American Journal of Polymer Science 2012, 2(6): 135-140
DOI: 10.5923/j.ajps.20120206.01

Preparation, Characterization and Electrical Study of (Carboxymethylated Polyvinyl Alcohol/ZnO) Nanocomposites

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Abstract ZnO nanostructures were synthesized in one step reaction at 80℃ without any extra treatments. ($Zn(NO_3)_2.6H_2O$) and (NaOH) were used for synthesis. Production of ZnO nanostructures occurred relatively in short time. The obtained ZnO nanostructures were characterized by X-ray diffraction (XRD) and the atomic force microscope AFM. Carboxymethyleted PVA (CPVA) has been prepared and characterized. (CPVA) were composite with different ZnO nanoparticles concentrations. The composites are cast into films. The dielectric constant properties of the films were measured with hp LCR meter.

Keywords ZnO Nanocomposites, Dielectric study of ZnO nanocomposite, Carboxymethylated Polyvinyl Alcohol/ZnO Nanocomposites, Electrical Study, Permittivity

1. Introduction

Polymer nanocomposites are the subject of increased interest because they combine the features of polymers with small quantities of nanoparticles (less than 5% by weight)[1]. Nanoparticles are defined as those particles having at least one dimension in the range of 1 to 100 nm.[2],[3].

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. In polar polymer (for example, PMMA, PVC, PA (Nylon), PC,.. etc..) the imbalance of electrons distribution on the molecules are created the dipoles and the presence of an electric field these dipoles will move to align with the field. This will create dipole polarization of the material. The movement of the dipoles will take a time element to the movement, which affects the magnitude of the conductivity value. Polymer nanocomposites provide advantages over micron-filled polymers like resistance to degradation, improvement in thermo-mechanical properties and no reduction in dielectric strength value[4],[5]. Nanoparticles have higher surface area-to-volume ratio than in micro particle size. The interfacial area leads to a significant volume fraction of polymer surrounding the nanoparticles that is affected by the particle surface and has properties different from polymer in the interaction zone[6]. Since this interaction zone is much more extensive for nanocomposites than for microcomposites, it can have significant impact on electrical and mechanical properties[7]. The effective permittivity and conductivity of a composite is a complicated function of the physical properties of the individual components, such as, shape and particle size distribution, porosity, volume loading and the interaction between the filler and the insulating matrix[8-12]. The permittivity is independent on the frequency, when the frequency of the external field approaches the characteristic frequency for the charge redistribution/reorientation process a strong frequency dependence of the permittivity is seen as a downward step in the real part of the permittivity and a peak in the imaginary part[13]. ZnO has been one of the most promising materials for electrical devices, including transparent conductive films, light emitting diodes and photocatalyst[14-17]. ZnO can be synthesized practically into different nano forms[18]. In this work ZnO was synthesized by hydrothermal method[19]. The formation of ZnO nanoparticles was characterized by x-ray diffraction (XRD) and Atomic Force Microscopy (AFM). Polyvinyl alcohol (PVA) is well known polymeric material with good chemical stability and hydrophilicity [20],[21] for which there have been many experiments using PVA for the fabrication of the reverse osmosis (RO) or nanofiltration membrane. PVA membrane shows low flux and low rejection due to the relative high thickness of PVA membrane[22],[23]. Such membrane and their composite need ensure adequate mechanical strength, PVA has been chemically modified to its carboxymethylated form using monochloroacitic acid (MCAA) and the product designated as CPVA[24]. The electrical properties of CPVA are

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Published online at http://journal.sapub.org/ajps

particularly important in view of the fact that there is no exploration of the characteristics of CPVE electric properties or any ZnO nano type composite with this polymer.

