



# Spectroscopic Studies, Thermal Behaviour and Ac Impedance Study of Chemically Synthesized Silver Doped Polyaniline / BaFe<sub>12</sub>O<sub>19</sub> Polymer Composite

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## Abstract

The present work is a study of a.c impedance response and thermal behaviour of IPANI/Ag/BaFe<sub>12</sub>O<sub>19</sub> (PAB) composites synthesized by in-situ oxidative interfacial polymerization using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as an oxidizing agent at 0-5<sup>o</sup>C. The synthesized polymer composites were examined by FT-IR, TGA-DTA and DSC techniques. The a.c conductivity properties of the composites were investigated in the frequency range varying from 5x10<sup>1</sup> – 5x10<sup>6</sup> Hz at room temperature using HIOKI make 3532-50 LCR Hi-tester. FT-IR profiles confirm the formation of ferrite composite. The endothermic regions in the DTA pattern are consistent with the change regions in the TG curve. The Cole-Cole plots observed in the form of exact semi-circles clearly suggests the Debye-type relaxation mechanism present in these materials.

**Keywords:** Barium ferrite; Composites; Impedance; Polyaniline; Thermal stability

## 1. Introduction

Polymers have been proved to be excellent host matrices for trapping nanoparticles of metals, metal oxides and its composites are extensively useful in diverse applications viz., transducers, sensors, electrodes, EMI shielding electrochromic devices etc., as they combine electrical characteristics of metals, mechanical and processing properties of polymers [1]. Conducting polymers has been observed as frontier area of research and prospective materials for technological applications since last decade [2-4]. The way of synthesis of polymer decides the conductivity, band gap, chemical structure, polymerization mechanism and ease of attachment and detachment of different functional groups. Barium ferrite, being an hard magnetic material plays a key role as promising magnetic fillers in polymer composite material which finds diverse applications in magnetic recording media and microwave devices. It has been of a great interest because of its super functional properties viz., high magnetic anisotropy, low cost, large saturation magnetization, high chemical and physical stability.

## 2. Experimental Method

Aniline (0.1M) monomer was dissolved in aqueous nitric acid (1M) solution in a beaker, an organic solvent; chloroform (10ml) was added to the beaker. Then, add 0.1M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution and Ag-NO<sub>3</sub> (0.1M) solution separately dropwise, along the sides of the beaker to start oxidation at room temperature for

about 2-4 hrs, a dark- greenish coloured precipitate was formed slowly at the junction and then gradually diffused into the aqueous phase. After 24 hr, a dark greenish colour polyaniline matrix doped with shiny silver particles is obtained and the same is collected and washed with ethanol. BaFe<sub>12</sub>O<sub>19</sub> powder was added to the polymer solution with vigorous stirring in order to keep the BaFe<sub>12</sub>O<sub>19</sub> particles suspended in to the entire polymer solution. The reaction mixture was allowed to proceed at 50C for about 3hrs. The precipitate obtained was vacuum filtered, followed by washing with milli-Q water and acetone. Following this procedure, different IPANI/Ag/BaFe<sub>12</sub>O<sub>19</sub> (PAB) composites were prepared by varying 10%, 20%, 30%, 40% and 50% by weight of BaFe<sub>12</sub>O<sub>19</sub> in IPANI/Ag matrix. The resulting composites were crushed in to fine grained powder and dried in oven at 800 C to gain constant weight. The obtained powder form of polymer composites are pressed to form pellets of 10 mm diameter and thickness which varies from 1.5 to 2.5 mm by applying pressure of 90 MPa in a hydraulic press. The pellets are coated with silver paste on either side of the circular surfaces to obtain better electrical contact.

