The structural and electrical properties
of polyaniline carbon nanotubes (PANI-CNTs) composite

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Carbon nanotubes (CNTs) doped polyaniline (PANI) nanocomposite was synthesized by chemical polymerization method in the presence of HCl medium. The structure of the PANI/CNTs composite was confirmed by X-ray diffraction (XRD) technique. The SEM results showed granular and tube like shape for PANI and CNTs respectively. The SEM characterization of PANI-CNTs composite revealed a uniform wrapping of CNTs by PANI forming a core-shell nanostructure. The temperature dependent dielectric measurements were performed in the frequency range of 0.1 kHz-1 MHz. Dielectric measurements revealed the strong interactions between PANI and CNT nanoparticles causing a beneficial effect on stability of the composites. The dielectric constant followed the Maxwell-Wagner interfacial polarization. The frequency dependent conductivity obeyed a power law of frequency. Temperature has an effect on dielectric constant values of composite sample. Heat treatment affected the dipole polarization by reducing the relaxation time and hence contributed to the enhancement of dielectric parameters. Dielectric properties of composites were found to be improved due to addition of carbon nanotubes, which can improve the formation of a more efficient network for charge transport mechanism in the base polyaniline matrix. The border between polyaniline and CNTs can play an important role in yielding a large dielectric constant in the nanocomposites.

1. Introduction

The conducting polymers are innovative materials allowing new advances in electronics due to their novel physical, chemical, electrical, and optical properties that could be changed according to desire. A small addition of impurity can lead their conductivity from semiconducting to metallic level. The conducting polymers have gained much attention due to presence of delocalized {π – electrons} in the polymer chain which results in unique optical and nonlinear optical properties [1-2] and behave like conductors typically when oxidized [3]. Because of these properties they can put into practical uses as energy storing devices, optical sensors, fuel cells and materials for solar energy conversion [4,5].

Among all conducting polymers, polyaniline (PANI) is the most attractive polymer regarding its low price, simple to synthesize, and highly stable chemically [6-7], improved thermal and atmospheric stability and enhanced conductivity [8]. These properties make it useful in technological applications such as optical sensors, solar cells, fuel cells, electromagnetic interference shielding, batteries, photovoltaic cells, biological sensors etc. The conductive polymer/composites have been synthesized preferably by using either HCl or H_2SO_4 with ammonium peroxy-disulphate, ferric ions, permanganate or dichromate anions, or hydrogen peroxide as an oxidant [9].

Over the past few years, the inorganic/polymer hybrid nanoscale materials have received great attention from the world of science and industry for its ability to make use of properties of nanosized material. They have extensive variety of potential applications in optoelectronic gadgets and in field effect transistors (FETs) [10]. The inorganic nanoscale fillers have high surface to

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volume proportion and in this way anticipated that will alter radically the optical and electrical properties of the polymer. All in all, the preparation of conducting polymer/CNT composites has an objective to observe synergetic effects. As on later, natural and inorganic crossover materials have been widely concentrated on because of their fascinating properties [11] in light of the fact they join the profitable properties of metals and polymers. Several methods have been devised to prepare polymer/nanoparticals composites like sol–gel strategy, in situ compound polymerization in watery arrangement, physical blending, emulsion engineering and sono-concoction process [12,13].

The successful electropolymerization of PANI/CNT whiskers [14] was first reported in 1999.Since then a lot of preparatory methods have been devised for synthesizing PANI/CNTs composites instead of direct physical solid state blending [15] or ultra-sonication of CNTs in PANI solutions of N-methyl-2-pyrrolidinone or Hydrochloric acid. Luiz C. Mariano, found that the field effect variation of the drain current is poor for the film using only PANI. Yet it improves with the CNT dispersion in the polymeric layer due to the morphological change of PANI during after the insertion of CNTs.

One of the simplest methods for the synthesis of polyanline in an acidic dispersion of multiwall carbon nanotubes (MWCNTs) or single-wall carbon nanotubes (SWCNTs) in the presence of an oxidant at room temperature is In-situ compound polymerization [16].

