Studies on Structural, Morphological, Electrical and Dielectric Property of Tin Oxide Doped Polyaniline [SnO_2/PANI]

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Abstract: *The amalgamation of PANI and metal oxide composites with regular dispersion is foreseen to ease extensive utilization of the material. In the current work, Polyaniline (PANI) & Tin oxide doped polyaniline (SnO_2/PANI) composite samples with various content of SnO_2 were prepared by using chemical oxidative polymerization technique by utilizing ammonium persulphate (APS) as oxidant in acidic medium at room temperature and HCl as catalyst. The structural and morphological aspects of the composites were characterized by XRD & SEM methods respectively. The impedance analyzer was used to measure the electrical properties (AC & DC) & dielectric properties. The AC conductivity, Dielectric constant of all composites was determined with varying frequency at ambient temperature and DC conductivity was analyzed with respect to varying temperature.*

Key Words: **Tin 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 enhancing scientific & technical interest and contributing the scope to prepare new polymer materials [1].

Conductive polymers are specified by a conjugated composition of alternative single and double bonds. Properties of the conjugated polymers are mainly attributable to the subsistence of π electrons delocalized on an extended segment of chain. The aspect divided by all of them emerges from the typical behavior of their π -electron system, the increased conductivity in oxidized or in reduced condition & reversible redox stimulation in a suitable environment [2].

Among all conducting polymers, polyaniline has a unique and wide range electrical, dielectric properties and good stability. Polyaniline is one of the peculiar polymers amongst the various conducting polymers in its extensive collection of electrical, electrochemical and optical characteristics, also it has good strength. The electrical and sensing characteristics of the polyaniline may be improved in by formation of composites with various types of particles. 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 green protonated emeraldine is the most important form of polyaniline which can be produced 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 confined across the area of various repetitive units. Because the charges which are confined are able to travel through chain of the polymer, they are considered as charge carriers in conducting polymers [4]. Tin comprises of two streams of compounds that is stannous/tin (II) compounds & stannic/tin (IV) compounds. Two of them have substantial oxidation state. Stannous oxide exists in blue black crystalline product. It exhibits thermal stability in air up to 385^0 C and above this temperature it gets converted into stannic oxide, a white colored compound. The tin oxide (SnO_2) finds applications in chemical industries especially in making tin salts which are used as reagents and SnO_2 is famous in petroleum industry. Amongst the available semiconductor metal oxides, SnO_2 is popularly used in gas sensing applications. The SnO_2 has iso-structural with rutile phase. Each single cell comprises of 2 Sn atoms and 4 O_2 molecules. Tin oxide nano particles are prepared through various chemical roots like coprecipitation, hydrothermal, sol gel, sono-chemical polymer, precursor method among others [5-6].

2. MATERIALS AND METHODS:

2.1. Materials and Methods:

Chemicals used to prepare polyaniline are aniline, hydrochloric acid (HCl), ammonium persulphate of analytical grade and are prepared by employing chemical oxidative polymerization method.

2.2. Preparation of Polyaniline:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at 0°C temperature. This mixture was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. Then 0.2 M of ammonium persulphate was mixed drop by drop into above solution. This solution was constantly mixed by using magnetic stirrer at constant RPM for 8 hrs under 0° C temperature. After 8 hrs the precipitate was separated out by filtering and cleaned with deionised water along with acetone. The obtained final suspension was dried for about 24 hours in oven at the temperature of 50° C. The final product was grinded into powder & obtained black colored powder.

2.3. Preparation of SnO_2/Polyaniline:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at 0°C temperature. This mixture was mixed by using magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. 0.2 M of ammonium persulphate was mixed drop wise to the mixture. Tin oxide (SnO_2) powder for different additive weight percentage (5%, 15%, 25%, 35% & 45%) is dissolved in the mass fraction to the above solution with constant RPM to suspend SnO_2 homogeneously and stirring of final solution is continued for another 8 hours at ambient temperature. After 8 hrs the precipitate was segregated out by filtering and purified with deionised water with acetone. The obtained final suspension was made to dry at 50°C for about 24 hrs by using oven. And then final product was grinded into powder [7].

