Study of Dielectric Properties of Silver Doped Polyaniline Composites

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Abstract- **The present work is an investigation of dielectric response of Polyaniline/Ag/Graphene/$SrTiO_3$ (PAGS) composite prepared by in-situ chemical oxidative interfacial polymerization using $(NH4)_2S_2O_8$ as an oxidant with varying (10, 20, 30, 40 and 50 wt%) of $SrTiO_3$ in IPANI matrix. The structural characterization of the samples was examined using FTIR, SEM and EDX techniques. The dielectric response of synthesized polymer composites were investigated at room temperature in the frequency range varying from $5x10^1$-$5x10^6$ Hz using HIOKI make 3532-50 LCR Hi-tester. The real (ε') and imaginary (ε'') dielectric constant decreases with increase in frequency and exhibits almost zero dielectric loss at higher frequencies, which infers that the composite is a lossless material at frequencies beyond 3Hz. The real part of electric modulus (M') features a dispersion tending towards maximum value and approaches almost zero at low frequencies.**

Keywords: **Composites; Polyaniline, dielectrics, Graphene**

I. INTRODUCTION

Over the last few years, conducting polymer composites have been studied with emerging ideas because of diverse applications in various electrical and electronic devices viz., sensors, microwave devices [1-2]. Polyaniline-metal oxide composites synthesized via chemical oxidative method have attracted a great interest in view of their technological and fundamental scientific importance, where metal oxide is associated with the polymer chain during polymer synthesis. In this method, no further doping is required after polymer synthesis and uniform distribution of metal oxide within a polymer matrix takes place without the aid of any surfactants. So that the desirable properties of the polymer can be modified and its applicability can be improved. The large number of reports were found in the literature that explains synthesis of polyaniline (PANI) and its blends [3].The synthesis and design of conducting polymer composites with graphene nanoparticle as an effective conductive filler are important for designing electro chromic devices and development of super capacitors with better specific capacitance that was recently reported by Zhang et.al [4].

II. EXPERIMENTAL

0.1M aniline was dissolved in 1M nitric acid in a beaker, chloroform (10ml) was added to it. Then, add 0.1M ammonium per sulphate solution and silver nitrate solution 0.1M separately drop wise, along the sides of the beaker to start oxidation at room temperature for about 3-4 hrs, a dark greenish colour polyaniline matrix doped with shiny silver particles is obtained. $SrTiO_3$ powder was added to polyaniline solution with constant stirring in a thermostat bath at 5^oC for about 3hr in order to keep the $SrTiO_3$ particles suspended in the solution. The precipitate obtained was vacuum filtered and dried in oven at 80^oC to gain constant weight. Following this procedure different IPANI/Ag/$SrTiO_3$ composites were prepared by varying 10, 20, 30, 40 and 50 wt% of $SrTiO_3$ in silver doped IPANI matrix**.** PAGS- 10, 20, 30, 40 & 50% composite was prepared by mixing graphene nanopowder mechanically with different compositions of IPANI/Ag/$SrTiO_3$ (10, 20, 30, 40 and 50wt %) composite. Firstly, the IPANI/Ag/$SrTiO_3$ polymer composite of different compositions (10, 20, 30, 40 & 50%) was powdered using mortar & pestle, manually. Then graphene nanoparticle in powder form was added to obtain powder form of composites, which are pressed in to conductive circular pellets [4].

III. RESULTS AND DISCUSSION

The significant peaks of IPANI observed in the FT-IR spectra recorded for PAGS-50% composite matches in accordance with the values reported in the literature [5-10] and are depicted in the below table 1. The characteristic vibrations at $3420cm^{-1}$ and $1564cm^{-1}$ are due to absorbed moisture and sp^2 hybridized C=C stretching in aromatic ring of graphene sheets [11-14]. $SrTiO_3$ exhibits characteristic broad bands at 541 and 1435 cm^{-1} which can be ascribed to Ti-O stretching vibration and carboxylate group stretching mode [7,15]. The

characteristic stretching frequencies in FT-IR spectra of the composite exhibits significant red shift, which suggests that, there is a weak vanderwaals force of interaction between the IPANI backbone and $SrTiO_3$ [15].