2. Experimental

2.1. Materials

Aniline (Merck) was distilled under reduced pressure and stored at low temperature prior to use. Ammonium per sulfate (APS) was obtained from SIGMA ALDRICH. Carbon Nanotubes (MWCNTs) were supplied by SIGMA ALDRICH and used as obtained.

2.2. Sample Preparation

Polyaniline and Carbon nanotubes(CNTs) doped polyaniline samples were prepared by using *In-situ* polymerization method with 20% of Multi-Walled Carbon Nanotubes in the presence of an oxidant $(NH_4)_2S_2O_8$ (APS).

2.3. Polyaniline synthesis process

5 ml Aniline was dissolved dropwise in 30 ml HCl solution and continuously stirred for 2-3 h in open atmosphere at room temperature. The pH of HCl aqueous solution was maintained between (0-1).11.9 g Ammonium per sulphate (APS) was added drop wise in HCl aqueous solution at 1:1 molar ratio and the solution is continuously stirred for 1-2 h.By adding Ammonium per sulphate (APS) in the solution, black greenish precipitates of polyaniline begin to develop.The solution of polyaniline was left over night in dark room for the complete polymerization.The solution was filtered and washed 3-5 times with distilled water to remove the acid and finally with ethanol for complete removal of HCl. The polyaniline precipitates were then put in a vacuum oven at 70 ^{0}C for 3-4 h and then dried sample was ground to fine powder.

2.4. Synthesis of Polyaniline/Carbon nanotubes composite

First 0.5g Multi-Walled Carbon nanotubes (MWCNTs) were sonicated to make them functionalize in 30 ml de-ionized water. Then MWCNTs were dispersed in 30 ml HCl solution and stirred for 1 hour. These were then sintered by using the centrifuge. The pH was maintained between 0-1. MWCNTs (20% by weight) were dissolved in 30 ml distilled water and put on magnetic stirrer.30 ml HCl was added in Multi-Walled Carbon Nanotubes (MWCNTs) solution. 5ml Aniline and 11.9 g APS were added in 30 ml distilled water separately. Now the aniline and APS solution were added in CNTs solution keeping the solution on constant stirring. For protonation 30 ml of HCl was added twice. The solution was left for 3-4 hour and after completion, a greenish black MWCNTs doped aniline solution was obtained. This solution was left over night for complete polymerization and then filtered to get precipitate of PANI/CNTs composite. The solution was washed several times with de-ionized water to remove the HCl. To dry the residue it was put in vacuum oven at 70°C for 3-4 h and finally ground to fine powder.

2.5. Measurements

X- rays powder diffraction analysis was carried out using an automated diffractometer, Panalytical X' Pert PRO equipped with Cu-Kα radiations (λ=1.54 A°). The instrument was operated at 40 kV and 30 mA and diffraction patterns of PANI and PANI/CNT composite samples mounted on a standard holder were recorded over the range of 10° to 80° with counting time of 0.5 s and the step size of 0.02°. The crystalline size was calculated from Scherer equation and d-spacing was calculated from Bragg's equation. Scanning electron microscopy was carried out on an EVO50 ZEISS instrument. Dielectric measurements were recorded on pressed pellets (made by a press machine by exerting 10 ton pressure in stainless steel die of 8 mm diameter in the frequency range 0.1 kHz-1MHz. The temperature was varied from 30℃ to 150℃. For conductivity measurements the samples were connected to a Keithley 2400 source meter using two point probe method. The dielectric constant of all the samples and reproducibility were checked.

3. Results and discussion

3.1. XRD Analysis

The XRD result for pure PANI reveals that it has no sharp peak except a broad peak. As described in literature this broad high-angle asymmetric scattering peak indicates amorphous nature of PANI. This result can be characterized by divergence from monomer planes at inter atomic level. These diffraction results for PANI are analogues to so-called rigid polymers owing lot of benzene rings [17].

The XRD result for pure Multi-Walled Carbon Nanotubes (MWCNTs) revealed peaks at 2θ values of 26.35° and 43.59° as shown in Fig. 1. The corresponding d-spacing values are 3.38 and 2.07Å respectively. The average grain size calculated by Scherer's equation was found to be 6.5 nm [18] and given in Table 1.