3. RESULTS AND DISCUSSIONS:

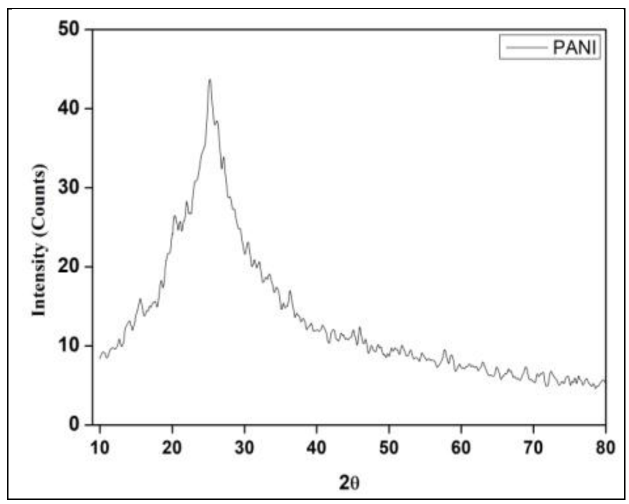
3.1. Structural Review:

The structural review of the sample was studied by XRD technique. Figure-1 (a-f) reveals XRD pattern of the PANI SnO_2/PANI for different additive weight percentage (5%, 15%, 25%, 35% & 45%) respectively. Generally polyaniline shows the amorphous nature. From pattern it reveals that, the synthesized pure polyaniline shows the prominent peak of pure polyaniline is in the range of 25^0-27^0 which is the characteristics of the PANI and confirms the development of PANI. Figure 2(b-f) also reveals the prominent peak of SnO_2 at 2θ values 27.08, 33.87, 38.13, 52.18, 55.42, 58.26, 61.66, 66.78 can be indexed to (110), (101), (200), (211), (220), (002), (310), (301) degree for different doping concentration (5%, 15%, 25%, 35% & 45%). It is also observed that, the intensity of the peaks is increasing from 800 counts to approximately 40000 counts as doping concentration increases. This increase in the magnitude of XRD peak may indicate that, tin oxide dispersed in the polyaniline matrix with broadness of the peaks remains same.

The standard crystalline size of PANI are evaluated to be approximately 17nm are calculated by using Debye - Scherrer formula,

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

Here D indicates standard crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, β is FWHM of the X-ray diffraction peak and & is Braggs' angle (deg.) and lattice strain was estimated to be 0.0088.



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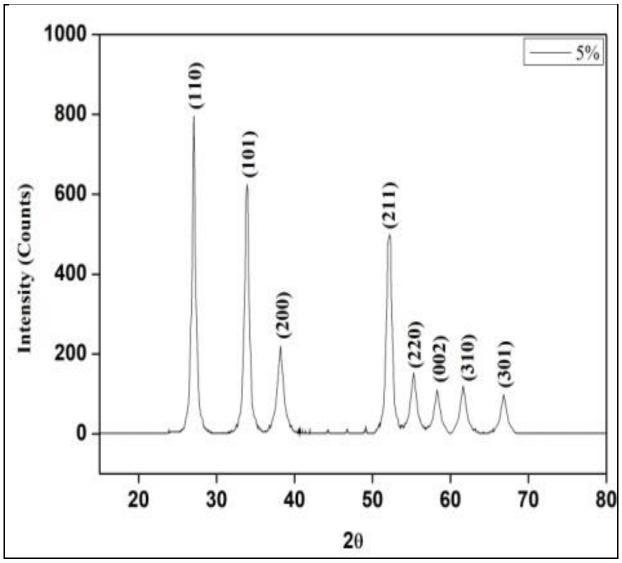

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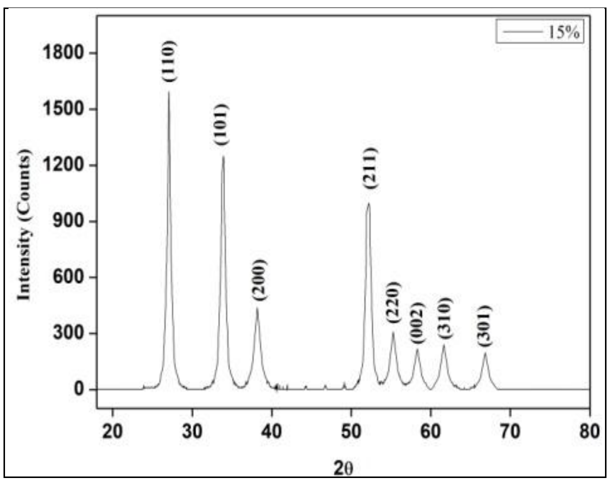

