



Electrical & dielectric studies of silver oxide doped polyaniline [AgO/PANI] nanocomposite

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Abstract

We have prepared Polyaniline (PANI) and metal oxide doped polyaniline (AgO/PANI) nano composites by incorporating silver oxide with conducting polymer (PANI) with 5%, 10%, 20%, 30%, 40% & 50% wt% of AgO via chemical oxidative polymerization method with APS as oxidant. X-ray diffraction & scanning electron microscopy (SEM) technique are used to investigate structural analysis and surface morphology of the prepared sample. The effect of silver oxide on PANI and the electrical properties (AC & DC) and dielectric properties were determined using impedance analyser. The AC conductivity, dielectric constant, dielectric loss and variation of $\tan\delta$ of all the composites were studied as a function of frequency at room temperature and DC conductivity were analysed as function of temperature.

Keywords: polyaniline, AC & DC conductivity, dielectric constant

1. Introduction

Conducting polymer composites are the future materials for emerging technologies as they possess a combination of unique properties of their constituents. The properties become more interesting when one of the components is in the nano range. Due to the synergistic effect of the polymer and the nano filler, the resulting materials are expected to display desirable properties with enhanced performance [1]. Polyaniline (PANI) was discovered over 150 years ago, it has only recently captured the attention of the scientific community due to its high electrical conductivity on treatment with protonic acids and became the most investigated conducting polymer since its discovery about three decades ago. It was first prepared in 1834 and has been the subject of mild research ever since [2]. However, the conducting properties of PANI were recognized and the number of research articles dealing with this conducting polymer grew rapidly since 1980s. Among all conducting polymers, PANI has a special representation due to its unique properties such as low cost of its monomers, ease of synthesis by chemical or electrochemical routes and high environmental stability. The specific advantages of PANI include the ability to tune its electrical properties easily by proton doping or simple versatile redox reactions. These features made PANI an attractive replacement material in many areas of applications such as electrodes, charge transfer and active layers, electrochromic displays, electromagnetic shielding as well as a growth template for neurons [3-4].

The properties of these conducting polymers can be modified by the addition of inorganic particles. Nano scale particles are more attractive due to intriguing properties arising from the nano size and large surface area. The insertion of nano scale fillers may improve the electrical and sensing properties of the

polymers [5]. In recent years, nano-sized metal particles have got much attention due to its unique optical, electrical and magnetic properties, which depends on the size and shape of the particle. Silver oxide (AgO) nano particles is a well-known material having vast applications in the field of oxidation catalysis [6-7], sensors [8], fuel cells [9], photovoltaic cells [10], all-optical switching devices, optical data storage systems [11] and as a diagnostic biological probes [12]. Many physical and chemical properties including luminescence, conductivity, and catalytic activity depend upon the size of nano scale materials.

2. Materials and Methods

2.1 Materials and Method

Aniline, hydrochloric acid (HCL) and ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ of analytic grade are used for synthesis of polyaniline and Silver oxide was used to prepare composite via chemical oxidative polymerization method.

2.2 Preparation of Polyaniline and AgO/PANI composite

In the first step, 0.2M of aniline solution and 1N of hydrochloric acid is taken in first beaker and stirred by magnetic stirrer for 2hrs at room for completion of the mixer. In second step, the solution of 0.2M of ammonium persulfate is taken in second beaker and it was added drop wise into the first beaker and continued the stirring for 8 hrs. In third step, continuous stirring of solution was filtered by Buchner funnel and washed with deionised water with acetone. In fourth step, final obtained product was dried in oven at 50 °C for 24 hrs. The dried sample was grinded into fine powder for further characterization. For preparation of AgO/PANI composite, continuation to the second step, silver oxide powder for different additive weight percentage (5%, 10%, 20%, 30%,

40% & 50%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the AgO homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. Then step four continued to obtain grinded powder.