The diffraction patterns of PANI/CNTs composite with 20% of MWCNTs content reveal peaks at 2θ values of 18.47°, 26.35° and 33.96° with average grain size of 30-40nm. The increases in crystallinity of PANI/CNTs composites conforms XRD pattern of PANI/CNTs crystalline nature composite and exactly match with the literature [19]. The crystallinity of the samples was manipulated by XRD (WAXs) formula [20] as given in Table 2. This shows that the crystallinity of the composite is higher than pure MWCNTs and is confirmed by figure. Because of amorphous nature of polyaniline mass to volume ratio of MWCNTs reduces which in result reduce the intensity of MWCNTs.

The characteristic distance between polymer chain may be affected by the size, shape and dimension of the dopants present in composite. This may enhance the electrical properties of the material due to (π-electron) delocalization [21].
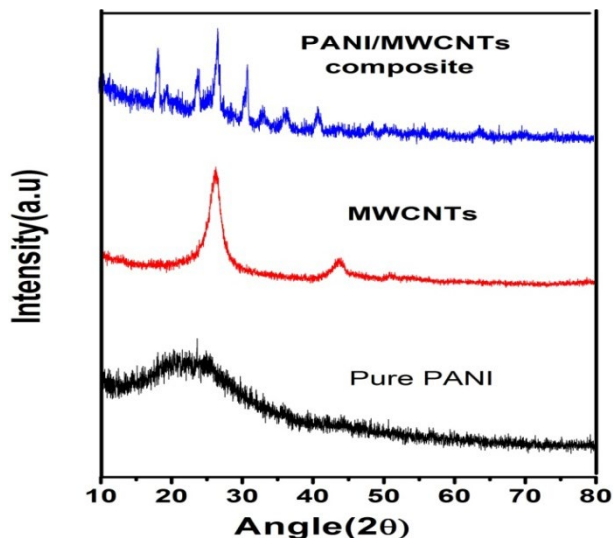
Fig. 1. Combined Diffraction results of pure PANI, MWCNTs and PANI/MWCNTs 20% composite.

3.2. Scanning Electron Microscopy (SEM)

Scanning Electron microscopy results were carried out by using intense narrow electron beam having a large depth of field. Very fine three-dimensional images of samples were obtained on a film known as micrograph. These proved helpful in understanding the morphological differences between the pure PANI, MWCNTs and PANI/MWCNTs 20%composite. The SEM images have been obtained to confirm the crystalline nature of Polyaniline doped MWCNTs as shown in Fig. 2.The SEM result for pure PANI shows its granular nature. The SEM result for pure CNTs represent its tube like shape. The SEM characterization of PANI-CNT composite reveals a uniform wrapping of CNT by PANI forming core-shell nanostructures and show that the composite is successfully synthesised that acts as conductive path and leads to high conductivity than pure PANI. Hence XRD pattern is confirmed.
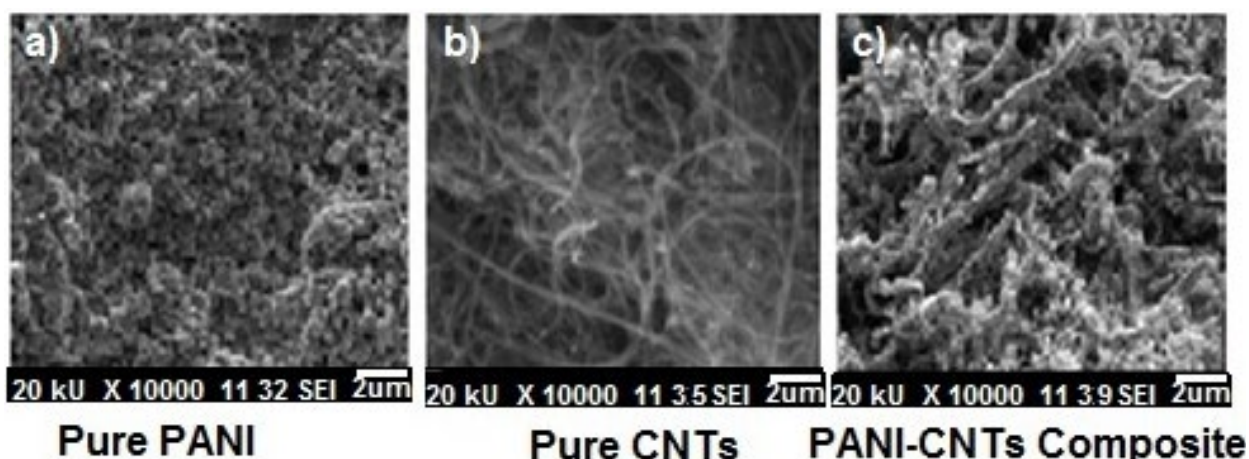