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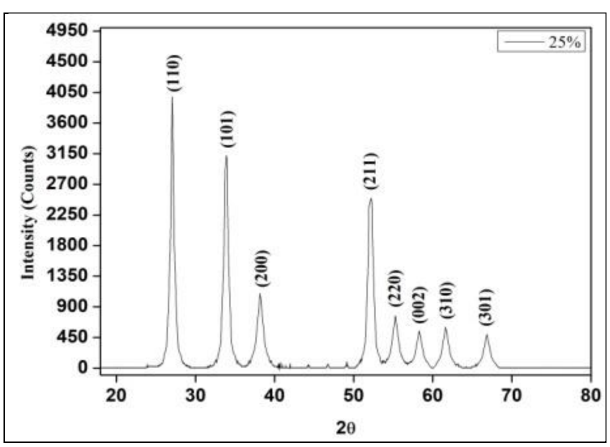

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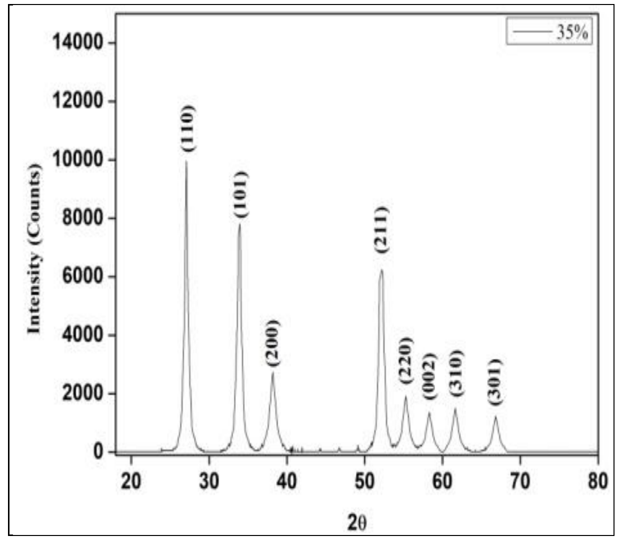

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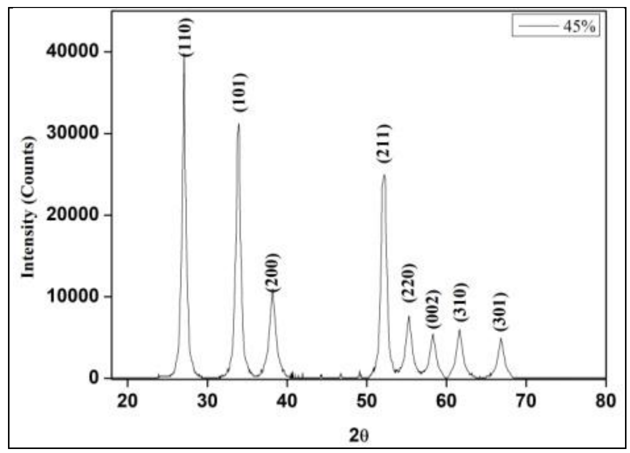
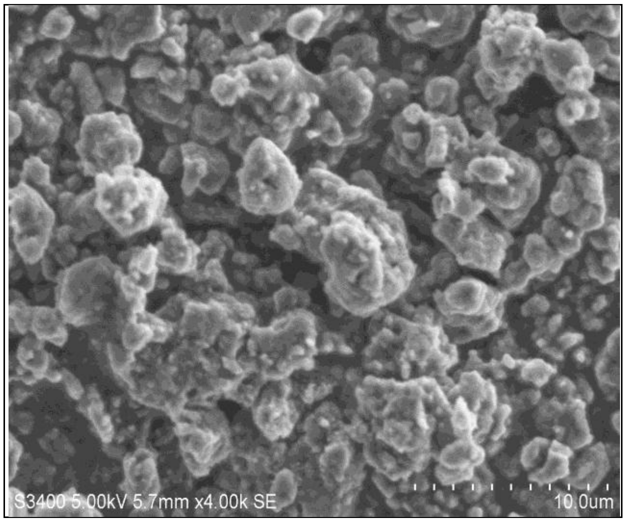