3. Result and Discussions

3.1 Structural Analysis

The structural analysis of the sample was studied by X-ray diffraction technique. Figure-1 shows the XRD pattern of the Pure PANI and Figure-2 (a-f) shows the XRD pattern of the AgO/PANI for different additive weight percentage (5%, 10%, 20%, 30%, 40% & 50%) respectively. Generally polyaniline is the amorphous in nature. From pattern it reveals that, the broad peak of the pure polyaniline indicates the amorphous nature of the sample. The sample shows crystalline in nature when it is doped with AgO and crystallinity increases when doping concentration increased from 5% to 50%. Figure-1 shows the prominent peak of pure polyaniline is in the range of 25-27°, which is characteristics peak of polyaniline. Figure-2 shows sharp peak of maximum intensity at 2θ values 32.7 degree and other weak peaks are 2θ values 54.7 & 58.9 degree and as doping concentration increases, the enhancement in the sharpness of the peaks and intensity of (111) reflection indicated the increase in the crystallinity of the PANI. The diffractions (111), (220) and (222) reflections related to the cubic structure of AgO (ICCD Card No: 00-41-1104). Along with (111) reflection at 2θ values 32.7 degree, an additional two diffraction peaks at 2θ values 44.1 and 54.8 degree are correspond to the (200) and (220) reflections of metallic silver (ICCD Card No: 00-004-0783). It is also

observed that, the intensity of the peaks is increasing from 45 counts to approximately 230 counts as doping concentration increased from 5% to 50%. This increase in the intensity of the XRD peak may suggest that, silver oxide dispersed in the polyaniline matrix.

The average crystalline size of the PANI are estimated to be approximately 20-30 nm are calculated by using Debye - Scherrer formula,

$$(D=K\lambda/(\beta \cos\theta))$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, β is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Bragg's angle (deg.).

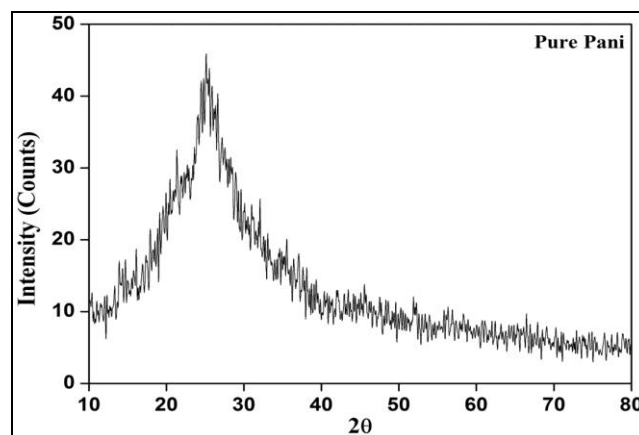


Fig 1: X-ray diffraction patterns of Pure Polyaniline.

