



Preparation Characterization and Electrical Study of Polymeric Mixture Nanocomposites

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ABSTRACT: Method at room temperature. SnO_2 nanostructures were synthesized by Sol-Gel $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and NH_4OH were used for synthesis. The polymeric mixture consist of three polymers; Poly Vinyl Acetate PVAc, Pecten, Poly Aniline PANI have been prepared at calculated amount. The polymeric mixture composite with different SnO_2 nanoparticles concentrations. The obtained SnO_2 nanoparticles ,polymeric mixture composite and polymer nanocomposite were characterized by FTIR ,X-ray diffraction(XRD) ,Atomic force microscope AFM and Scanning electron microscope SEM .The composites are cast into films .The dielectric constant properties of the films were measured with HP LCR meter .The electrical conductivity values for films increase with applied frequency increasing. Also, the electrical conductivity is discussed in terms of the Arrhenius plot, the electrical conductivity is plotted against the inverse temperature for polymeric mixture composite and polymer nanocomposite at different applied frequencies.

I. INTRODUCTION

Polymer nano composites are the subject of increased interest because they combine the features of polymers with small quantities of nanoparticles [1]. Nanoparticles are defined are those particle having at least one dimension in the range of 1 to 100 nm [2]. The structure of the polymer is very important to determine, if it is polar or non -polar and this influences the dielectric and electrical properties of the polymer [3]. Conducting polymers are electronically conducting organic materials [4]. They possess an extended π -conjugation along the polymer backbone and exhibit semiconducting behaviour [5]. Conducting polymers exhibit the electrical and optical properties of the metal and retain the attractive mechanical properties of polymers leading to wide range of technological applications[6]. The superiority of polyaniline over all other conducting polymer are reported by Badra and et al[7]. PANI is taken as matrix materials for many work[8], because not only it is highly stable in air and in some solvent, but also exhibits dramatic changes in its electronic structure and physical properties .Polymerization of PANI in the presence of mixture of PVAc and Pecten leads to a more unique mixture because of the additional interaction to a hydrogen bonding between the hydroxyl and carboxylic groups in pectin and PVAc with the same group in PANI. Tin dioxide (SnO_2) is an important oxide semiconductor material, which has been widely used in many applications such as catalysts agent [9], hazardous gas sensors [10], heat reflecting mirrors [11], and visitors [12], transparent conducting electrodes for solar cells [13], and optoelectronic devices [14]. Tin dioxide-based gas sensor devices are very important in developing n-type semiconductor sensors, which can be utilized to detect various inflammable and harmful gases such as hydrogen (H_2), carbon monoxide (CO), ethanol and methanol. Semiconductor sensors exhibit changes in electrical resistivity in the presence of small concentrations of certain gases. Sensors consisting of fine particles of metal oxides usually exhibit high sensitivity compared to their counterparts made of larger particles. The most important factor affecting the sensitivity of gas sensors is the actual crystallite size of the sensing materials [15].

II. EXPERIMENTAL

A. Preparation of SnO_2 Nanoparticles

The resulting opal in a typical synthesis [16], a transparent sol solution was prepared by dissolving 3.5 g of tin tetrachloride pent hydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) in 100 mL distilled water under vigorous stirring. 4 mL of an aqueous ammonia solution was added to the above solution by drop wise under stirring gels were filtered and washed with methanol to remove impurities, and dried over 80°C for 5 h in order to remove water molecules. Finally, ash colored tin oxide nanopowders were formed at 400°C for 2h. the crystalline structure and morphology of SnO_2 powder was assessed by XRD, (Shimadzu XRD-6000) was with copper radiation ($\text{Cu K}\alpha_1$, 1.5406 Å)

B. Polymeric Mixture Composite Preparation

prepared by in situ chemical oxidation polymerization of aniline monomer in the presence of PVAc and Pecten solution .In a typical The synthesis process, aniline hydrochloride was dissolved in a few distilled water then it was added to 500 ml of the prepared polymers mixture solution(PVAc and Pecten solution) with high stirring for one hour by used mechanical stirring (1000 cycle / min). Sodium Persulphate solution was added to the mixture by drop wise with high stirring, the mixture was allowed to react for one hour under constant stirring at -3°C After a while, the colour of



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solution changed to greenish black and that the first evidence be Polyaniline in polymeric composite and blended with other polymers ,and so we obtained a homogeneous solution consisting of three polymers mixed with each other . It was found that the film which contains 25 percentage of polyaniline in polymers mixtures is the best film can be obtained through a homogeneous ,powerful ,soft and conductive electrical can be relied upon in the preparation of nanocomposite polymeric film.