(f) **Figure-1**: XRD pattern of PANI & SnO_2 Composite

3.2. Morphological Study:

Figure-2 (a-f) illustrates the surface morphology of pure polyaniline and SnO_2/PANI (5%, 15%, 25%, 35% & 45%) respectively. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM image of SnO_2/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.



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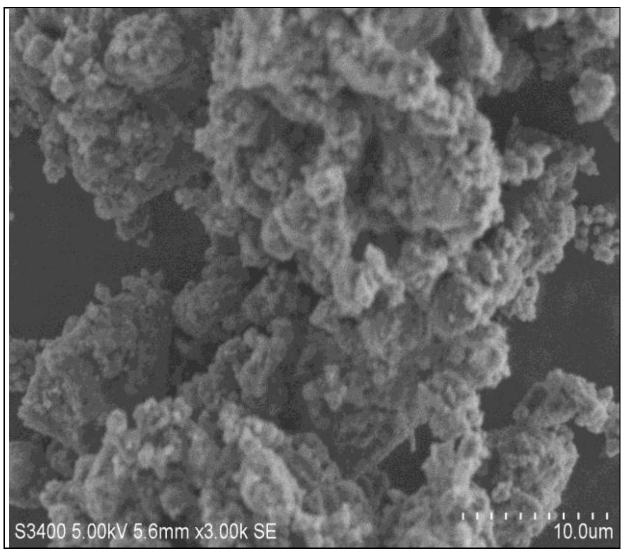

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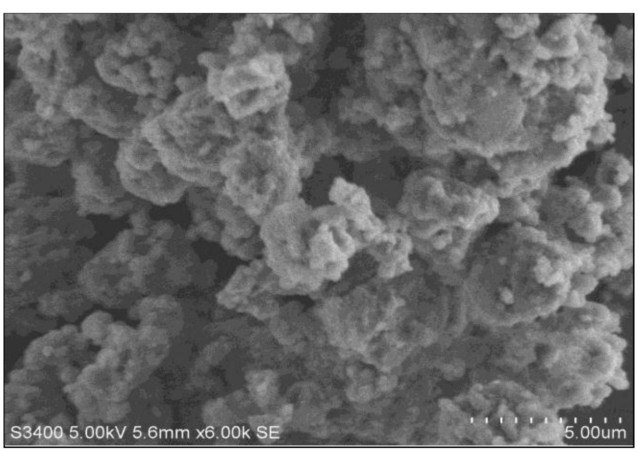

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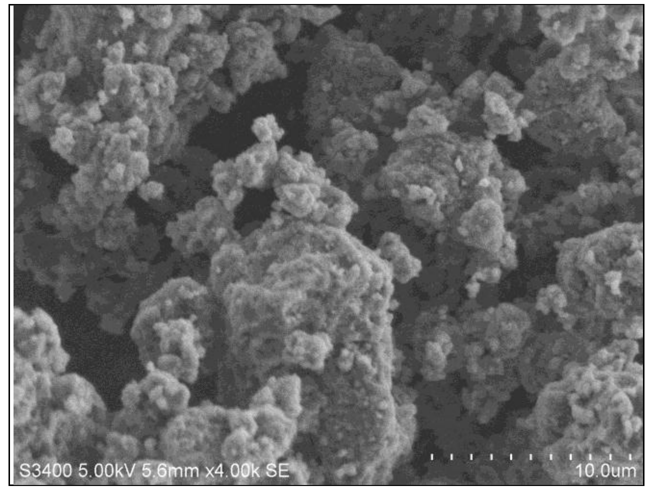