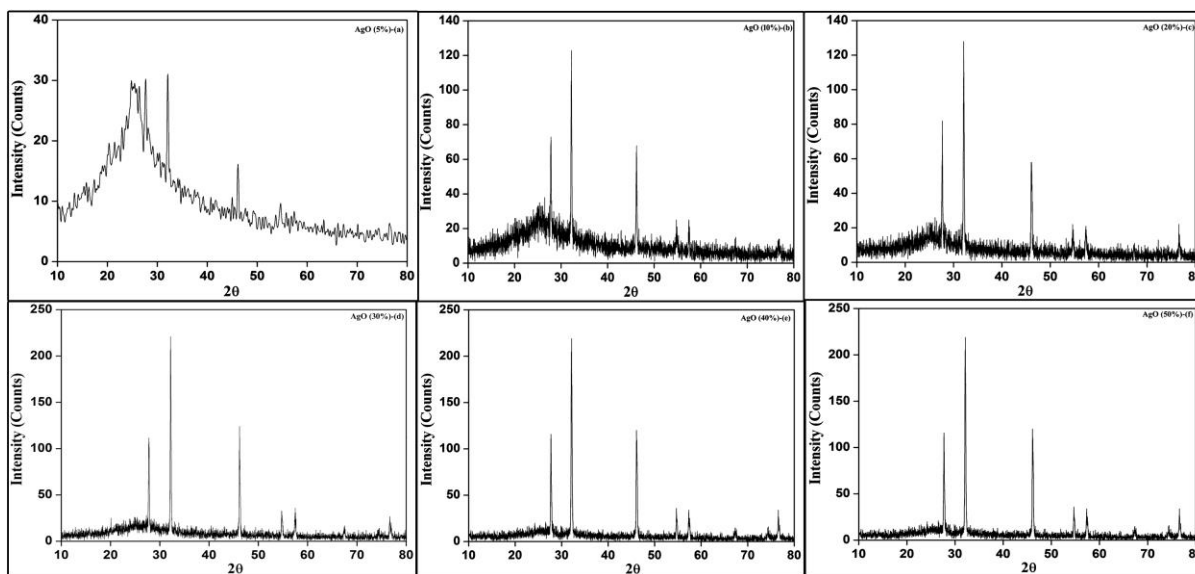


Fig 2: X-ray diffraction patterns of (a) AgO (5%)/PANI, (b) AgO (10%)/PANI, (c) AgO (20%)/PANI, (d) AgO (30%)/PANI, (e) AgO (40%)/PANI, (f) AgO (50%)/PANI.

3.2 Morphological Study

Figure-3 illustrates the surface morphology of pure polyaniline and Figure-4 (a-f) illustrates the surface morphology AgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) respectively. The SEM image of PANI shows uniform

morphology with semi-crystalline like structure. The SEM image of AgO/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface

morphologies with diverse sizes. Also observed that, percentage of composites doesn't affect the morphological image considerably. The average grain size was calculated as 30-40nm. The average grain size was determined by the linear intercept technique. A number of lines were drawn on a photograph and number of intercepts between the test line and grain boundaries were counted. The average grain size was calculated by using

$$D = \frac{1.56 \times C}{M \times N}$$

Where, D- Average grain size, N- Number of intercepts and M- Magnification of the photograph.