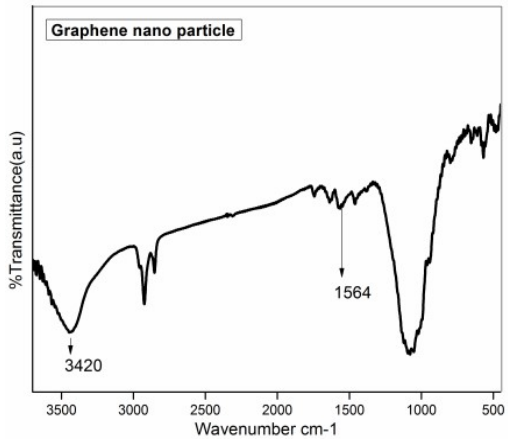

Figure 1a

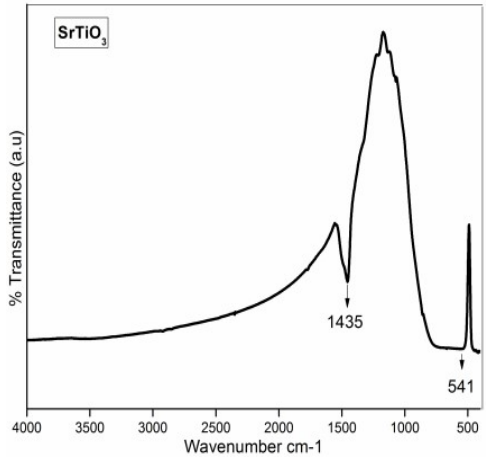

Figure 1b

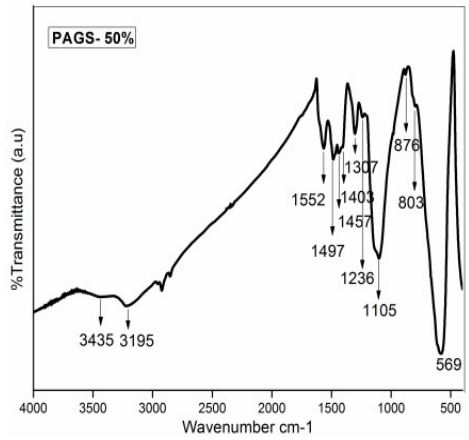

Figure 1c

Figure 1 Shows FTIR spectra (a) Graphene nanoparticle, (b) pure $SrTiO_3$ and (c) PAGS-50% composite.

TABLE 1

Table 1 Shows IR bands and its assignments of IPANI in the PAGS-50% composite

IR Frequencies (cm^{-1})	Band Assignments
3195	N-H stretching mode of aniline
1497	Quinoid ring stretching modes
1457	Benzenoid ring stretching modes
1307	C-N and C=N stretching modes of IPANI
1236	Polaronic structure of IPANI
1105	C-H out-plane deformation of IPANI
803	C-H in-plane deformation of IPANI

It is observed from SEM photograph, that $SrTiO_3$ shows clusters and cubic granular morphology of almost 2µm in size**.** The SEM image of composite shows, a clear view of oriented structure where in almost all $SrTiO_3$ particles are seen as embedded in the polymer matrix. Hence, it shows that fine grains of $SrTiO_3$ cubes when incorporated with IPANI matrix tend to coalesce and form agglomerates of size 10 µm with the overlapping platelet-like structure of graphene sheets, mostly arranged in parallel plane orientation and stacked together.

