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Electrical & dielectric studies of Silver oxide/Polyaniline nanocomposites influenced by ammonium dichromate

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Abstract

The combination of polyaniline and metal oxide composites with uniform distribution is expected to facilitate wider applications of the material. In this study, Polyaniline (PANI) and Silver oxide doped polyaniline (AgO/PANI) with different molar concentration were prepared by chemical oxidation route using ammonium dichromate $(NH_4)_2Cr_2O_7$ (ADC) as oxidant and HCL as catalyst. The structural and surface morphology of the nanocomposites were characterized by XRD & SEM technique. The electrical properties (AC & DC) and dielectric properties were determined using impedance analyser. The AC conductivity, dielectric constant, dielectric loss and variation of tanδ of all the composites were studied as a function of frequency at room temperature and DC conductivity were analysed as function of temperature.

Keywords: silver oxide/polyaniline composite, x-ray diffraction, electrical conductivity and dielectric permittivity

1. Introduction

Among the many materials, conducting polymer has unique properties such as electrical, optical and magnetic property, due to this reason polymers increasing scientific and technical interest and offering the opportunity to prepare new polymer materials [1].

Conducting polymers are characterized by a conjugated structure of alternating single and double bonds. The feature shared by all them originates from the common nature of their π -electron system, an enhanced conductivity in oxidized or in reduced state and reversible redox activation in a suitable environment [2].

Among all the conducting polymers, polyaniline has a unique and wide range electrical, dielectric properties and good stability. Hence polyaniline have been considered as prominent new materials for the fabrication of the devices. Polyaniline (PANI) is an important conducting polymer because of its high conductivity in doped state. PANI has wide range of application due to its flexible properties in different area. Such some applications are solar cell, LED, sensors, radiation absorbers and electromagnetic shields. It is possible to alter the properties of the PANI by the process of doping metal oxide or various types of particles with polyaniline. It is one of so called polyaniline composite, in which conductivity results from a process of partial oxidation or reduction [3]. There are many oxidation forms of the polyaniline, among these the most important form of polyaniline is green protonated emeraldine which can prepare by using chemical oxidative polymerization method. When the metal oxide or various types of particles are doped with polyaniline, the charge-transfer reaction takes place between polyaniline and doping agent. The bond length and angles changes when charges are removed from the polyaniline upon chemical doping. The charge is localized over the region of several repeating units. Since the localized charges can move along the polymer chain, they are regarded as charge carriers in conducting polymer [4]. Ammonium persulfate (APS), Ammonium Dichromate (ADC) was used as an oxidant to minimize the presence of residual aniline and to obtain the best yield of PANI.

Silver oxide (AgO) is the chemical compound with fine dry powder of a brownish-black colour. It is a three-dimensional polymer and is not readily soluble in most solvents and which slightly hydrolyzes only in water. When AgO hydrolyzes in water, it gives the water a distinctive metallic taste. AgO is soluble in dilute nitric acid and which is easily attacked by acids. Silver is multivalent forms of various phases like Ag_2O, Ag_3O_4, Ag_4O_3, and $Ag_2O_3$by interacting with oxygen [5]. These oxides have different crystalline structures leading to a variety of physiochemical, electrochemical, electronic and optical properties. The most observable and stable phases are AgO and Ag_2O [6]. The recent development in AgO is for its potential use in optical memories. Fortiu and Weitzman [7] reported that silver oxide has band gap of 1.2 eV while other studies have shown that Ag_xO films have a wide range of energy band gap of between 1.2 and 3.4 eV [8, 9]. This wide range of band gap is as a result of different stoichiometries, crystalline phases, and properties arising from different deposition techniques.

2. Materials and Method

Chemicals used to prepare polyaniline are aniline, hydrochloric acid (HCL), ammonium dichromate $(NH_4)_2Cr_2O_7$ of analytical grade and synthesized by employing chemical oxidative polymerization method.

2.1 Preparation of Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of Hydrochloric acid at 0°C temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.25 M of ammonium dichromate $(NH_4)_2Cr_2O_7$ was added drop wise into the mixer. This reaction mixer was continuously stirred in magnetic stirrer at constant RPM for 8 hrs under 0° C temperature. After 8 hrs the precipitate was separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder and obtained black coloured powder

2.2 Preparation of AgO/Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at 0°C temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.25 M ammonium dichromate was added drop wise into the mixer. Silver oxide (AgO) 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 0°C temperature. After 8 hrs the precipitate was separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50°C for 24 hrs. The final product was grinded into powder [10].