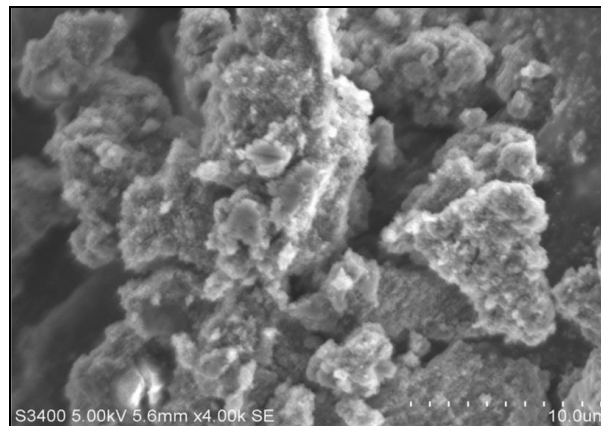


Fig 3: SEM micrographs of Pure Polyaniline

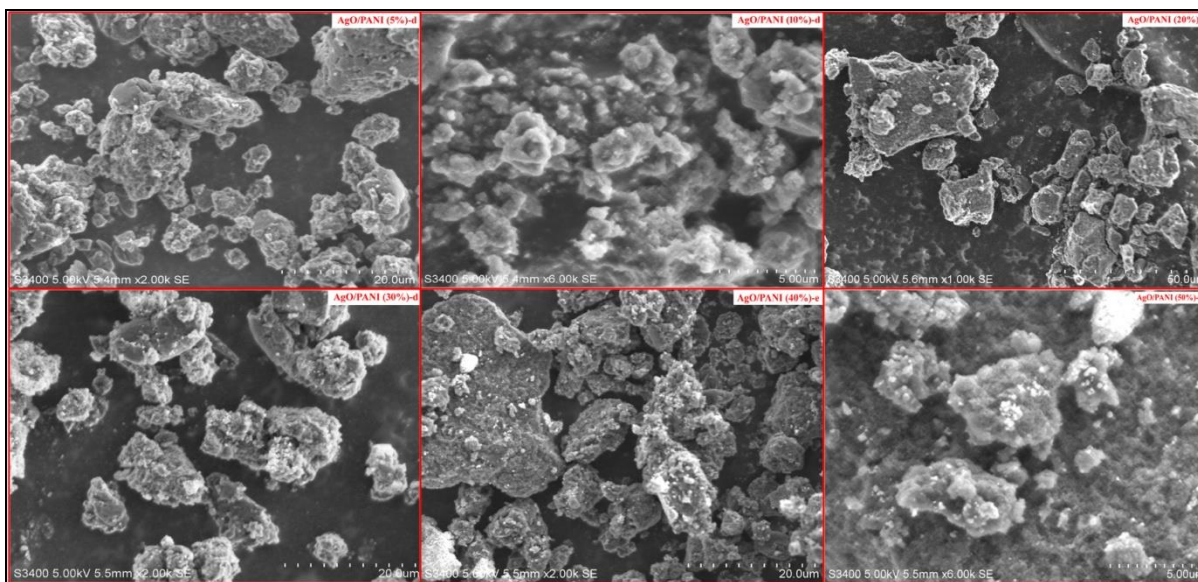


Fig 4: SEM micrographs of (a) AgO (5%)/PANI, (b) AgO (10%)/PANI, (c) AgO (20%)/PANI, (d) AgO (30%)/PANI, (e) AgO (40%)/PANI, (f) AgO (50%)/PANI.

3.3 Electrical Conductivity

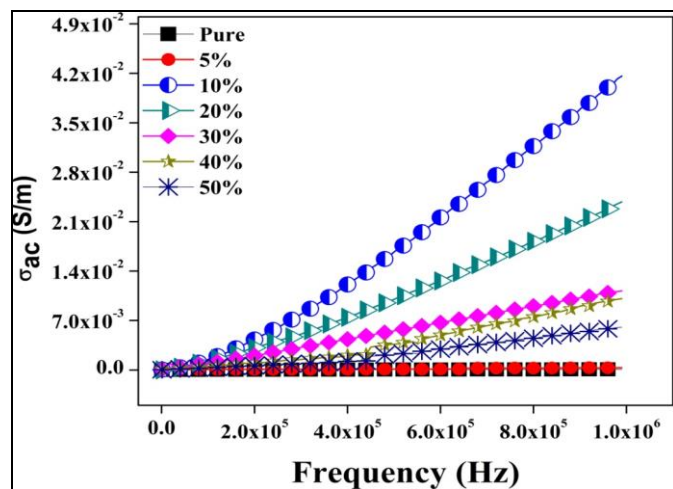
3.3.1 AC Conductivity

The frequency dependent conductivity for disordered materials such as polymers can be due to interfacial polarization at contacts and grain boundaries of the sample [13]. Figure- 5 shows the frequency dependence of σ_{AC} conductivity as a function of frequency for pure PANI and AgO/PANI composites with different wt%. The conductivity of all the studied samples are observed at room temperature. In all cases it observed that, the σ_{AC} conductivity increases as frequency increased from 1 KHz to 1MHz. It is reported previously that, polyaniline has electrical conductivity ranges between 10^{-10} and 10^3 S/cm depending on the acid dopant and fillers [14]. From plots it is observed that, the conductivity of all composites are higher than that of pure polyaniline. This observed high conductivity of the composites may due to the distribution of silver oxide in the polyaniline matrix. The variation of the conductivity of polyaniline and composites at 1 KHz, 500 KHz and 1 MHz shown in table-I. Previously