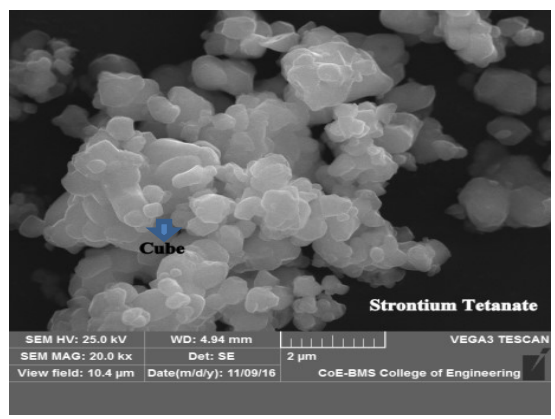

Figure 2a

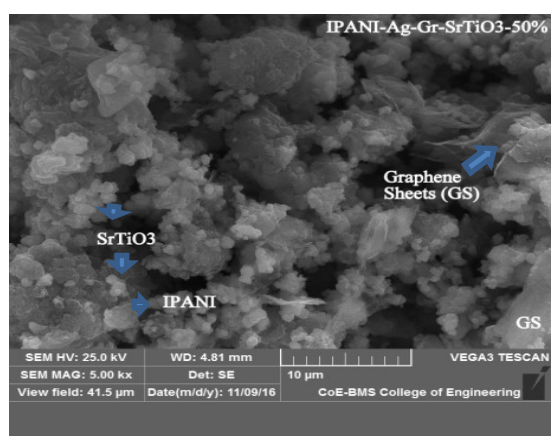

Figure 2b

The fine structures of the composites are found to be slightly agglomerated and the traces of graphene wafer like structures were also seen in the composite. Thus, SEM studies confirm the presence of graphene and $SrTiO_3$ in IPANI matrix, which is a direct evidence for the formation of the composite.

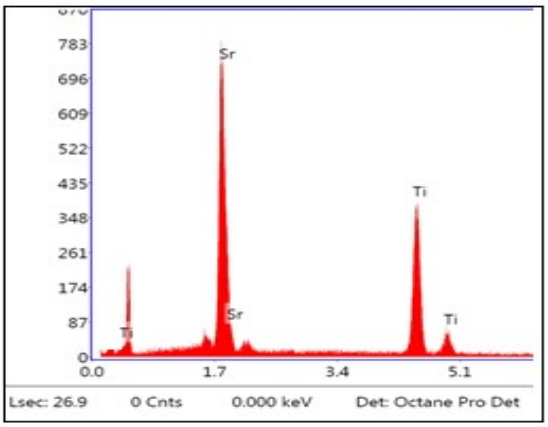

Figure 2c

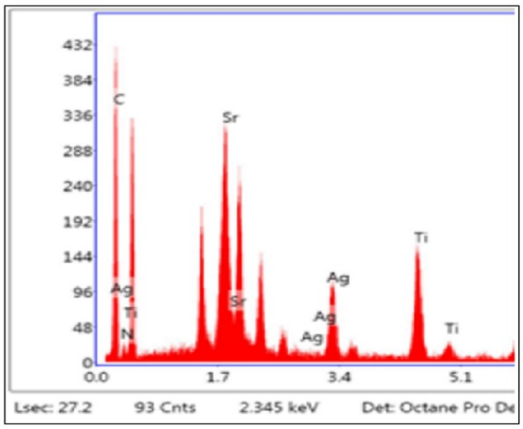

Figure 2d

Figure 2 Shows SEM micrographs of (a) pure Strontium titanate (b) PAGS-50% composite, EDX spectra of (c) Pure Strontium titanate (d) PAGS-50% composite.

TABLE 2

Table 2 Shows the weight% of Sr, Ti, Ag and elements (C, N and O) obtained from EDX analysis.

Sample	EDX (Weight %)					
	C (K)	N (K)	Ag (L)	O (K)	Sr (L)	Ti (K)
$SrTiO_3$	-	-	-	28.69	49.53	22
PAGS-50%	42.38	3.06	1.2	38.54	11.01	4.88

The chemical composition analysis of the examined samples is depicted in the table 2 and 3. EDX spectrum of pure $SrTiO_3$ witnesses the presence of Sr and Ti metals. However, no other peaks of impurities were observed. The peaks observed at 0.3277 keV for K lines of C and at 4.736 keV for K lines of Ti and at 1.744 keV for L lines of Sr elements. An overlapping broad peak of O and Ti of $SrTiO_3$ is observed at about 0.422 keV. EDX spectra of PAGS-50% composite exhibited the characteristic peaks of elemental C, Ti, Sr, N, O and Ag. The corresponding EDX results suggest that the $SrTiO_3$ and silver doped IPANI nanoparticle composites were successfully coated on the surface of graphene sheet by this method. From the chemical compositions obtained from the EDX spectra, it can be concluded that $SrTiO_3$ cubes are homogenously distributed in between the stacks of graphene layer and those $SrTiO_3$ nano cubes act as spacer between two graphene layers.