C. Preparation of Polymer Nanocomposite

Four 40 ml beakers were prepared with 25percentage of poly aniline (12.5g in 100 ml distilled water PVAc, 5 g in 100 ml distilled water Pecten and 0.367 g of Aniline chloride and 0.8070 g of Ammonium persulphate) and mixed completely under constant stirring for one hour at room temperature .Each composite was mixed ultrasonically for 30 minutes with different MWCNT composites weights (0,0.007,0.014 and 0,028g). The films prepared by solution casting .The specimen size was (5x10x10 cm), then the films let dry at 50°C for 120 hour. At the expiry of this time, the films were ready which were peeled off the casting glass plate. After drying the films ,measured the electrical conductivity to the nanocomposite films by LCR meter .It found that the highest electrical conductivity was the film containing of 4 % Percentage of MWCNT ,that is why this ratio selected for this study .

D. Swelling Test

It was found that the weight of films don't change when it putting in water for more than 7 days, this prove that the films don't absorb water or get it any swelling.

E. Dielectric Constant Measurement

The above fabricated films were cut into 2x1.5 cm pieces to fit a homemade Silver electrode for characterization by measuring the dielectric properties. Precision LCR meter HP 4274 A connected with HP 4275 A and with Test Fixture HP 16047 A at frequency range 10² Hz to 10⁵ Hz was used. The dielectric parameter as a function of frequency is described by the complex permittivity.

$$\epsilon^*(\omega) = \epsilon'(\omega) - \epsilon''(\omega) \dots\dots\dots(1)$$

where the real part ϵ' and imaginary part ϵ'' are the components for the energy storage and energy loss, respectively, in each cycle of the electric field. The measured capacitance C was used to calculate the dielectric constant, ϵ' using the following expression

$$\epsilon' = \frac{Cd}{\epsilon^0 A} \dots\dots\dots (2)$$

Where d is the thickness between the two electrodes, A is the area of the electrodes, ϵ^0 is the permittivity of the free space, = 8.85x 10⁻¹²/N. m² and (ω) is the angular frequency ($\omega = 2\pi f$), f is applied frequency }The dielectric loss ($\epsilon''(\omega)$) is described with eq. (3),were $\tan \theta(\omega)$ is tangent delta [17]

$$\epsilon''(\omega) = \epsilon'(\omega). \tan \theta(\omega) \dots\dots\dots(3)$$

Electrical conductivity of prepared films are calculated by following equation

$$\sigma = \epsilon' \times \epsilon^0 \dots\dots\dots(4)$$

III. Results and Discussion

A. FT-IR Characterization

Evidence of polymeric mixture composite and nanocomposite was provided by FT-IR spectroscopy, as shown in the spectrum of Figure 1A and 1B respectively .As we see the characteristic absorption band at 1400 cm⁻¹ for (C-N) in polyaniline[18],the band at1188 cm⁻¹ attributed to(C-N⁺) group, which caused electrical conductive .The bands at 3321,3131cm⁻¹ for aromatic(C-H) and (O-H) at acetate group, respectively .The peak at 1111cm⁻¹ for (C-O-C) in Pecten. Figure 1C shows the FTIR spectra of the synthesized nanomaterials. The spectrum show Sn-O strong absorption band near 667.513 cm⁻¹ [19]. The peaks at 3383 and (OH) and(C=C) residues, probably due to atmospheric moisture [20] [21].