reported that, the ac conductivity of pure polyaniline was found to be approximately 3×10^{-7} S/m at 1 KHz and it increases to 6.5×10^{-6} S/m at 1 MHz [15]. Compared to previously reported, the conductivity was found to be higher for polyaniline at both the frequency 1 KHz and 1 MHz may be due to the variation aniline, oxidant and HCL in synthesis process. The conductivity of the polyaniline found to be 3.79×10^{-6} S/m, 5.11×10^{-5} S/m and 8.88×10^{-5} S/m which increases as doping increased then reaches to the value 4.93×10^{-5} S/m, 2.17×10^{-3} S/m and 0.60×10^{-2} S/m for the measured frequency 1 KHz, 500 KHz and 1 MHz respectively. Among the composites, the conductivity of the composite 30% is found to be maximum (9.03×10^{-5} S/m) at 1 KHz frequency and composite 10% is found to be maximum of about 1.61×10^{-2} S/m & 4.16×10^{-2} S/m at 500Khz and 1MHz frequency respectively. This may be due to the extended chain length of polyaniline which facilitate the hopping of charge carriers when the content of 10% & 30% AgO.

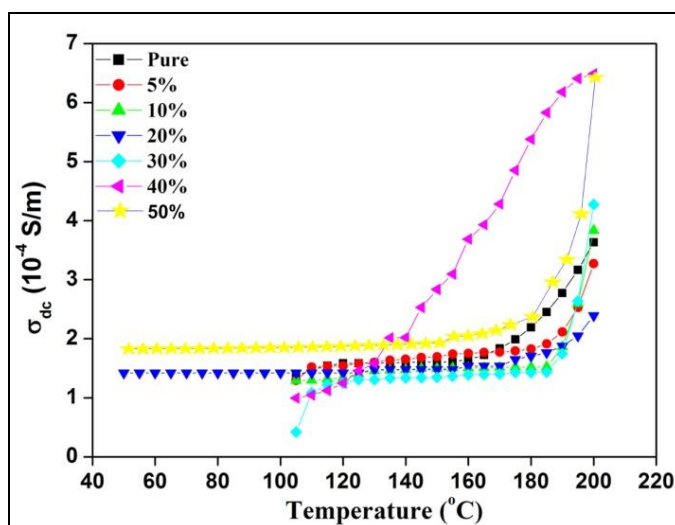
Table 1: Variation ac conductivity as function of composition at 1 KHz, 500 KHz and 1 MHz frequency.

Sample	Conductivity (σ_{ac}) S/m At 1 KHz	Conductivity (σ_{ac}) S/m At 500 KHz	Conductivity (σ_{ac}) S/m At 1 MHz
Pure PANI	3.79×10^{-6}	5.11×10^{-5}	8.88×10^{-5}
PANI/AgO (5%)	8.38×10^{-6}	1.20×10^{-4}	3.28×10^{-4}
PANI/AgO (10%)	5.32×10^{-5}	1.61×10^{-2}	4.16×10^{-2}
PANI/AgO (20%)	9.23×10^{-6}	9.77×10^{-3}	2.38×10^{-2}
PANI/AgO (30%)	9.03×10^{-5}	5.40×10^{-3}	1.12×10^{-2}
PANI/AgO (40%)	8.29×10^{-5}	3.62×10^{-3}	1.01×10^{-2}
PANI/AgO (50%)	4.93×10^{-5}	2.17×10^{-3}	0.60×10^{-2}

**Fig 5:** AC conductivity of Polyaniline and composites as function of Frequency

3.3.2 DC Conductivity

To illustrate the effect of AgO on the DC- conductivity of polyaniline material, a comparison of pure PANI and PANI/AgO composite was made. The temperature dependence DC electrical conductivity of pure PANI & AgO/PANI composites was carried out from 40°C temperature to 200°C on silver paste coated pellets with thickness ranging from 1-2 mm. Figure-6 shows the variation of dc electrical conductivity as a function of temperature for pure polyaniline & polyaniline composites. It is observed that in all cases, dc conductivity of the PANI increases with increase in the temperature indicates semiconductor behaviour of PANI sample and it is found to be 1.4×10^{-4} S/m at 40 °C, which increases to 3.4×10^{-4} S/m at 200 °C for pure polyaniline. In addition, the dc conductivity is smaller in case of composites 5%, 10%, 20% & 30% and higher in case of composites 40% & 50%. As is known the most common green polyaniline emeraldine salt has conductivity on a semiconductor level of the order of 100 Scm^{-1} [16].