3. Results and Discussions

3.1 Structural Analysis

The structural analysis of the sample was studies by X-ray diffraction technique. Figure-1 shows the XRD pattern of the Pure PANI and Figure-2 (a, b, c, d, e & 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 synthesized pure polyaniline is semi-crystalline. The semi-crystalline nature of polyaniline obtained may be due to ammonium dichromate used in the synthesis as oxidant and it is crystalline as doping percentage increases due to the presence of Ago in the polyaniline. Figure-1 shows the prominent peak of pure polyaniline is in the range of 25-27°. Figure-2 (a, b, c, d, e & f) shows the prominent peak of AgO at 2θ values 32.19, 32.16, 32.26, 32.12 and 32.33 degree for different doping concentration (5%, 10%, 20%, 30%, 40% & 50%). It is also observed that, the intensity of the peaks is increasing from 70 counts to approximately 600 counts as doping concentration increases. This increase in the intensity of the XRD peak may suggest that, silver oxide dispersed in the polyaniline matrix with broadness of the peaks remains same.

The average crystalline size of the PANI are estimated to be approximately 17nm 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 Braggs' angle (deg.) and lattice strain was estimated to be 0.0088.

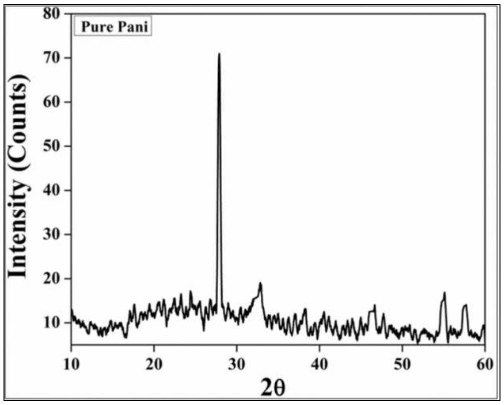

Fig 1: X-ray diffraction patterns of Pure Polyaniline.

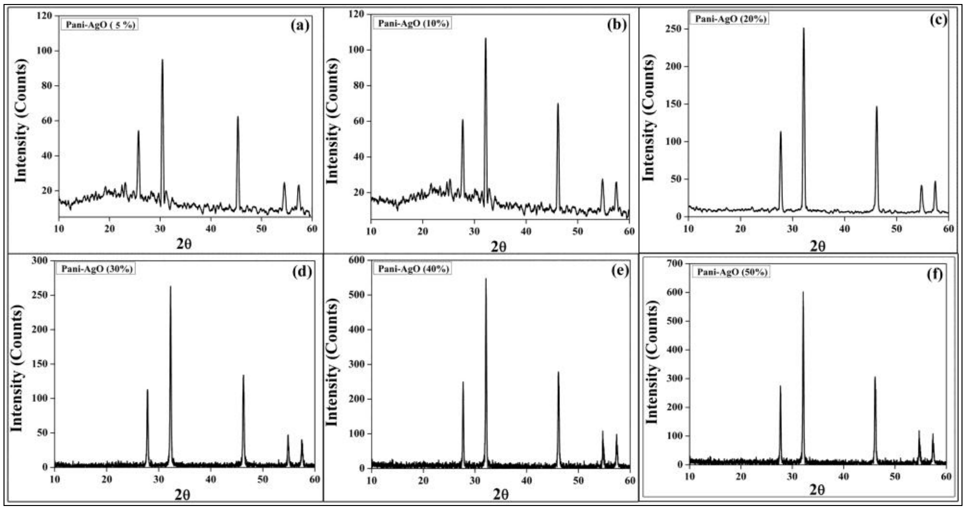

Figure-2: X-ray diffraction patterns of (a) AgO(5%)/PANI, (b) AgO (10%)/PANI, (c) AgO (20%)/PANI, (d) AgO (30%)/PANI, (e) AgO (40%)/PANI, (f) AgO (50%)/PANI.

3.2 Morphological Study

Figure-3 illustrates the surface morphology of pure polyaniline and Figure-4 (a, b, c, d, e & 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 20-30nm.