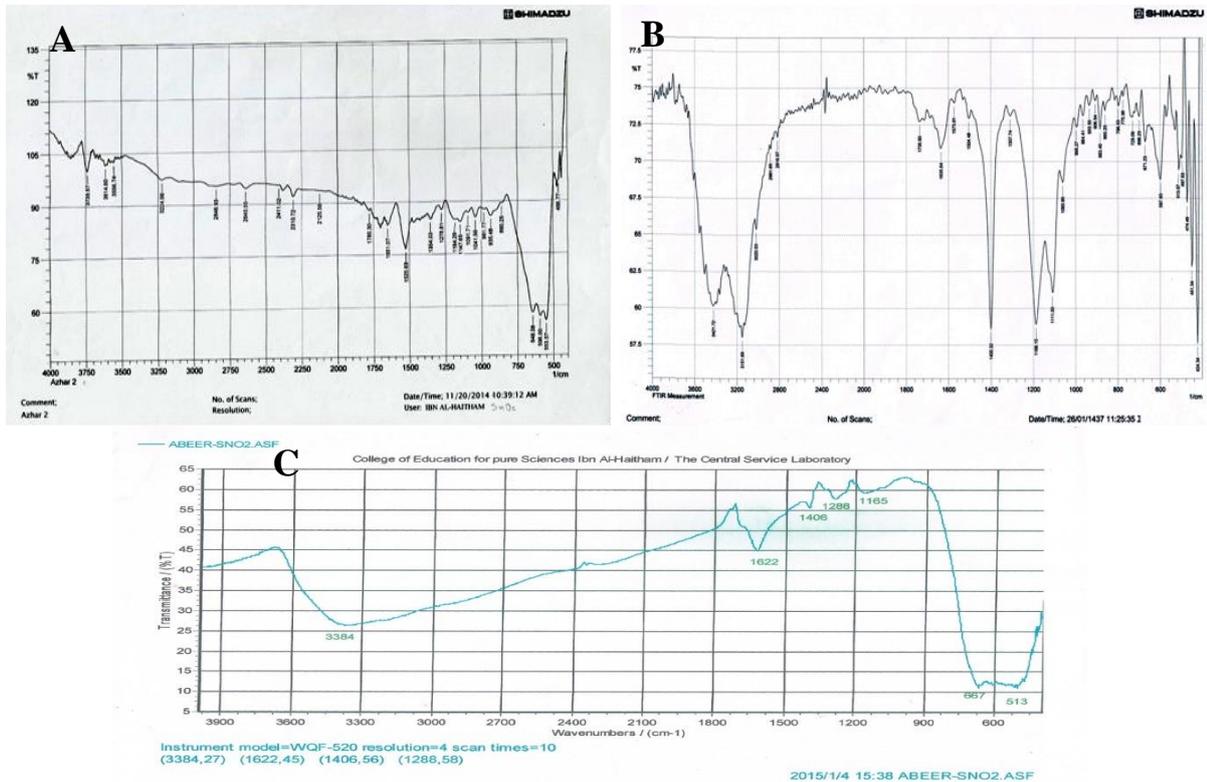


Figure 1. FTIR spectrum A: polymeric mixture composite, B: polymer nanocomposite and C: FTIR spectrum of SnO₂

B. Characterization of SnO₂ nanoparticles and Prepared Composites with X- Ray Diffraction (XRD)

The XRD spectra of SnO₂ nanoparticles are shown in Figure 2. A series of characteristic peaks: (22.28 ,33.86,51.81 and 65.08 degree) are observed, and they are in accordance with the SnO₂ structure polycrystalline (tetragonal). No peaks of impurity were observed, suggesting that the high purity SnO₂ was obtained. In addition, the peak is widened implying that the particle size is very small according to the Debye–Scherrer formula:

$$D = \frac{K\lambda}{B \cos\theta} \dots\dots\dots(5)$$

where K is the Scherrer constant taken as 0.94, λ the X-ray wavelength (CuKα₁ = 0.15406 nm), B the peak width of half-maximum, and θ is the Bragg diffraction angle. The crystallite size D is about(5.3,5.6 and7.4) nm calculate using the Debye–Scherrer formula. The XRD spectra the polymeric mixture composite is shown in Figure 3.Three clear peaks are appear In this Figure(19.88,25.12 and 14.0 degree),while Figure 4 is gave the XRD spectra of the polymer nanocomposite ,which gave a series of peaks (23.8,36.62 and 48.12 degree)