Fig. 2 SEM results for a)PANI, b)MWCNTs and c)PANI/MWCNTs composite.

3.3. Dielectric constant and Dielectric Loss

We know that the dielectric constant is directly proportional to capacitance and given by the equation;

$$\varepsilon' = Cd/A\varepsilon_0$$

Fig. 3, 5 and 7 shows the variation of dielectric constant within frequency range of 0.1 kHz - 1MHz for pure PANI, MWCNTs and PANI/MWCNTs 20% composite.
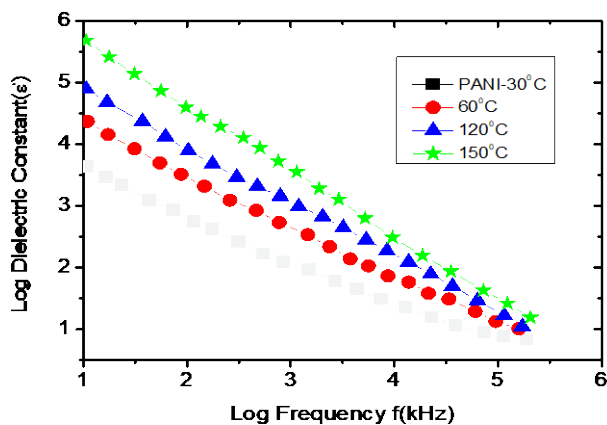
The dielectric loss is expressed as;

$$\varepsilon'' = \varepsilon' \tan\delta$$

The above relation shows that the dielectric loss is directly proportional to the dielectric constant so satisfies the same results as for the dielectric constant.

Figs.4, 6 and8shows the variation of dielectric loss in a frequency range of 1 kHz - 1MHz for pure PANI, MWCNTs and PANI/MWCNTs 20% composite.

Fig. 3. Log ε′ vs Log f for pure PANI.
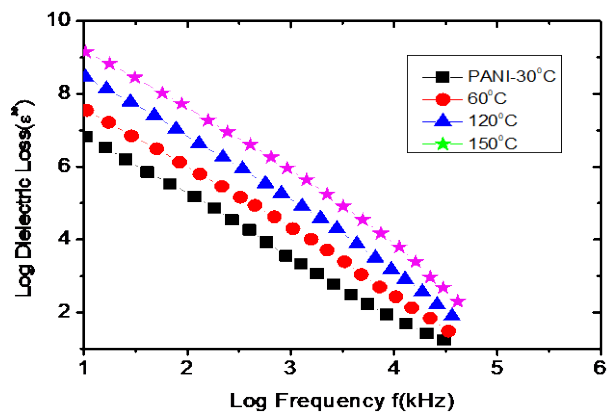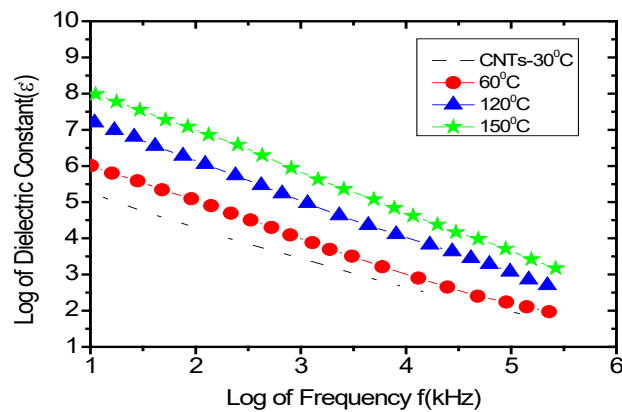

Fig. 4. Log ε″vs Log f for pure PANI.