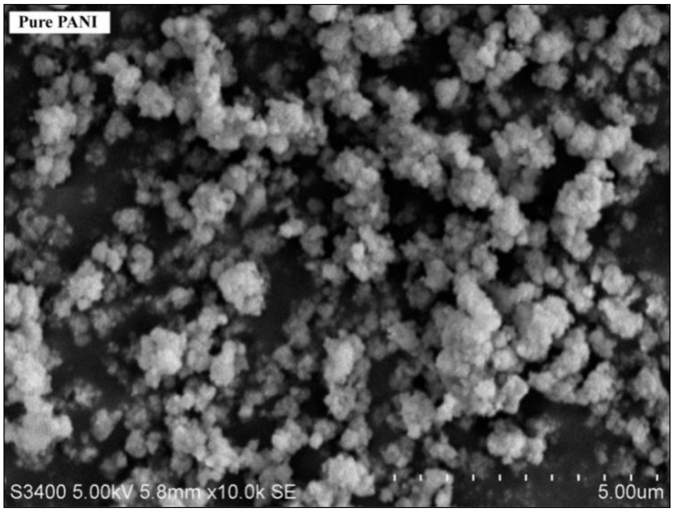

Fig 3: SEM micrographs of Pure Polyaniline

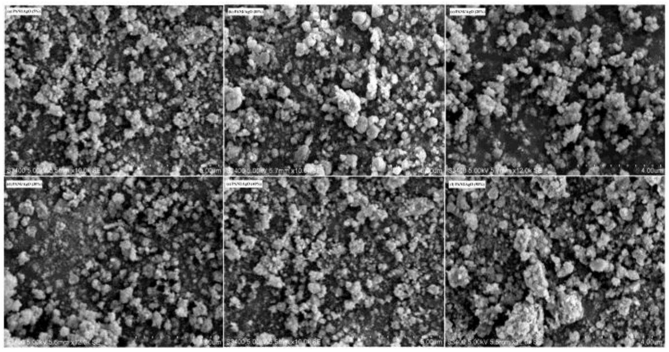

Figure-4: SEM micrographs of (a) AgO(5%)/PANI, (b) AgO (10%)/PANI,m (c) AgO (20%)/PANI, (d) AgO (30%)/PANI, (e) AgO (40%)/PANI, (f) AgO (50%)/PANI.

3.3 Electrical Conductivity

3.3.1 AC Conductivity

The AC electrical conductivity of pure PANI & AgO/PANI composites was carried out at 1KHz–1MHz frequency in room temperature, AgO/PANI pallets were coated with silver paste with thickness ranging from 2-5 mm. Figure-5 shows the AC conductivity (σ_{ac}) as a function of frequency for pure polyaniline and AgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) respectively. 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 [11]. As frequency increased from 1KHz–1MHz, it is found that, the AC conductivity of PANI increases gradually. It is evident that the AC-conductivity is frequency dependent and enhanced linearly with an increase of the frequency. This indicates that there may be charge carriers which can be transported by hopping through the defect sites along the polymer chain [12]. Also it is observed from plots that, the conductivity also increases as concentration of silver oxide increases from 5% to 40% i.e., the conductivity is greater than the pure polyaniline at 1KHz. Then shows decrease in conductivity as concentration of silver oxide increases to 50% i.e., the conductivity lesser then pure polyaniline at 1KHz. The increase and decreasing in the conductivity of the PANI and composites were shown in figure-6 as function of additive weight percents of silver oxide. It is also observed from figure-6 that, the ac conductivity of PANI composite (20%) was found to be high among all other composites for both 1 KHz and 1 MHz frequency and it increases from 7.41 x 10^{-6} S/m to 2.3 x 10^{-2} S/m. The anomaly in the conductivity behaviour of these composites may be due to the variation in the distribution of silver oxide in polyaniline. Previously reported that, the ac conductivity of pure polyaniline (ammonium persulphate as oxidant) was found to be approximately 3x10^{-7} S/m at 1 KHz and it increases to 6.5x 10^{-6} S/m at 1 MHz [13]. Compared to pure polyaniline (ammonium persulphate as oxidant), the conductivity of pure polyaniline (ammonium dichromate as oxidant) is found to be less.