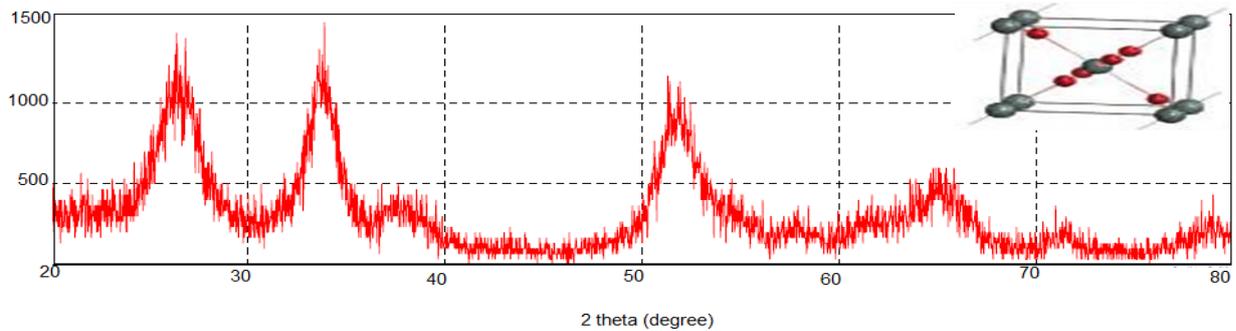


Figure 2 . XRD pattern of nanoparticles SnO₂ powder and the tetragonal structure of SnO₂ crystal

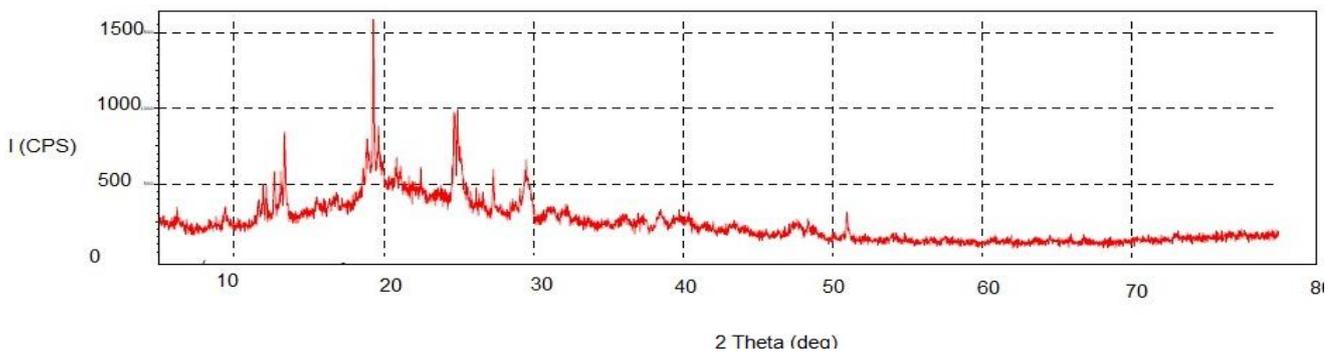


Figure 3 . XRD pattern of polymeric mixture composite

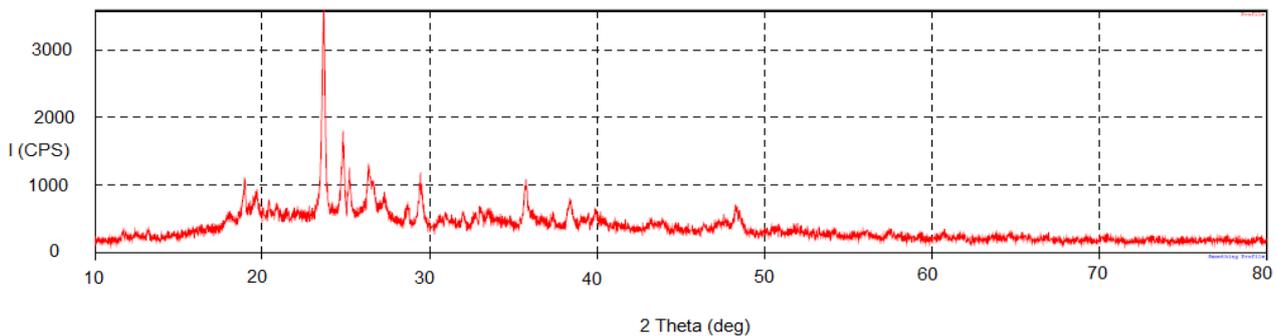


Figure 4 . XRD pattern of polymer nanocomposite

C. Atomic Force Microscopy

The Atomic Force Microscopy (AFM) image (Figure 5A) represents SnO₂ nanoparticles. The particle size histogram was performed and shown as in Figure (5). The particles which are to a large extent well-separated from one another throughout the field of the micrograph. Figure (5B) show the maximum particle diameter; were less than (50.6 nm). Figure 6 and 7 shown AFM image of the polymeric mixture composite and nanocomposite at two and three dimensional, respectively.