Fig.5.Log ε´ vs Log f for pure MWCNTs.
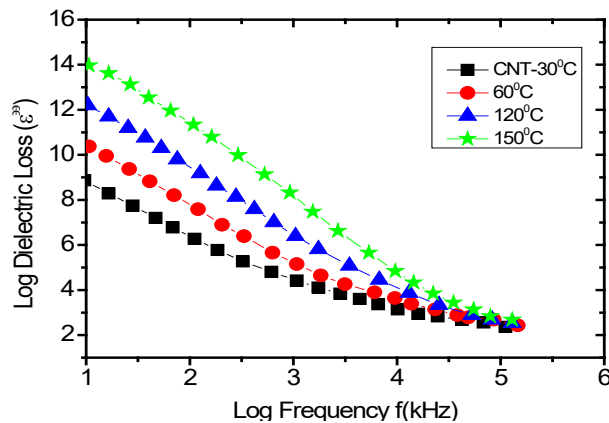
Fig. 6. Log ɛ″vs Log f for pure MWCNTs.

Figs. 3 and 4 shows the results for pure PANI and confirm that $\varepsilon´$ and $\acute{\varepsilon}$ varies inversely with frequency. Temperature also affected the ε' values of polymers [22]. As the temperature increased the intermolecular forces between the polymer chains were broken which caused an increase in thermal agitation. This heating treatment affected the dipoles polarization by reducing the relaxation time and polymer chains preferred to align in phase with the changing frequency and hence contributed to the enhancement of the dielectric constant. Fig. 5 and 6 represent the results of relative permittivity ε' and dielectric loss $\acute{\varepsilon}$ for the MWCNT at different temperatures as a function of frequency. These results show that ε' and $\acute{\varepsilon}$ have higher values at lower frequencies and go on decreasing with the rise in frequency for all temperatures [23]. This increase is also characterized by the deposition of additional charge carriers at the interfaces, which can increase the net dipoles on interfaces. This increase in electrical dipoles will play a crucial role to vary the net polarization of the ionic medium that helps to boost the relative permittivity [24]. However because the
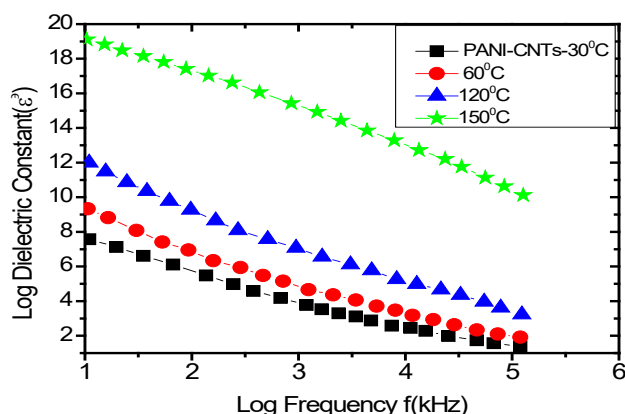
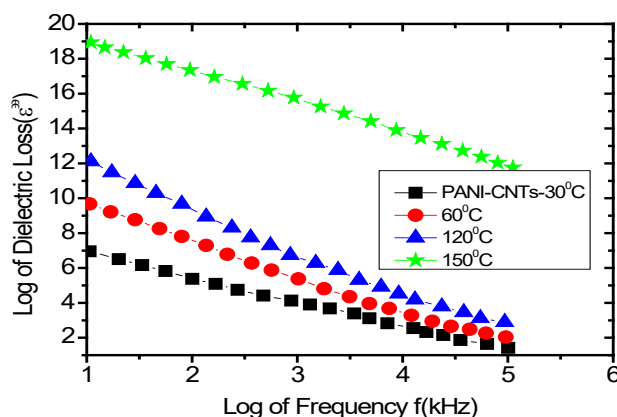*Fig. 7. Log ε′ vs Log f for PANI/ MWCNTs 20% composite.*

Fig. 8. Log ε″ vs Log f for PANI/ MWCNTs 20% composite.