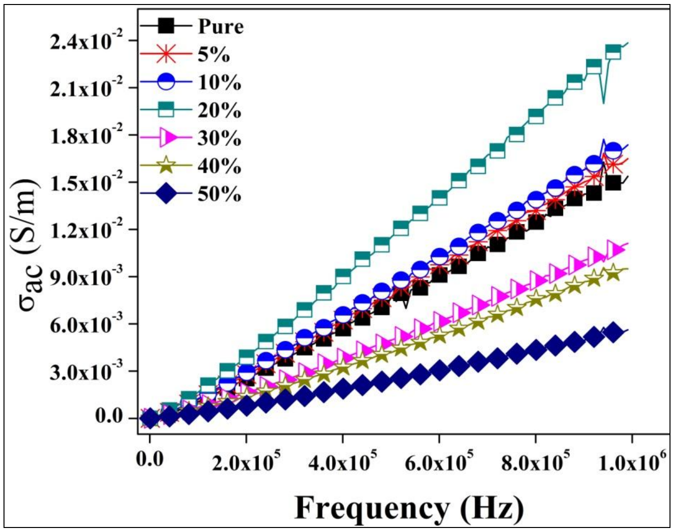

Fig 5: AC conductivity of Polyaniline and composites as function of Frequency

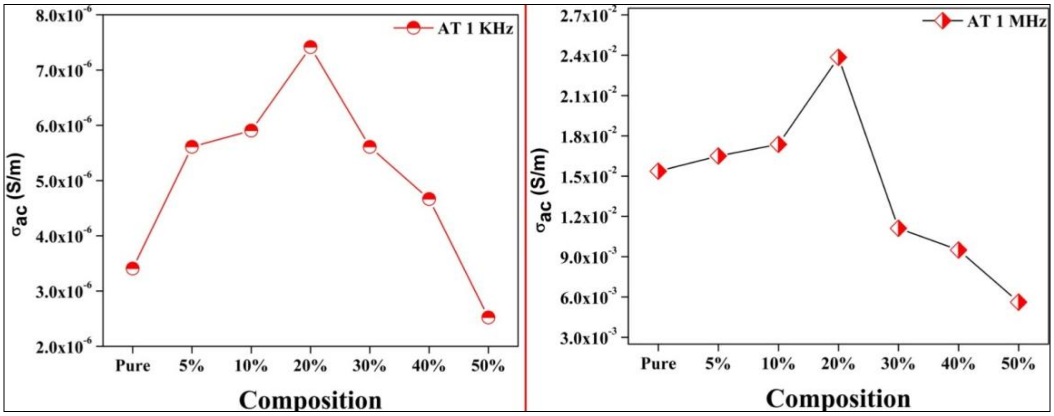

Fig 6: Variation of AC conductivity of PANI & Composites at 1 KHz & 1 MHz Frequency

3.3.2 DC Conductivity

The temperature dependence DC electrical conductivity of pure PANI & AgO/PANI composites was carried out from room temperature to 200°C on silver paste coated pellets with thickness ranging from 2-5 mm. Figure-7 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 and it is found to be 4.06 x 10^{-9} S/m at 30 °C, which increases to 4.07 x 10^{-5} S/m at 200 °C for pure polyaniline. The dc conductivity found to be 1.56 x 10^{-9} S/m at 30 °C and which increases to 4.06 x 10-7 S/m at 200 °C for composite (50%). From above it is clear that, the conductivity decreases as concentration of silver oxide increases from 5% to 50% in the polyaniline matrix. The decrease in the dc conductivity may due to the distribution of silver oxide and ADC in polyaniline. It is observed from figure that, conductivity of PANI showing in two phases i.e., the conductivity in the range 30 °C – 140 °C and 150 °C to 200 °C. The first phase conductivity is almost constant which may be due to inter-chain transport of charge carriers, i.e., hopping of charge carriers between the polymer chains and is usually observed at intermediate temperature. But, at high temperature region, (phase two) there is an sudden increase in the conductivity with increase in temperature due to intra-chain transport of charge carriers which can be described by the band conduction mechanism and is usually it is observed at high temperatures as reported by authors in their previous work [14, 16]. The localized states that forms extended band like structures may act in trapping the carriers from extended states.