TABLE 3

Table 3 Shows the atomic% of Sr,Ti, Ag and elements (C, N and O) obtained from EDX analysis

Sample	EDX (Atomic %)					
	C (K)	N (K)	Ag (L)	O (K)	Sr (L)	Ti (K)
$SrTiO_3$	-	-	-	32.14	39.89	27.99
PAGS-50%	55.27	3.42	0.5	37.73	1.97	1.59

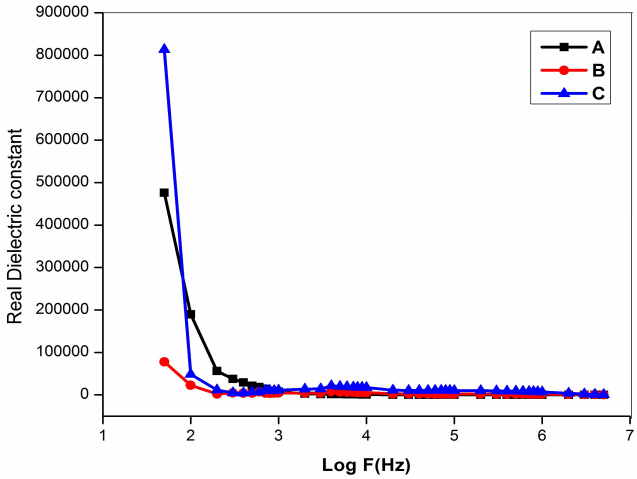

Figure 3a

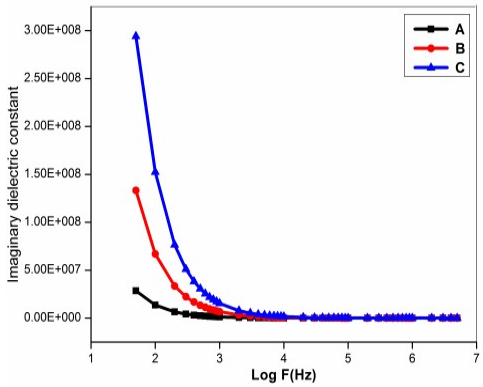

Figure 3b

The values of ε' decreases with increase in frequency and remains almost same after 3Hz. At higher frequencies, the value of ε' is low, because the relaxation mechanism is relatively slow compare to molecular vibration. 50wt% shows high value of ε' at lower frequencies and remains almost same at higher frequencies compared to that of 10wt% and 30wt% and the high value of ε' may be due to dielectric relaxations [27-29]. However, the value of ε" decreases for 10wt%, 30wt % and 50wt% with increase in frequency and remains almost same after 3.5 Hz, which is a characteristic of Debye relaxation mechanism. 50wt% shows high value of ε" at lower frequencies and remains almost same at higher frequencies compared to that of 10wt% and 30wt%.The dielectric tangent loss values for the PAGS-10%, 40% & 50% composite shows higher at lower frequencies and decreases with increase in frequency up to 3.5Hz and thereafter remains almost same. It is observed that, the 50wt% composite shows higher values of dielectric loss compared to that of 10wt% and 40wt%. This is due to increase in interfacial interactions between the IPANI and $SrTiO_3$, which is in direct evidence with FT-IR studies, leading to maximum space charge polarization [25-26].

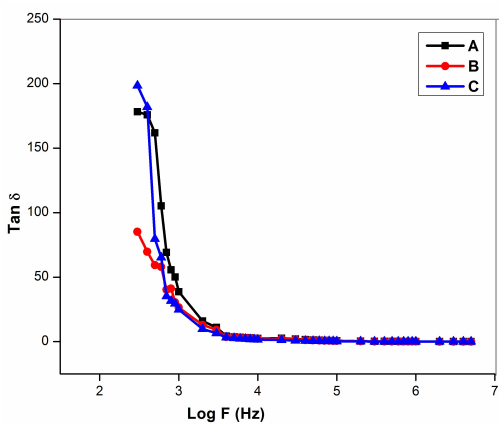

Figure 3c

Figure 3 shows the (a) variation of real dielectric constant (ε') as function of logarithmic frequency for PAGS-10%, 30% & 50% composite, (b) variation of imaginary dielectric constant (ε") as function of logarithmic frequency for PAGS-10%, 30% & 50% composite and (c) variation of dielectric tangent loss as a function of logarithmic frequency for PAGS-10%, 40% & 50% composites at room temperature.