**Fig 6:** DC conductivity of Polyaniline and composites as function of Temperature.

3.4 Dielectric Studies

The dielectric properties of materials, namely permittivity, are typically measured as a function of frequency and are called dielectric/ impedance spectroscopy. The permittivity values show the interaction of an external field with the electric dipole moment of the sample (Griffiths 1999, Baker-Jarvis, *et al.* 2010, Yaw 2012). Dielectric measurement is an important tool to understand the material behaviour especially at high frequencies because it can provide the electrical or magnetic characteristics of the materials, which is a critical parameter

required to implement the material in many applications. Measurement of dielectric properties involves measurements of the complex relative permittivity (ϵ), which consists of a real part and an imaginary part. The real part of the complex permittivity, also known as the dielectric constant is a measure of the amount of energy from an external electrical field stored in the material. The imaginary part is zero for lossless materials and is also known as loss factor. It is a measure of the amount of energy loss from the material due to an external electric field. The dielectric parameters were evaluated by

measuring equivalent parallel capacitance C_p and dissipation factor $\tan\delta$ by using the equation,

$$\epsilon' = \frac{C_p}{C_0} \&$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

or

$$\epsilon' = \epsilon'' \tan \delta$$

The term $\tan\delta$ is called loss tangent and it represents the ratio of the imaginary part to the real part of the complex permittivity.

Where $C_0 = \epsilon_0 A/t$, is the geometrical capacitance of vacuum of the same dimensions as the sample. A and t are the area and thickness of the sample respectively and f the measuring frequency. C_p is the capacitance measured, ϵ' the real dielectric constant and ϵ'' the imaginary dielectric constant.

3.4.1 Variation of real dielectric constant (ϵ')

Figure-7 shows the variation of dielectric constant ϵ' as a function of frequency for different wt% of polyaniline /AgO composites. Dielectric constant of polyaniline and polyaniline composites decreases as frequency increases over the measured frequency range 1 KHz to 1 MHz, which is a typical characteristic of disordered conducting polymer. In all the cases it is observed that, the dielectric constant is relatively high at low frequency (1 KHz) compared to polyaniline and further it decreases with increase in applied frequency. For 10wt% dielectric constant is high at low frequency among all the composites and decreases linearly up to 1MHz with increase in frequency. The observed behaviour may be due to Debye like relaxation mechanism which is taking place in these materials. Previously reported that, the dielectric constant of polyaniline found to be approximately 122.38 at frequency 1KHz and which decreases to approximately 85.68 at 500 KHz. Table-II shows the variation real dielectric constant (ϵ') as function of composition at 1KHz, 500KHz and 1 MHz^[17].

Table 2: shows the variation real dielectric constant (ϵ') as function of composition at 1 KHz, 500 KHz and 1 MHz

Sample	ϵ' at 1 KHz	ϵ' at 500 KHz	ϵ' at 1 MHz
Pure PANI	140.64	33.41	33.10
PANI/AgO (5%)	644.90	23.63	22.86
PANI/AgO (10%)	167924.66	61.55	60.22
PANI/AgO (20%)	1162.39	28.99	28.20
PANI/AgO (30%)	12231.74	79.11	75.86
PANI/AgO (40%)	12309.65	41.28	38.11
PANI/AgO (50%)	10970.78	37.15	34.30