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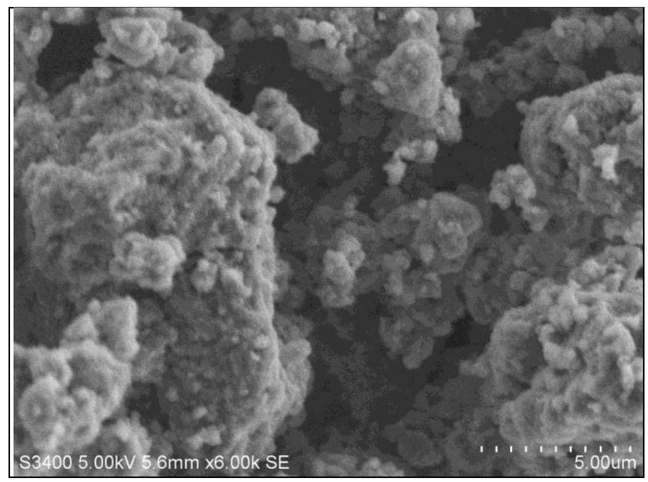

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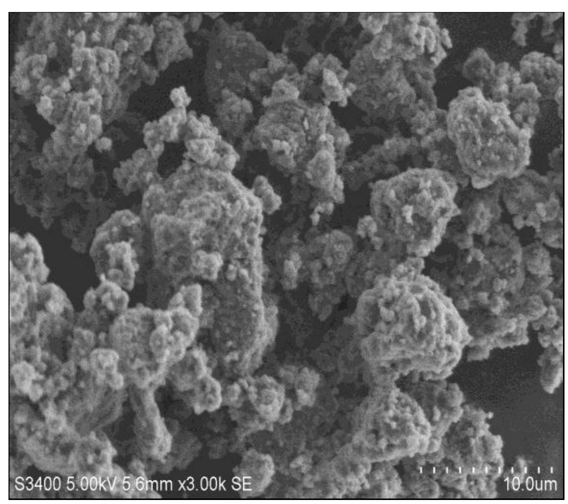

(f)

Figure-2: SEM images of PANI & SnO_2/PANI Composites

3.3. AC Conductivity:

The AC electrical conductivity of pure polyaniline & SnO_2/PANI composites was carried out at 1KHz–1MHz frequency in room temperature, SnO_2/PANI pallets were coated with silver paste with thickness ranging from 2-5 mm. Figure-3 reveals the AC conductivity (σ_{ac}) which varies according to the variation of frequency for pure polyaniline and SnO_2/PANI (5%, 15%, 25%, 35% & 45%) respectively. It is reported previously that, polyaniline has electrical conductivity which confines between the range of 10^{-10} and 10^{3} S/cm depending on acid doping agents & filler materials [8]. As frequency increased from 1 KHz–1MHz, it can be found that, the AC conductivity of PANI extends gradually. Undoubtedly it can be understood that AC-conductivity is dependent on frequency and is linearly increased with an increase of the frequency. This specifies that there might be presence of the particles which carry the charge and can be transferred by bouncing through the dislocated areas through chain of polymer [9]. Also it is observed from plots that, the conductivity also increases as concentration of tin oxide increases from 5% to 45% i.e., the conductivity is greater than the pure polyaniline at 1 KHz & 1 MHz frequency. The extension in the conductivity of the polyaniline and composites were revealed in figure-4 as function of additive weight percents of tin oxide. Additionally from figure-4 it is noticed that, the AC conductivity of PANI composite (50%) was found to be high among all other composites for both 1 KHz and 1 MHz frequency. The variation in conductivity behaviour of these composites possibly owes to change in the dispersal of tin 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 the frequency of 1 KHz and it extends to $6.5x\ 10^{-6}$ S/m at 1 MHz [10].

