. Both these transitions are exothermic. One transition has transition temperature of 246°C and another 466°C, corresponding to two transitions of TG.

TG curve of composite shows three transition. The first transition is from ambient temperature to 68°C, with a weight loss of 3.31 % which is due to loss of moisture. The second transition is initiating from 68°C and stops at 248°C, with a weight loss of 8.67 % and accounts for the removal of urea molecules of dopant. Third transition is a big one initiating from 248°C and ends at 386°C with a weight loss of 72.52% which is because of loss of organic moieties of C, H and N of Ppy part of composite and ammonia of dopant. TG curve runs parallel to x-axis beyond 512°C, which is due to inorganic moiety CoCl_2 of dopant whose decomposition temperature is beyond the analysis range, hence indicates stability of the composite. DSC of composite shows an exothermic peak at transition temperature of 444°C, with a heat flow of 19.27 W/g.

On comparing thermograms of dopant, Ppy and composite, it is evident that dopant and composite shows thermal stability beyond 500°C unlike pure Ppy which shows complete decomposition before 500°C, hence proves that dopant has been inserted into the composite and has increased the thermal stability of the composite material.

Conclusion

Successful synthesis of composite of polypyrrole based on the synthesized adduct $[\text{Co}(\text{H}_2\text{N-CO-NH}_2)_2(\text{NH}_3)_2\text{Cl}_2]$ has been proved by FTIR, XRD, SEM and TG/DSC analysis. FTIR of dopant exhibits monodentate character of urea and its coordination with cobalt occurs via the neutral oxygen of carbonyl. Moreover octahedral geometry has been proposed for the dopant. FTIR spectral peaks of composite confirm the

presence of dopant crystals. XRD reveals semi-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. SEM analysis suggests amorphous and semi-crystalline nature of Ppy and Ppy composite, respectively. TG and DSC analysis inferred that dopant has been inserted into Ppy matrix and has increased the thermal stability of the composite material; hence the material can serve for high temperature application purposes.

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