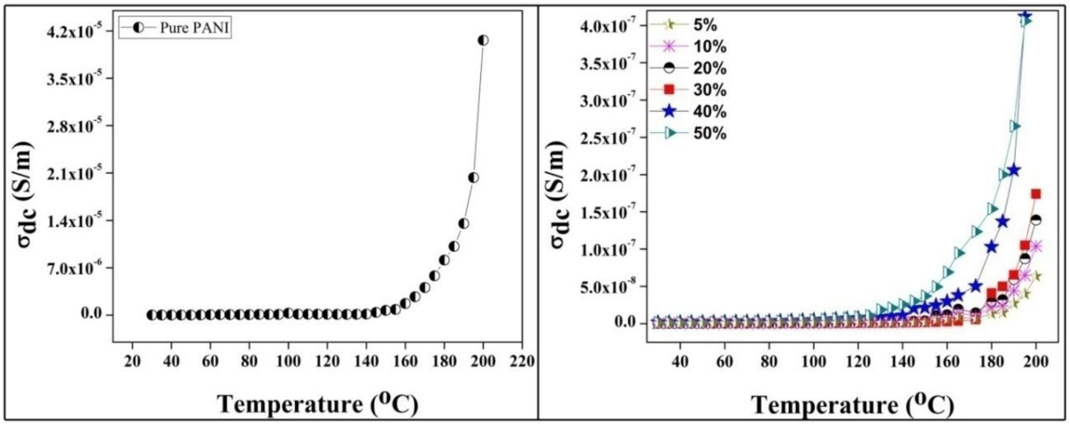

Fig 7: DC conductivity of Polyaniline and composites as function of Temperature

3.4 Dielectric Studies

3.4.1 Variation of real dielectric constant (ε')

Figure-8 show the variation of dielectric constant (ε') as a function of frequency for polyaniline and polyaniline composites at room temperature (RT) in the frequency range of 1KHz to 1MHz. It is observed that, obtaining higher value of dielectric constant at low frequency range. Debye type relaxation mechanism may be responsible for higher value of dielectric constant at low frequency. Dielectric constant of polyaniline and polyaniline composites decreases as frequency increases over the measured frequency range 1KHz to 1MHz, which is a typical characteristic of disordered conducting polymer. The decrease in the real dielectric constant takes in two part as low frequency range and higher end frequency range, i.e., the variation of ε' in the range 1x10^{3} Hz to 2 x 10^{5} Hz and 2 x 10^{5} to 1x 10^{6} Hz. In the first part, the dielectric constant decreases suddenly up to 2 x 10^{5} Hz and in the second part it maintains almost constant values of ε' up to 1 MHz. Figure-9 shows the variation of dielectric constant as function of additive weight percentage of silver oxide and it is clear that, the dielectric constant of the composite increases as concentration of silver oxide increases in the polyaniline matrix up to the composite 30% and then it decreases gradually for the composites 40% - 50% for the frequency 1KHz. It is observed that, among the composites, the dielectric constant is found to be maximum for composite 30% at 1KHz and 20% at 1MHz and also the value of dielectric constant for composites 5%- 30% is found to be higher in value and for composite 40%-50% is found to be lesser in value compared to pure polyaniline in 1KHz & 1MHz frequency.

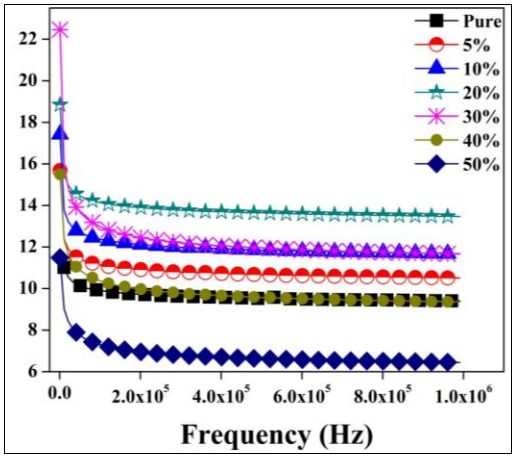

Fig 8: Variation of **D**ielectric constant (ε′) of Polyaniline and composites as function of frequency