Frequency gets higher values, the dipoles don not have enough relaxation time to follow the applied electrical field; therefore surface polarization is expected to decrease which results in reduction of ε′ values. At higher frequencies, atomic or electronic polarization is typically playing an important role [25]. Fig. (7&8) describe the variation in ε′ and ε̈ for PANI/MWCNTs 20% for all temperatures at different frequencies. As stated earlier that the increase in temperature, increases the mobility of charge carriers which in turn increases the polarizability of the composite. This increase in polarizability contributes to enhance the dielectric constant [26]. It has been observed that ε′ will increase by dispersing nanoscale particles in polymer materials.

The dielectric function ε* in complex form can be described as

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where ε′ is the real part and ε″ is the imaginary part of this complex function.

Literally ε′ is stored energy and ε″ is energy dissipated in each cycle of alternating field. At low frequencies for all temperatures, relative permittivity has higher values whereas at higher frequencies the values of relative permittivity are nearly constant [27]. This increase in relative permittivity and loss is related to the localized mobile charges that may contribute in the formation of interfacial dipoles due to electric polarization. At higher values of frequencies, dipoles do not have enough relaxation time (T_r) to be aligned along the field and hence do not depend upon frequency [28].While at low frequencies, dipoles have ample time to arrange themselves in the direction of applied field and hence we observe a frequency dependent behavior. The mechanism that contributes to dielectric properties is due to interaction of electric field with electronic,

interfacial, dipolar and atomic polarization which in turn is because of charge transport mechanism at the valance states of cations [29].

The higher values of (ε') and (ε'') at reduced frequencies is usually attributed to Maxwell Wagner polarization in heterogeneous systems. Maxwell-Wagner surface polarization model [30-31] is accustomed to justify the reduction in relative permittivity with increasing frequency. J.R. Gaines et al has reported that with the rise in frequencies, the surface polarization does not occur as the carriers displacement is smaller than the size of conducting regime and therefore ε' decreases with the rise in frequency and also permittivity loss decreases with rise in relative permittivity [32].

Table 3. The measured average relative permittivity and average permittivity Loss for PANI, MWCNTs and PANI/MWCNTs 20% composite in frequency range (1Hz-1MHz).

Material	Average relative permittivity (ε')	Average permittivity Loss (ε'')
PANI	3.99	6.38
MWCNTs	5.52	5.6
PANI/MWCNTs	8.35	8.75

3.4. Tangent Loss

The energy dissipated in an insulating material can be measured by the phase (δ) relation of current and applied voltage as
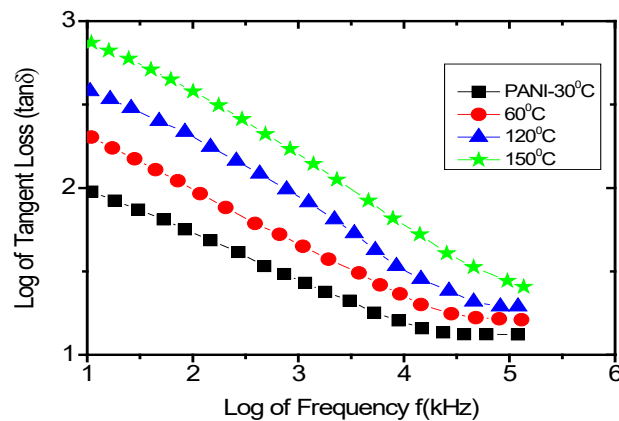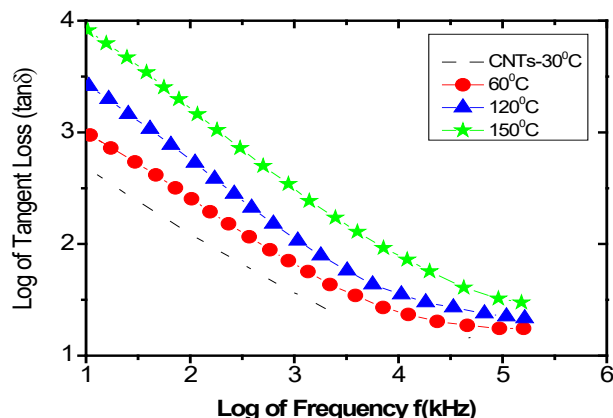

Fig. 9. Log tanδ vs Log f for Pure PANI.