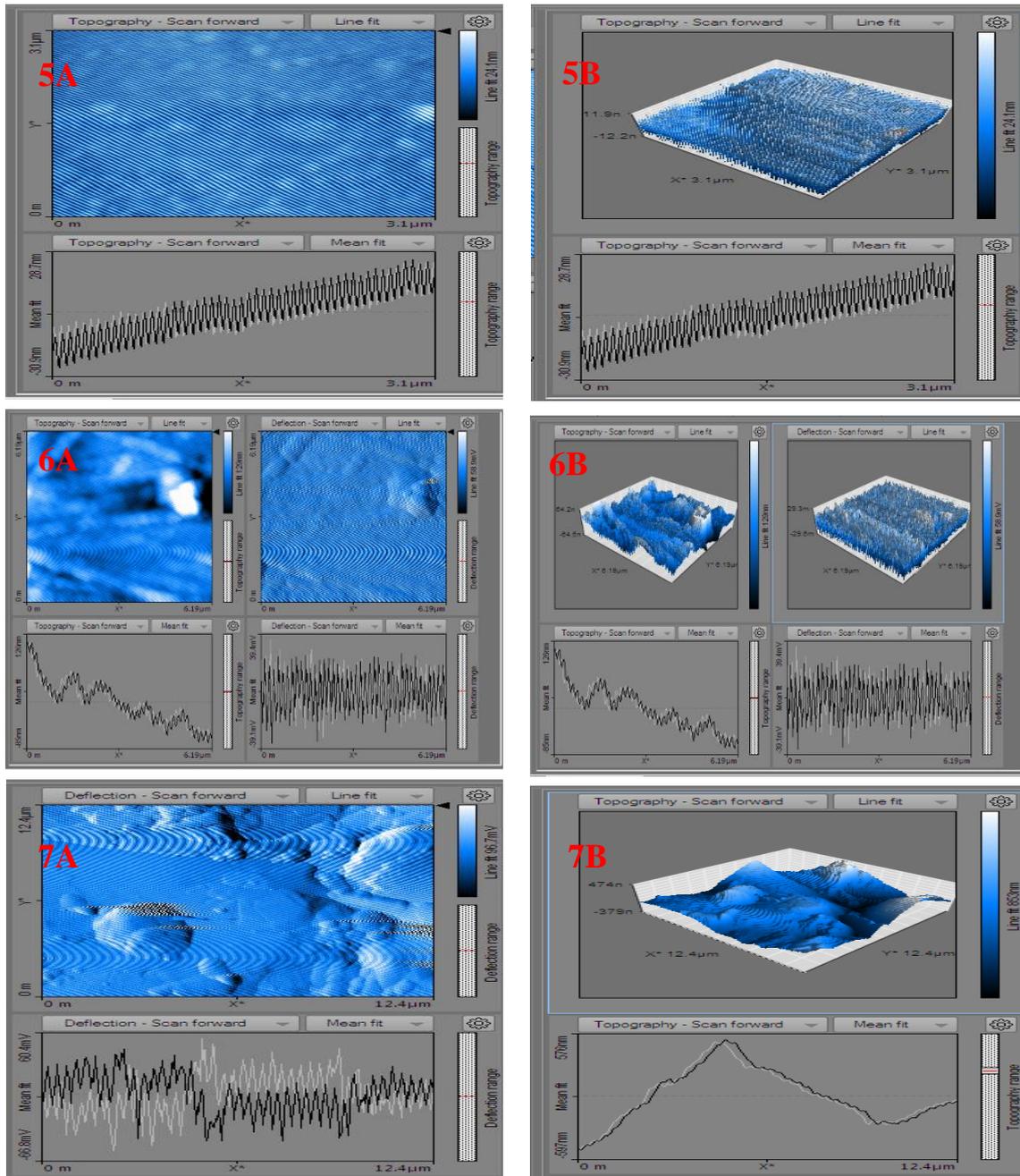


Figure 5 . AFM image of the SnO_2 2D and 3D , Figure 6 AFM of polymeric mixture composite. 6A 2D, 6B 3D Figure 7 AFM of polymer nano composite 7A 2D,7B 3D

D. Scanning Electronic Microscopy SEM

SEM image of SnO_2 nanoparticles, polymeric mixture composite and nanocomposite are shown in figures 8,9A and 9B respectively. Nanocomposite shows the homogeneous coating of polymeric mixture onto the SnO_2 nanoparticles indicating that SnO_2 nanoparticles were well dispersed in matrix of polymers mixture. Rough surface and increased diameter of

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nanocomposite indicated the coating of the polymeric mixture over all nanoparticles. The element analysis of SnO₂ nanoparticles shows the high purity of this compound.