## 3. Results and Discussion

### 3.1. FT-IR studies

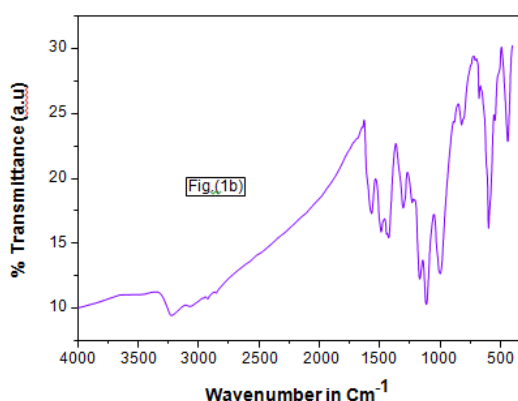
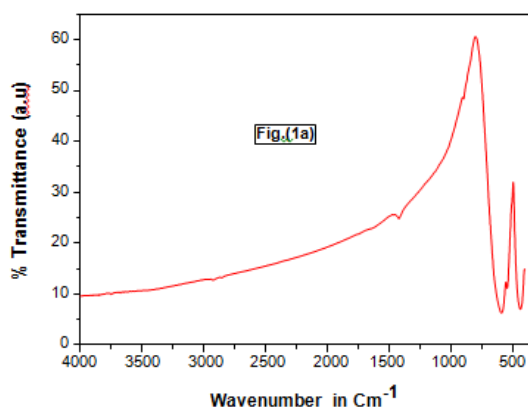
The characteristic absorption bands of IPANI observed in the FT-IR spectra recorded for PAB-50% composite are in agreement with the values reported in the literature [5-7,13-14], indicating that IPANI is formed in the composite and the corresponding band assignments are depicted in the table 1. In figure 1a, the peaks observed at 579

and 456cm<sup>-1</sup> correspond to typical Fe–O bond stretching in the BaFe<sub>12</sub>O<sub>19</sub> structure [8-11] and refers to intrinsic vibrations of the

tetrahedral and octahedral sites of BaFe<sub>12</sub>O<sub>19</sub>, respectively [7]. FT-IR spectra of the composite reflects the characteristic peak of Fe-O stretching vibration bands at 580 and 426cm<sup>-1</sup> and confirms the presence of BaFe<sub>12</sub>O<sub>19</sub> in the composite. By careful observation of the FT-IR spectra of the composite, it is noted that, the characteristic stretching frequencies of IPANI and BaFe<sub>12</sub>O<sub>19</sub> exhibits slightly blue shift, indicating that IPANI particles are well encapsulated by BaFe<sub>12</sub>O<sub>19</sub> [12].

**Table 1: FT-IR band assignments of IPANI in PAB-50% composite.**

IR Frequencies (cm <sup>-1</sup> )	Band Assignments
3201	N-H stretching mode of aniline
1558	Quinoid ring stretching modes
1487	Benzenoid ring stretching vibrations
1301	Asymmetric C-N stretching modes of benzenoid ring
1222	Conducting protonated form of IPANI
1114	C-H in plane bending vibrations
820	C-H out of plane deformation of p-disubstituted benzene ring



**Fig. 1** Shows FT-IR spectra of (a) Barium Ferrite, (b) PAB-50% composite

### 3.2. Thermal studies

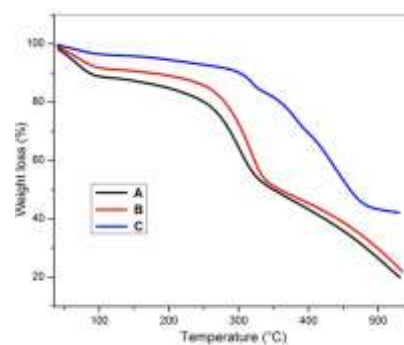
The TG thermogram of IPANI shows, initial weight loss of about 3.90% below 150°C ascribed to the removal of absorbed water molecules and acid dopants on the surface of the polymer [15] and the major weight loss of 9.89% is occurred from 300-400°C due to degradation of polymer backbone [16]. Similar behaviour in the degradation process was also observed for doped silver