Fig. 10. Log tanδ vs Log f for PURE MWCNTs.

$$D(\omega) = \tan\delta = \varepsilon''/\varepsilon'$$

wheretanδ is the loss tangent.

In insulating materials, the energy dissipation is due to the fact that the alternating field E(ω) leads ahead to loss tangent D(ω) by an angle (δ). This phase (δ) is 90° for free space however if an insulator is inserted between the plates of a capacitor then (δ) changes from 90°. The deviation of D(ω) from 90° is called dielectric loss factor.
This increase in tangent loss at low frequencies and reduction in tangent loss at higher frequency for polymer and polymer/nanoscale composite of known concentration are shown in Fig. 9, 10 and 11. The decrease in dielectric loss factor with increasing frequency at numerous temperatures is a typical characteristic of conjugated compounds. Hence our results reasonably follow the literature [33].
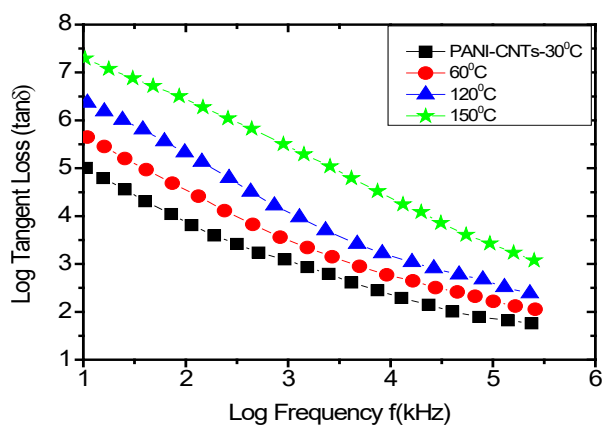

Fig. 11.Log tanδ vs Log f for 20% PANI/MWCNTs composite.

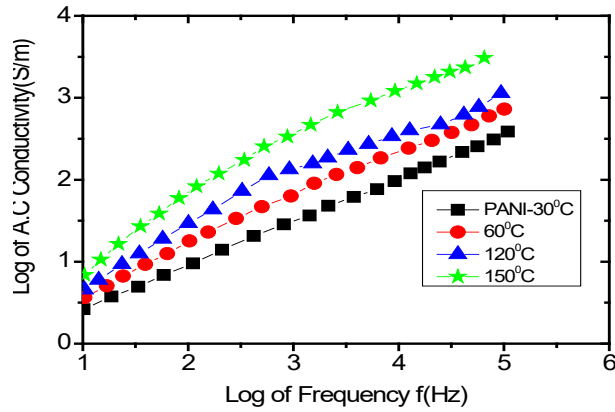*Fig. 12. Log σ$_{ac}$ vs Log f for pure PANI.*

3.5. A.C conductivity(σ_{ac})

A.C conductivity of material is given by

$$\sigma_{ac} = \omega \, \varepsilon_o \, \varepsilon''$$

as

$$\omega = 2\pi f$$

$\varepsilon'' = \varepsilon' \tan\delta$ where $\tan\delta$ is the loss tangent then A.C conductivity is given by

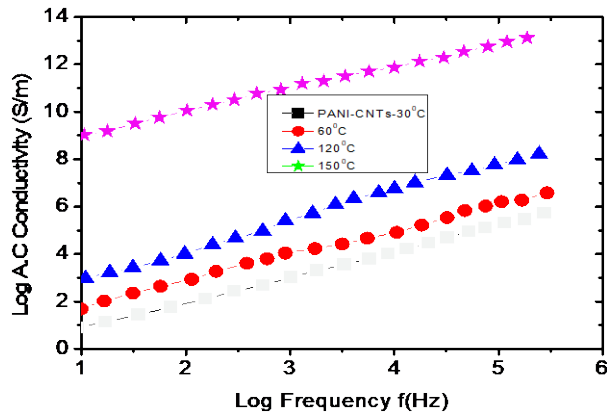$$\sigma_{ac} = 2\pi f \varepsilon_o \, \varepsilon' \tan\delta$$

Fig. 13. Log σ$_{ac}$ vs Log f for PANI/MWCNTs 20% composite.