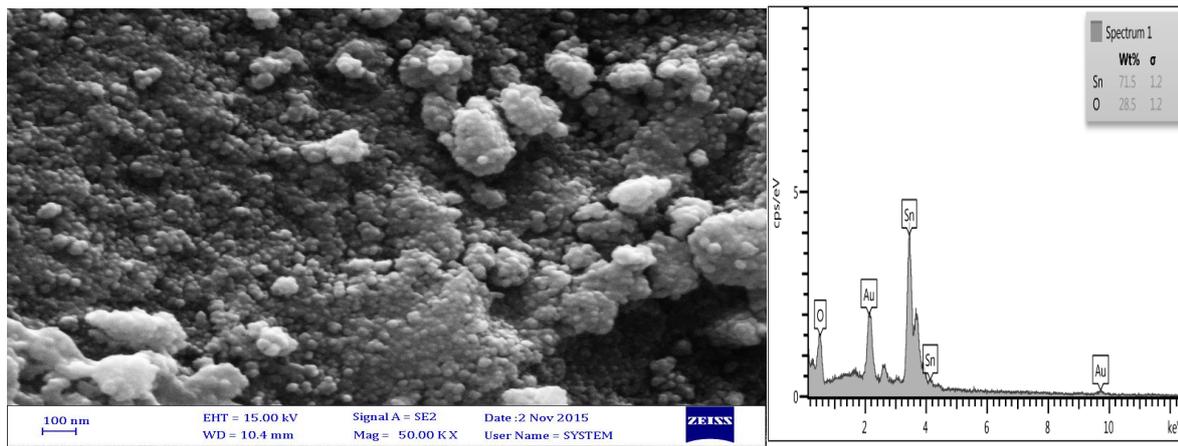


Figure 8. SEM image and element analysis of SnO₂ nanoparticles

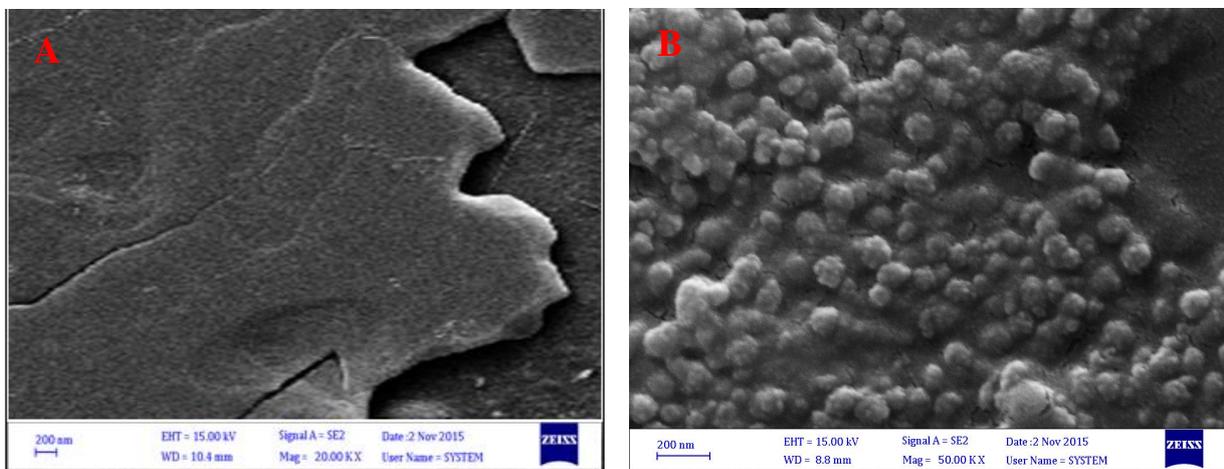


Figure 9. A SEM image of polymeric composite, B :SEM image of polymer nanocomposite