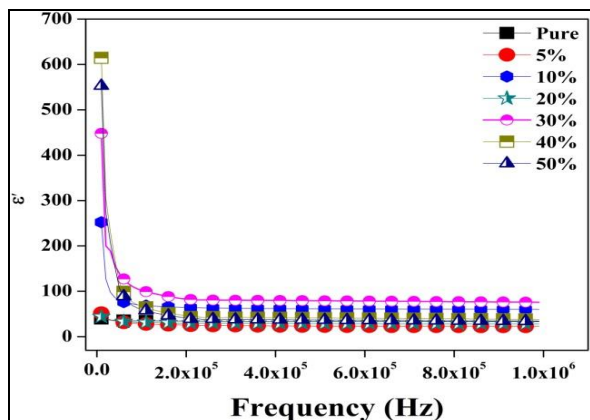


Fig 7: Variation of Dielectric constant (ϵ') of Polyaniline and composites as function of frequency

3.4.2 Variation of imaginary dielectric constant (ϵ'')

Figure-8 shows the variation of ϵ'' as function of frequency in the range 1 KHz to 1MHz for polyaniline and polyaniline composites. In all cases the value of ϵ'' decreases as frequency increases over a measured frequency 1KHz to 1MHz in two phases, i.e. in the range 1.0×10^3 Hz to 2.0×10^5 Hz and then from 2.0×10^5 Hz to 1M Hz frequency. The variation of ϵ'' at 1 KHz, 500 KHz & 1 MHz is shown in table-3. It is clear that, the imaginary part of dielectric constant is dependent of composition of silver oxide. The value of ϵ'' if found to be maximum for composite 10% at 1 KHz frequency and composite 50% is maximum at frequency 500KHz and 1MHz. The value of ϵ'' of all the composites are higher than polyaniline.

Table 3: shows the variation ϵ'' as function of composition at 1 KHz, 500 KHz and 1 MHz

Sample	ϵ'' at 1 KHz	ϵ'' at 500 KHz	ϵ'' at 1 MHz
Pure PANI	592.33	1.87	1.61
PANI/AgO (5%)	912.66	4.37	5.96
PANI/AgO (10%)	37.43×10^5	6.39	4.79
PANI/AgO (20%)	3243.34	2.34	1.83
PANI/AgO (30%)	1130.54	31.83	25.15
PANI/AgO (40%)	1400.54	51.15	38.38
PANI/AgO (50%)	1500	61.38	46.05

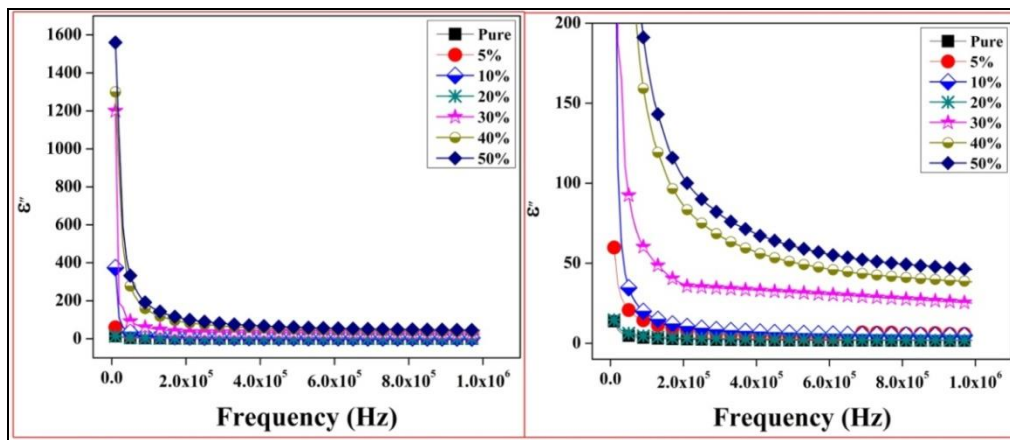


Fig 8: Variation of Dielectric constant (ϵ'') of Polyaniline and composites as function of frequency

3.4.3 Variation of $\tan\delta$

The Variation of $\tan\delta$ as a function of frequency for pure polyaniline and composites are shown in figure-9. The loss tangent for pure PANI has a rather value of 3.99 at 1 KHz, which decreases with increasing frequency and reaching a value of 0.048 at 1MHz. The observed value of dielectric loss at low frequency an all cases may be due to the high value of resistance caused by grain boundaries. In first phase of the

frequency 1 KHz to 2×10^5 Hz, the value of $\tan\delta$ decreases suddenly and in second phase of frequency 2×10^5 Hz to 1 MHz, the value of $\tan\delta$ decreases gradually and maintains constant value further. The variation of $\tan\delta$ at different frequency is given in table-III. From table it is clear that, composite 20% id found to be maximum among the composites also greater than polyaniline at frequency 1 KHz.