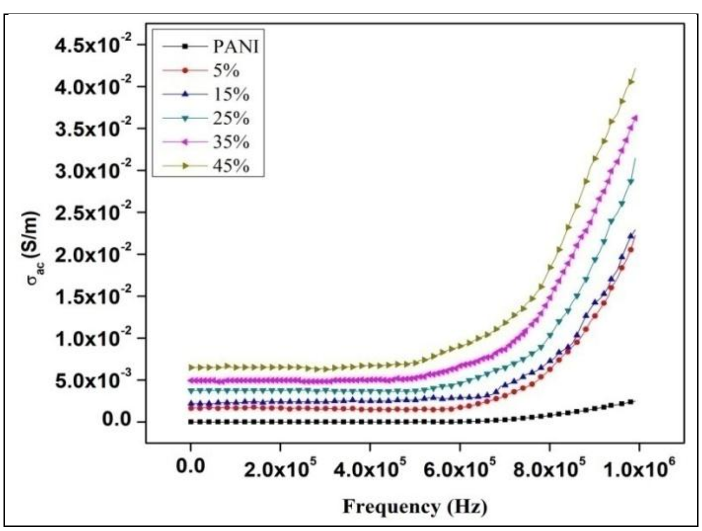

Figure-3: AC conductivity of PANI & SnO_2/PANI Composite

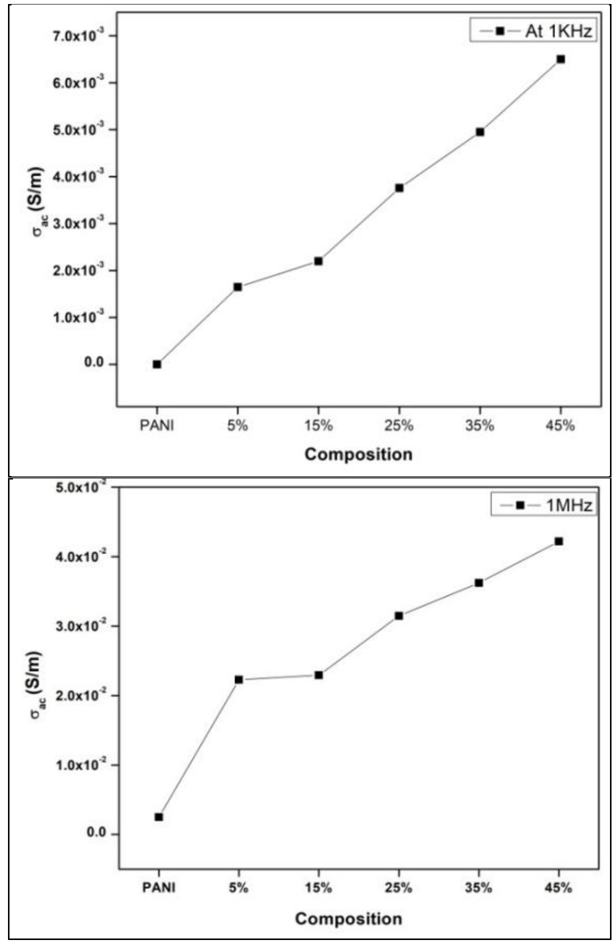

Figure-4: AC conductivity with respect to composition of PANI & SnO_2/PANI Composite

3.4. DC Conductivity:

The DC electrical conductivity which is dependent on temperature of pure PANI & SnO_2/PANI composites was carried out from room temperature to 180°C on silver paste coated pellets with thickness ranging from 2mm - 5mm. Figure-5 reveals the increase of DC electrical conductivity with respect to varying temperature for pure polyaniline & SnO_2/polyaniline composites. It can be noticed that in all cases, DC electrical conductivity of the PANI enhances with increment in the temperature and it is found to be $7.34\ x\ 10^{-5}$ S/m at 30 °C, which increases to $7.52\ x\ 10^{-4}$ S/m at 180°C for pure polyaniline. From this it is evident that, the conductivity decreases as concentration of tin oxide increases from 5% to 45% in the polyaniline matrix. The decrement in DC electrical conductivity may be owing to the distribution of tin oxide and APS in polyaniline. It is noticed from figure that, conductivity of PANI showing in two phases i.e., the conductivity in the extent of 30 °C – 140 °C and 150 °C to 180 °C. The first phase conductivity is almost constant which is because of inter-chain transfer of particles which carry charge, and is usually noticed at transitional temperature. But, at high thermal energy region, (phase two) we can see the sudden enhancement in the conductivity with increment in temperature and this is because of intra-chain transfer of particles which carry the charge and can be explained by band conduction phenomenon and is generally noticed at greater temperatures as reported by authors in their previous work [11-13]. The localized states that manifests elongated band like structures may proceed in trapping the particles which carry the charges from extensive states.