E. Electrical Properties

The dielectric properties of materials are mainly determined by their polarizabilities at a given frequency. For multicomponent systems, when free charge carriers migrate through the material, space charges build up at the interfaces of the constituents owing to the mismatch of the conductivities and dielectric constants of the materials at the interfaces [26]. This is called interfacial polarization. The interfacial polarization in polymers having structural inhomogeneities (e.g., Nanoparticles) can be identified by low-frequency dielectric measurement based on Maxwell – Wagner–Sillar’s method [26]. The changes in the permittivity values as a function of frequency are attributed to dielectric relaxations especially at low frequency which due to micro-Brownian motion of the whole chain (segmental movement). Nevertheless, these changes are also affected by the interfacial polarization process known as Maxwell–Wagner–Sillar, which exists in heterogeneous dielectric materials and is produced by the travelling of charge carriers [22].

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In order to study the effect of different frequencies on different filler concentrations with the dependence of relaxation processes, effective permittivity was used. Figure 10 and 11 show the real and imaginary part of the permittivity respectively obtained through Equations (1-3) [23] as a function of frequency. It can be seen from Figures 10 and 11 that the effective permittivity is increased for all polymer composites with decreasing frequency. Permittivity is a frequency dependent parameter in the (PANI, PVAc, Pecten) polymers systems. The permittivity of polymeric mixture system is governed by the number of orientable dipoles present in the system and their ability to orient under an applied electric field [24], [25]. Usually, the molecular groups which are attached perpendicular to the longitudinal polymer chain contribute to the dielectric relaxation mechanisms. At lower frequencies of applied voltage, all the free dipolar functional groups in the PANI Chain can orient themselves resulting in a higher permittivity value at these frequencies. As the electric field frequency increases, the bigger dipolar groups find it difficult to orient at the same pace as the alternating field, so the contributions of these dipolar groups to the permittivity goes on in a continuously decreasing permittivity of the polymeric mixture system at higher frequencies. Similarly, the inherent permittivity's in SnO₂ nanoparticles also decrease with increasing frequencies of the applied field [26],[27]. This combined decreasing effect of the permittivity for both polymeric mixture and the filler particles result in a decrease in the effective permittivity of the polymeric mixture composites when the frequency of the applied field increases. SnO₂ displays strong Ionic polarization due to Sn⁴⁺ and O²⁻ ions and therefore has a high value of static permittivity [27]. Therefore, in the range of frequencies under study SnO₂, dielectric behaviours should have an influence on the resultant dielectric behaviours of (polymeric mixture) composite. In figure 10 the real permittivity slope variations with respect to frequency can be considered to be very minimal, since the nanocomposites permittivity slope is almost the same as that of polymeric mixture in frequency range more than 3.5x10³ Hz, but at frequencies less than 3.5x10³ Hz, there is a noticeable change in the permittivity slope. This observation of the steepness of the permittivity slope at frequencies lower than 3.5x10³ Hz is due to the influence of filler SnO₂ nanoparticles. Figure 11 show the variations of imaginary permittivity with respect to frequency, the steepness changes of the imaginary permittivity slope were observed at frequency less than 3.3x10³Hz and this is identified with work of Tsangaris G.et.al, [28]. Figure 12 (a and b) shows the increasing in electrical conductivity for polymer nanocomposite than in polymeric mixture composite.