The electric modulus is the reciprocal of the permittivity in complex form was found using the equation [31]:

$$M^* = \frac{1}{\epsilon^*} = M' + M''$$

Where M' and m" are the real and imaginary parts of electric modulus and is calculated by the equation:

$$M' = \varepsilon' / ((\varepsilon')^2 + (\varepsilon'')^2)$$

$$M'' = \varepsilon'' / ((\varepsilon')^2 + (\varepsilon'')^2)$$

The real part of electric modulus versus frequency profile of IPANI and PAGS composites exhibited relaxation mechanisms at high frequencies. At high frequency, the real part of electric modulus, M' shows dispersion while at low frequency it tends to zero which shows the low contribution of electrode polarization to M'. At high frequency, dielectric relaxation peaks take place when the hopping frequency of the localized electric charge carriers becomes approximately equal to that of the externally applied ac electric field. At lower frequencies the real part of electric modulus exhibit low value which may be due to the large value of capacitance associated with the electrode polarization and at high frequency it shows high values as a consequence of low value of capacitance [32]. At higher frequencies, 50wt% composite shows significantly higher value of M' (1.61218×10^{-8} at 6.69Hz) compared to 10wt% (8.78573×10^{-9} at 6.69Hz). However, at higher frequencies IPANI shows high value of M' which may be due to the low value of capacitance associated with the electrode polarization compared to that of PAGS-10% &50% composites.

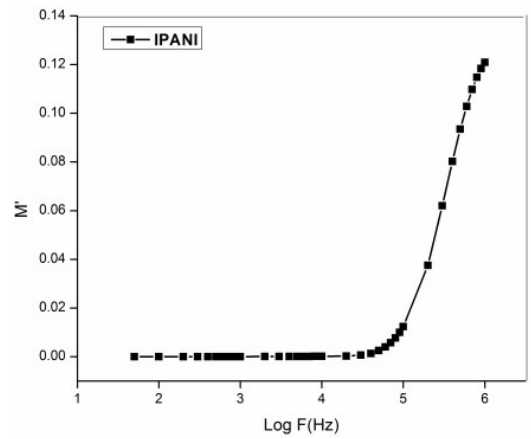

Figure 4a

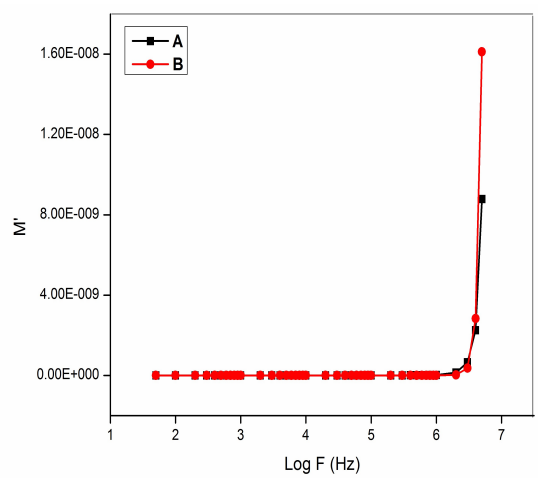

Figure 4b

Figure 4 shows the (a) variation of real part of electrical modulus (M') as function of logarithmic frequency for bulk IPANI, (b) variation of real part of electrical modulus (M') as function of logarithmic frequency for A-B. PAGS-10% & 50% composites at room temperature.

IV. Conclusion

In the present study, we reported the facile synthesis of PAGS composite via in-situ chemical oxidative interfacial polymerization route using $(NH_4)_2S_2O_8$ as an oxidizing agent. FT-IR studies give the direct evidence for the interfacial interactions between IPANI and $SrTiO_3$. Dielectric studies confirmed that the synthesized PAGS composites behave as dielectric materials at lower frequencies. However, it exhibits almost zero dielectric loss which suggests that the composite is lossless material at frequencies beyond 3 Hz. PAGS-50% composite showed highest dielectric behavior at lower frequencies, this may be due to maximum space charge polarization, resulting in the role of dielectric response for the better electrical properties.

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