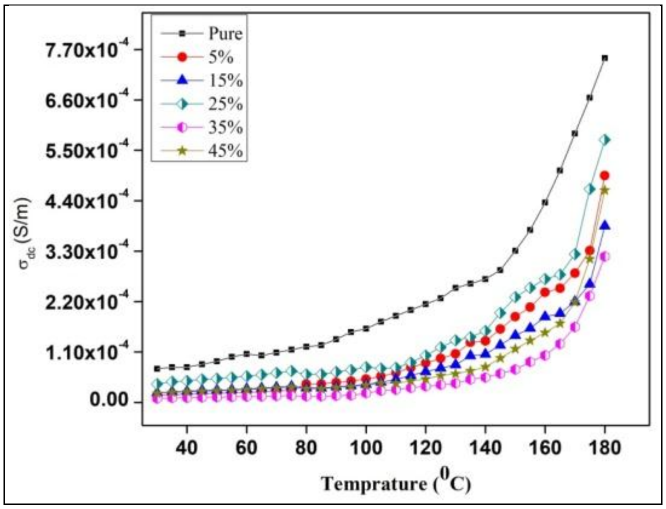

Figure-5: DC conductivity of PANI & SnO_2/PANI Composite

3.5. Dielectric Constant:

Figure 6 reveals the variation of dielectric constant ε' with respect to varying frequency for polyaniline and SnO_2/PANI composites at different weight percentage. It can be visualized in various cases that, dielectric constant is a bsolutely greater at lesser frequency & diminishes with increment in supplied frequency. This kind of behavior might be because of Debye like relaxation phenomenon which occurs in this kind of materials [14].

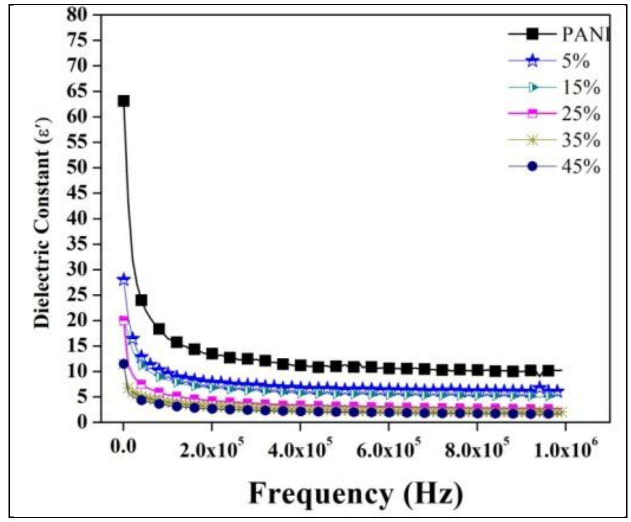

Figure-6: Dielectric constant of PANI & SnO_2/PANI Composite

4. CONCLUSION:

In this current work, we have successfully prepared the conducting polymer, PANI and its composites i.e. PANI / SnO_2, in 5, 15, 25, 35 & 45 weight percentages using chemical oxidative polymerization method. XRD pattern of polyaniline reveals the existence of amorphous nature in polyaniline and regularly arranged crystalline nature of polyaniline composites. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM micrograph of SnO_2/PANI reveals 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. AC conductivity measured with respect to the change in frequency displayed enhancement in conductivity with increment in the SnO_2 content. It can be noticed that, DC conductivity of the PANI enhances with increment in the temperature i.e., it is found to be 7.34 x 10^{-5} S/m at 30 °C, which increases to 7.52 x 10^{-4} S/m at 180°C for pure polyaniline. From this it is evident that, conductivity decreases as there is increment in the concentration of tin oxide from 5% to 45% in the polyaniline matrix. It is visualized in various cases that, dielectric constant is absolutely greater at lesser frequency & diminishes with increment in supplied frequency.

ACKNOWLEDGEMENTS:

The authors are thankful to Poojya Dr. Sharanabaswappa Appaji, President, Sharnbasveshwar Vidya Vardhak Sangha, Kalburagi, Prof. Dr. V.D Mytri, Principal Appa Institute of Engineering and Technology, Kalburagi and Dr.

Sangshetty Kalyane Professor, VGST Research Centre of Bhalki by providing Basic Work, Bhalki, Bidar, Karnataka for the encouragement during the process of carrying out this work.

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