The above relations show that σ_{ac} increases with the rise in frequency. Maxwell-Wagner model explained this frequency dependent behavior [34,35].

Fig.12 and 13showsthat the A.C conductivity increases as the frequency increase for all the temperatures. It has been observed that Polymer/Nanotubes composite has higher A.C conductivity than pure PANI.

The frequency dependent conductivity σ(ω) of disordered solid materials such as monomer/CNT composites can be approximated by an empirical law named as "universal power law".

$$\sigma_{ac}(\omega, T) = A\,(T)\,\omega^s$$

Where A is a pre-exponential factor and S is frequency exponent 0<S<1. Electrical conduction will be dc conduction or frequency independent if s=0 and if s≤1 electrical conduction will be frequency dependent or ac conductivity. It has been found that there is electron tunneling if S is independent of T but depends on f and in case of small polarons tunneling S increases with T while for large polarons tunneling S decreases first then increases with T [36].
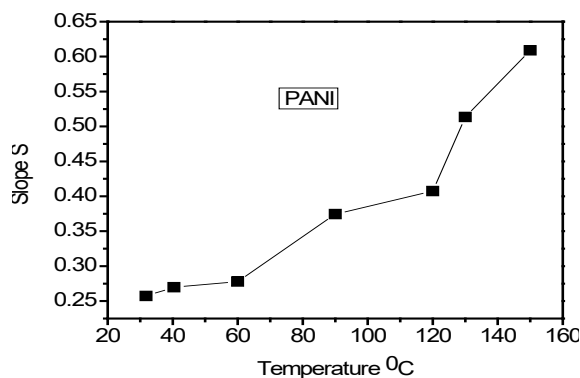

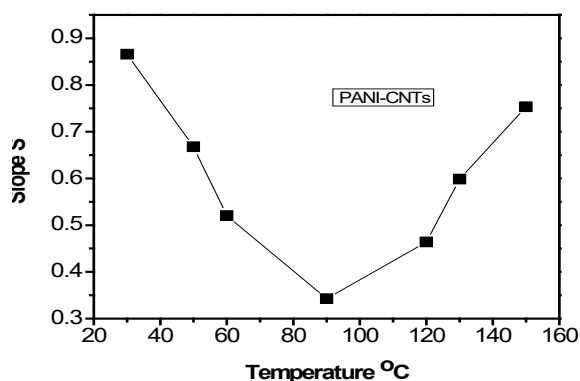*Fig. 14. Slope S vs Temperature for PURE PANI.*

Fig. 15. Slope S vs Temperature for PANI-CNTs Composite.

In our case the values of s for best linear fit lies between 0.2567 and 0.609 (T= 30-150^{0}C) for Pure PANI and 0.3427 and 0.8659 (T= 30-150^{0}C) for PANI-CNTs composite. It indicates that the studied samples follow charge hopping mechanism and exhibit ac conduction. In our case S decreases with T. Therefore from this trend of S it may be concluded that large polarons hoping is taking place. The rise of conductivity with rise of frequency and temperature is common response of polymeric samples. It is due to the tremendous increase of the mobility of charge carriers. Frequency dependent conductivity increases with rise in temperature which may be due to trapped charges. It has been observed that with the increase in frequency the AC conductivity increases due to large jump probability.

4. Conclusions

Polymer/nanosized particles have been synthesized successfully in open air at room temperature (27±5)^{0}C and hence *in-situ* chemical polymerization is best suitable method for synthesis of PANI and MWCNTs doped PANI. It was confirmed by XRD pattern that nanosized

MWCNTs are crystals and pure PANI is with amorphous nature. While crystalline nature was exhibited by PANI/MWCNTs 20% composite. The SEM characterization of PANI-CNTs composite revealed a uniform wrapping of CNTs by PANI forming a core-shell nanostructure. This structure acted as a conductive path and lead to high value of conductivity than pure PANI.An inverse relation was found between dielectric measurements and frequency at various temperatures. On average the values of relative permittivity, permittivity loss and dielectric loss factor for all samples were found to increase with temperature.

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