Table 3: shows the variation $\tan\delta$ as function of composition at 1 KHz, 500 KHz and 1 MHz

Sample	$\tan\delta$ at 1 KHz	$\tan\delta$ at 500 KHz	$\tan\delta$ at 1 MHz
Pure PANI	3.99	0.056	0.048
PANI/AgO (5%)	1.40	0.185	0.115
PANI/AgO (10%)	20.04	0.10	0.079
PANI/AgO (20%)	2.57	0.080	0.065
PANI/AgO (30%)	2.81	0.457	0.432
PANI/AgO (40%)	4.92	0.485	0.473
PANI/AgO (50%)	2.53	0.582	0.568

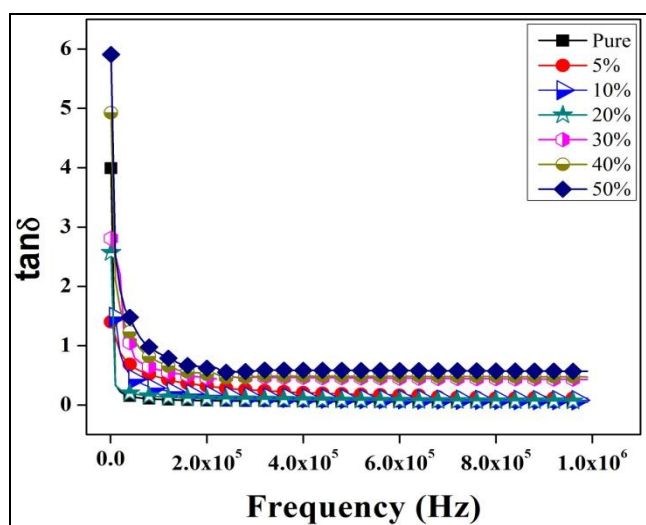


Fig 9: Variation of $\tan\delta$ of Polyaniline and composites as function of frequency

4. Conclusion

Polyaniline and Ago/PANI were successfully synthesized by the chemical oxidative method. The result of XRD and SEM shows the formation of the composites and indicates the

interaction between PANI and AgO. The average crystalline size of the PANI are estimated to be approximately 20-30 nm by XRD technique. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM image of AgO/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes.

From AC conductivity it is observed that, the conductivity of all composites are higher than that of pure polyaniline. The maximum conductivity is achieved 4.16×10^{-2} S/m for composites 10% at 1MHz frequency. The temperature dependence DC electrical conductivity of pure PANI & AgO/PANI composites was carried out from 40°C temperature to 200°C and increases with increase in the temperature indicates semiconductor behaviour of PANI sample. DC conductivity is found to be higher for in case of composites 40% & 50%. It is observed that the real dielectric constant (ϵ'), imaginary dielectric constant (ϵ''), dielectric loss tangent in case of polyaniline and composites decreases as a function of frequency. The sample (polyaniline) used exhibits small value of dielectric loss at higher frequency over the measured frequency range 1 KHz to 1 MHz. For 10wt%

dielectric constant is high at low frequency among all the composites and decreases linearly up to 1 MHz with increase in frequency. The imaginary part of dielectric constant is dependent of composition of silver oxide. The value of ϵ'' is found to be maximum for composite 10% at 1 KHz frequency and composite 50% is maximum at frequency 500KHz and 1MHz. The value of $\tan\delta$ for composite 20% is found to be maximum among the composites also greater than polyaniline at frequency 1 KHz.

5. References

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