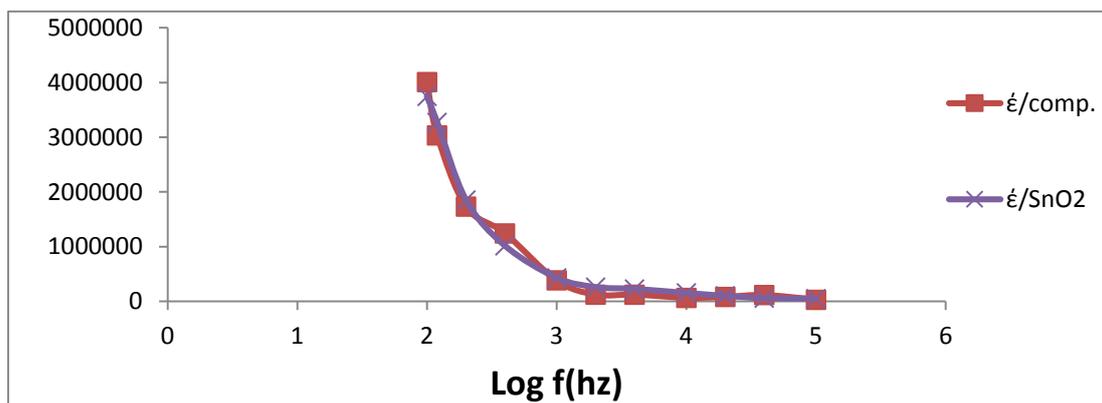


Figure 10. Variations of real permittivity with respect to frequency of polymeric mixture and polymer nanocomposite

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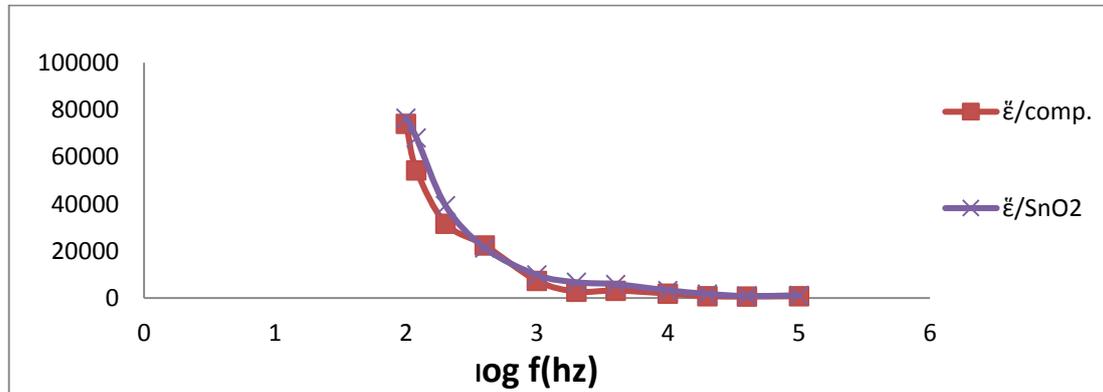


Figure 11. Variations of imaginary permittivity with respect to frequency of polymeric mixture and polymer nanocomposite.

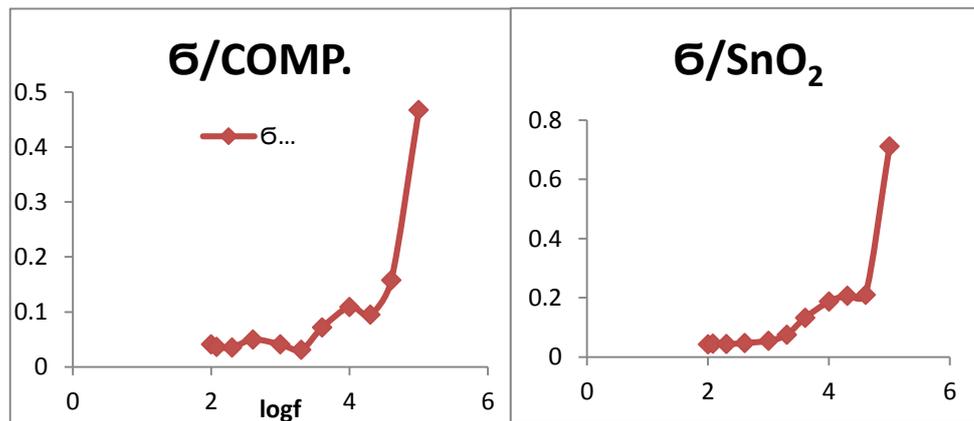


Figure 12 .(a and b) Electrical conductivities of polymeric mixture composite and nanocomposite, respectively.

IV. CONCLUSION

In this study, the dielectric behaviour of the polymeric mixture composite and polymer nanocomposite films has been investigated. The results show that the dopant composition has great influence on the magnitude of dielectric properties. The results also show that the composite polymer films have both electric and electronic properties. The composite polymer films exhibit the combination of intrinsic dielectric anisotropy as a result of the competition of free charges and electronic polarization corresponded to PANI matrix . Electrical conductivity of the composition of nanoparticles is increased than that of polymeric mixture composite ,which indicates high availability of free charges.

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