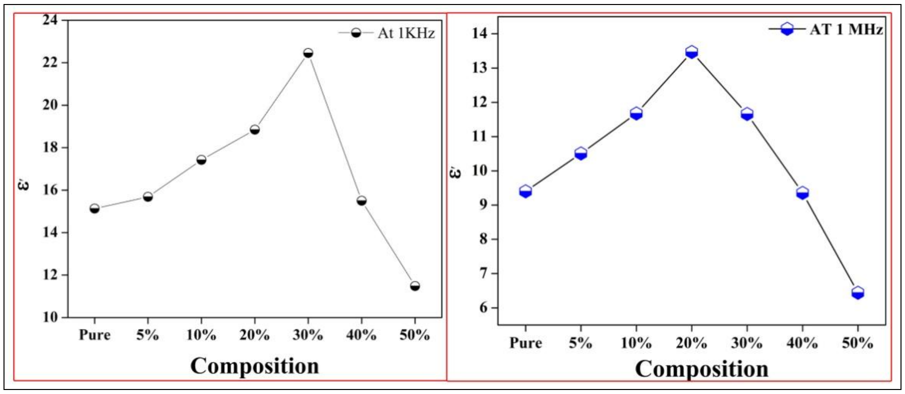

Fig 9: Variation of Dielectric constant (ε′) of Pani & Composites at 1 KHz & 1 MHz Frequency.

3.4.2. Variation of imaginary dielectric constant (ε'')

Figure-10 shows the variation of imaginary part of the dielectric constant (ε'') with frequency 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. In the first phase, the value of ε'' decreases suddenly and then shows gradually constant value in the second phase. Figure-11 shows the imaginary dielectric constant (ε'') as function of additive weight percentage of silver oxide and it is clear that, the imaginary part of dielectric constant is dependent of composition of silver oxide. Then the dielectric constant of the composite decreases as concentration of silver oxide increases in the polyaniline matrix up to the composite 20% and then it increases for the composites 30% for the frequency 1 KHz. It is observed that, the dielectric constant is found to be maximum for composite 30% in the frequency 1 KHz. For frequency 1 KHz, the value of dielectric constant for composites 5% to 50% is found to be less in value except composite 30% compared to pure polyaniline. Then for frequency 1 MHz, all the composites have higher value compared to pure polyaniline. The variation of the imaginary part of dielectric constant in composites compared to polyaniline may responsible for distribution of AgO in polyaniline.

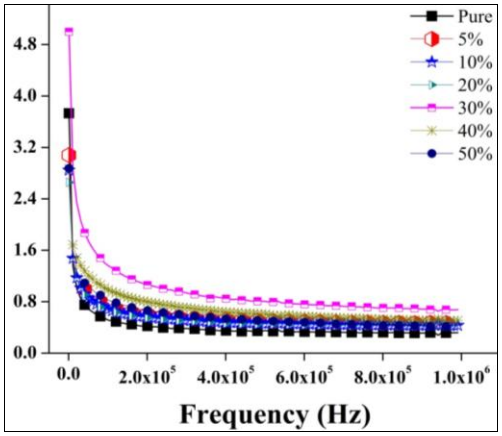

Fig 10: imaginary dielectric constant of polyaniline and AgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of frequency

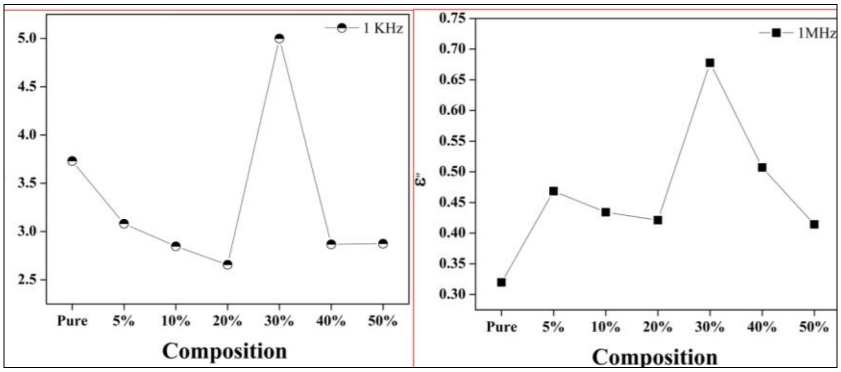

Fig 11: Dielectric constant (ε″) of Pani & Composites at 1 KHz & 1 MHz Frequency.

3.4.3 Variation of tanδ

The Variation of tanδ as a function of frequency for pure polyaniline and composites are shown in figure-12. The loss tangent for pure PANI has a rather value of 0.25 at 1KHz, which decreases with increasing frequency and reaching a value of 0.033 at 1MHz. The observed high 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 x 10^5 Hz, the value of tanδ decreases suddenly and in second phase of frequency 2x 10^5 Hz to 1 MHz, the value of tanδ decreases gradually and maintains constant value further. Figure-13 shows the variation of tanδ as function of additive weight percentage. It is clear that, the value of tanδ is minimum for composite 20% for both the frequency 1 KHz & 1 MHz.