IPANI, it shows higher onset degradation temperatures compared to IPANI due to the presence of more thermally stable silver particles [19]. BaFe<sub>12</sub>O<sub>19</sub> with exceptionally high thermal stability, showed two stage weight loss behavior in the range 40<sup>0</sup> to 450<sup>0</sup>C, the first step weight loss of about 0.14% below 100<sup>0</sup>C due to moisture, and there- after degradation process proceeds up to 450<sup>0</sup>C with a weight loss of about 0.2%. The TG thermo gram of PAB-50% composite exhibit four distinctive decomposition patterns, from ambient temperature to 4500C, the first step weight loss of 1.2% below 1000C is due to expulsion of water molecules and impurities, second step weight loss of 4.76% occurs in the range 300-3500C, the third step weight loss of 6.7% in the range 350- 4000C is mostly attributed to IPANI [17] and the fourth step weight loss of 8.5% takes place beyond 4000C, which is due to decomposition of barium ferrite particles. The onset temperatures for four degradation stages of the composite position rate of the polymer when combined with BaFe<sub>12</sub>O<sub>19</sub> and IPANI. IPANI undergoes rapid thermal degradation at 301.050C; however the composite is stable up to 434.580C. This suggests that, the composite is thermally more stable compared to bulk IPANI. From the table 2, it is clear that, BaFe<sub>12</sub>O<sub>19</sub> is thermally stable up to 435.340 C, upon addition of barium ferrite in to the IPANI-Ag matrix retains the thermal stability of the composite. Comparing the thermal behavior of the synthesized PAB-50% composite with that of IPANI, indicates a notable shift of the endothermic peak from are 69.350, 318.730, 382.650 and 434.580C respectively. The decom- silver nano particle is found to be different from that of the bulk 301.050-434.580C due to the presence of IPANI [17-18].

**Table 2: Weight loss% and Onset Temperatures of synthesized polymer sample**

Sample	Steps	Onset temperature (°C)	
		% Weight Loss	
IPANI	1	3.90	69.3
	2	9.89	301.05
IPANI/Ag	1	2.90	70.5
	2	12.13	317.17
BaFe <sub>12</sub> O <sub>19</sub>	1	0.14	71.82
	2	0.20	435.24
PAB - 50%	1	1.20	69.35
	2	4.76	318.73
	3	6.70	382.65
	4	8.50	434.58

The DSC curves of Silver doped IPANI shows exhibited a little exothermic hump around 300°C attributed to crystallization of silver nano particles and broad endotherm at 250°C, due to loss of moisture and other volatile compounds. IPANI completely decomposes above 300 °C, showing a broad exothermic peak at 325 °C and broad endothermic peak in the range 350- 400°C related to morphological changes at higher temperatures [22]



**Fig. 2(a)**

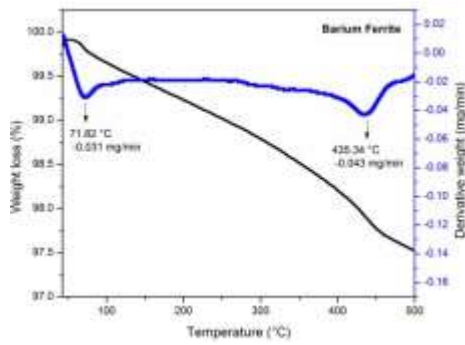


Fig. 2(b)

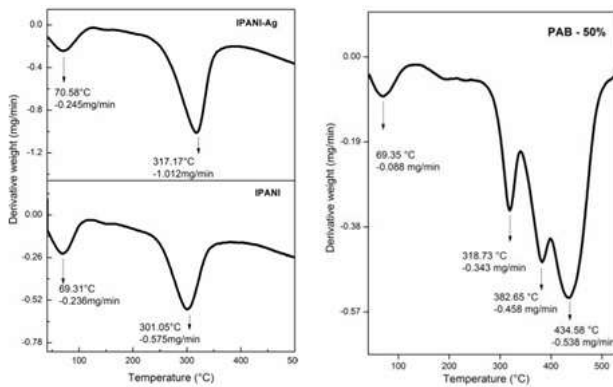


Fig. 2(c)

Fig. 2(d)

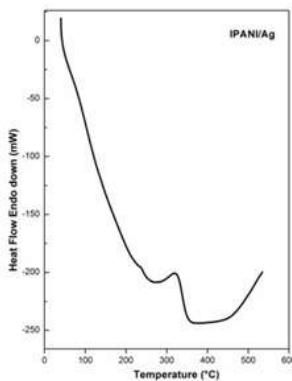


Fig. 2(e)