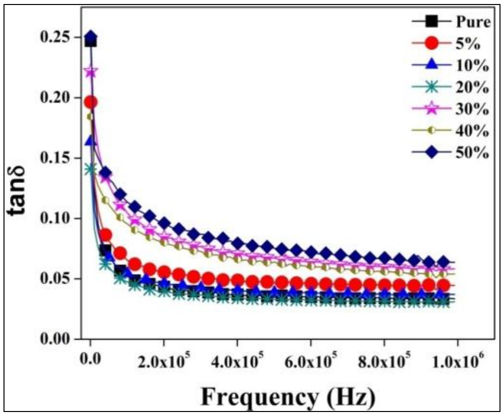

Fig 12: Variation of Dielectric loss tangent (tanδ) of polyaniline and AgO/PANI (5%, 10%, 20%, 30%, 40% & 50%) as a function of frequency

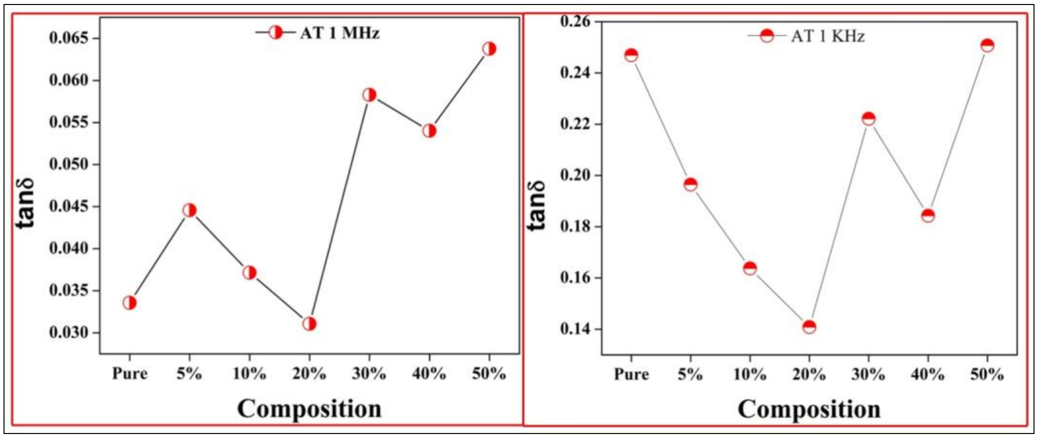

Fig 13: Variation of Dielectric loss tangent (tanδ) of PANI & Composites at 1 KHz & 1 MHz Frequency.

4. Conclusion

In this paper, the synthesis of polyaniline, composite formation (AgO/PANI), variation of structural and morphological changes of AgO/PANI composites has been investigated. The AgO/PANI composites can be fabricated by in situ polymerization of aniline in the presence of AgO via chemical oxidative method. Results showed that the average grain size of 20-30nm, the dispersion of silver oxide in the PANI matrix and clear indication of silver oxide peaks in PANI was evidenced by SEM and XRD examinations; there was interaction between PANI and AgO particle from FT-IR spectra analysis. The AC conductivity of PANI shows the conductivity increases with increasing frequency from 1KHz–1MHz. It is evident that the AC-conductivity is frequency dependent and enhanced linearly with an increase of the frequency and the conductivity of composite (20%) was found to be high among all other composites. DC conductivity of the PANI increases with increase in the temperature and it is found to be 4.06 x 10^{-9} S/m at 30 °C, which increases to 4.07 x 10^{-5} S/m at 200 °C for pure polyaniline and the conductivity decreases as concentration of silver oxide increases from 5% to 50% in the polyaniline matrix. The decrease in the dc conductivity may due to the distribution of silver oxide. The composites showed some interesting dielectric response of high dielectric constant at low frequency region and dependence on content of AgO in PANI matrix. It is observed that at low frequencies, the dielectric constant was found to decrease with increasing frequency and then above 2 x 10^5 Hz dielectric constant is found to decreasing gradually and maintains constant up to 1 MHz.

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