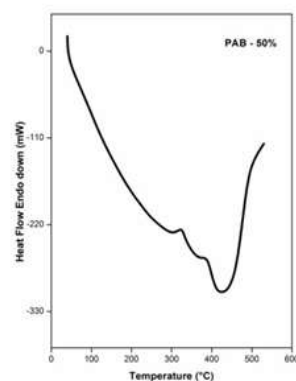


Fig. 2(f)

**Fig. 2** Shows (a) TGA curves of A. IPANI, B. IPANI-Ag, C. PAB-50% composite (b) TGA-DTA pattern of  $\text{BaFe}_{12}\text{O}_{19}$  (c-d) Derivative weight loss pattern of IPANI, IPANI-Ag, and PAB-50% composite, which suggests most apparent weight loss steps corresponding to endothermic peaks in the region 50- 450 °C (e-f) DSC curves of IPANI/Ag and PAB-50% composite.

The DSC curves of the composite shows weak endotherm at 270°C is due to loss of moisture, dopants and other volatile compounds. The trace is then followed by endotherm around 350°, due to de-composition of IPANI backbone [23]. The sharp endotherm observed in the range 400- 450°C can be attributed to the degradation of barium ferrite particles.

#### AC impedance study

Fig. 3a shows the variation of a.c impedance,  $Z$  with logarithmic frequency for PAB-30%, 40% & 50% composites at room temperature. It is observed that,  $Z$  values decreases with increase in frequency and at higher frequencies the values of  $Z$  merges beyond the fre-

quency 5.8 Hz for all the wt% of the composites, this may be due to the polarization effect [ 20, 21].

The variation of real ( $Z'$ ) and imaginary ( $Z''$ ) parts of the complex impedance plotted as a function of applied a.c frequency for PAB-30%,40%&50% composites are shown in Fig. 3b. It is seen that the values of  $Z'$  remains constant at lower frequencies forming a high value plateau. At higher frequencies a sudden fall in the  $Z'$  is observed which forms a lower plateau region as the frequencies approaches the microwave range. The observed behaviour of  $Z'$  as a function of frequency is due to the resistive contribution of the material. The values of  $Z''$  in all the samples remain constant at lower frequencies forming a lower-value plateau, whereas at higher frequencies  $Z''$  shows a relaxation peak. The value of frequency at which the relaxation peak observed depends upon the wt% of barium ferrite particles present in the composite. As the applied frequency approaches to microwave region,  $Z''$  values again forms a low value plateau.

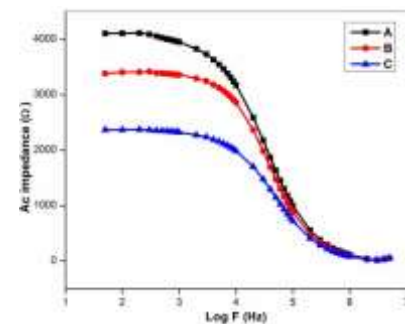


Fig. 3(a)

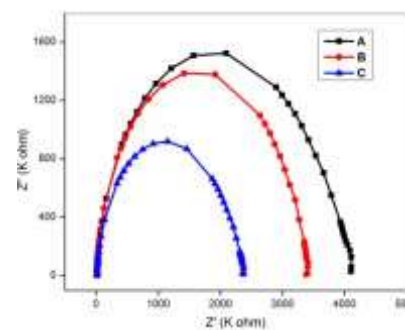


Fig. 3(b)

**Fig. 3** Shows (a) Variation of a.c impedance with the logarithmic frequency for PAB -30%, 40% & 50% composite at room temperature and (b) Cole-Cole plots for PAB -30%,40% & 50% composite

#### 4. Conclusion

In the present work, IPANI/Ag/ $\text{BaFe}_{12}\text{O}_{19}$  composites were successfully synthesized by in-situ chemical oxidative interfacial polymerization using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidant. By careful observation of DSC profile of the composite, it can be noticed that, a shift of endothermic peaks notably towards higher temperature side suggesting that the composite is thermally more stable. The increased thermal stability may be attributed to the formation of interpenetrating polymer network with barium ferrite particle embedded with silver nano particles, which are confirmed by FT-IR studies. Ac impedance studies of PAB-30%, 40% & 50% composite shows semicircles on a complex plane impedance plot, indicating that the composite obeyed Debye model with single relaxation.

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