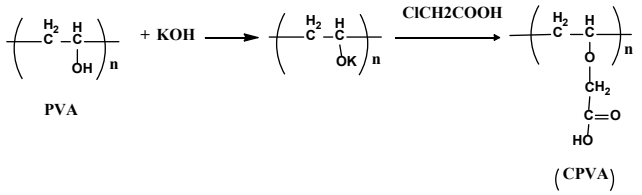
2. Experimental

2.1. Preparation of ZnO Nanoparticles

ZnO nanoparticles were prepared according to[25]. All reagents used in this work, NaOH and $Zn(NO_3)_2.6H_2O$, were imported from Sigma Aldrich. A solution of 1M-NaOH was prepared by dissolving 40 gm of NaOH in one liter of deionized water in 2 liter beaker and was heated at 80℃ with stirring. A solution of 0.5M- $Zn(NO_3)_2.6H_2O$ (250 ml)was added to the basic solution and the reaction mixture was kept stirred and heated at 80℃, for three hours. The suspended solution formed from the above mixture was separated with a centrifuge to obtain ZnO which was washed several times with deionized water. The ZnO product was dried at 80℃ in oven for several hours, the yield was about 91%. The crystalline structure and morphology of ZnO powder was assessed by XRD. (Shimadzu XRD-6000) was with copper radiation (Cu K_α, 1.5406 Å) as incident radiation and with Atomic Force Microscopy (AFM).

2.2. Preparation of carboxy methylated PVA (CPVA)

Condensation of Polyvinyl Alcohol PVA (MW 72000 Dalton) with monochloroacitic acid (MCAA) (from Aldrich) .PVA was dissolved in the desired amount of aqueous potassium hydroxide solution and heated in a water bath. The calculated amount of the MCAA was then added (1:2:: OH: MCAA) and the reaction mixture was stirred at 65℃ for 3h.



Scheme 1. Synthesis of CPVA by the reaction of PVA and MCAA

At the end of the reaction the mixture (Scheme 1.) was acidified with 0.1N hydrochloric acid. The product was precipitated with methanol. It was then dissolved in distilled water and re-precipitated from the solution using methanol as non-solvent. The process was repeated till the polymer became free of chloride ions[24].

2.3. CPVA with ZnO Nanocomposites Film Fabrication

Three grams CPVA , was dissolved completely in 120 ml distilled water under constant stirring for one hour while the mixture was heated up till 50℃ then the mixture was left to cool down to (24℃) and the stirring was carried out to ensure the homogeneity of the composition. The obtained CPVA solution was divided in six equalled parts and each part was mixed ultrasonically for 20 min, with various concentrations of ZnO nanoparticles (0.0%, 0.0008%, 0.004%, 0.008%, 0.018%, 0.038%). To cast the film, the mixture for each ZnO nanoparticles concentration was poured into a 12x6 cm casting glass plate and let to dry at room temperature for 140 hours. At the expiry of this time, the films were peeled off the casting glass plate.

2.4. Dielectric Constant Measurements

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 10^2 Hz to 10^5 Hz was used. The dielectric parameter as a function of frequency is described by the complex permittivity.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega) \quad (1)$$

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.

$$\varepsilon' = \frac{Cd}{\varepsilon_\circ A} \quad (2)$$

where d is the thickness between the two electrodes, A is the area of the electrodes, $\varepsilon_\circ$ 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 (ε"(ω)) is described with eq. (3):

$$\varepsilon''(\omega) = \varepsilon'(\omega).tan\theta\ (\omega) \quad (3)$$

$tan\ \theta\ (\omega)$ is tangent delta[27]. The electric modulus is the reciprocal of the permittivity in complex form[28] was found using eq. (4):

$$M^* = \frac{1}{\varepsilon} = M' + M'' \quad (4)$$

Where M′ and M" are the real and imaginary part of dielectric modulus and it was calculated by Eq. (5and 6):

$$M' = \frac{\varepsilon'}{\varepsilon'^2+\varepsilon''^2} \quad (5)$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2+\varepsilon''^2} \quad (6)$$

3. Results and Discussion

3.1. FT-IR Characterization of CPVA

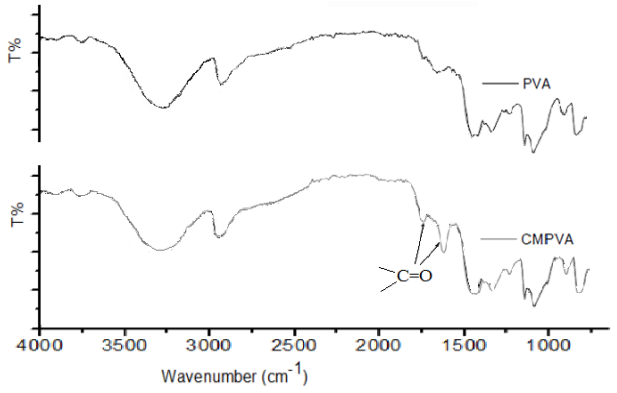


Figure 1. FTIR spectra of PVA and carboxymethylated PVA (CPVA)

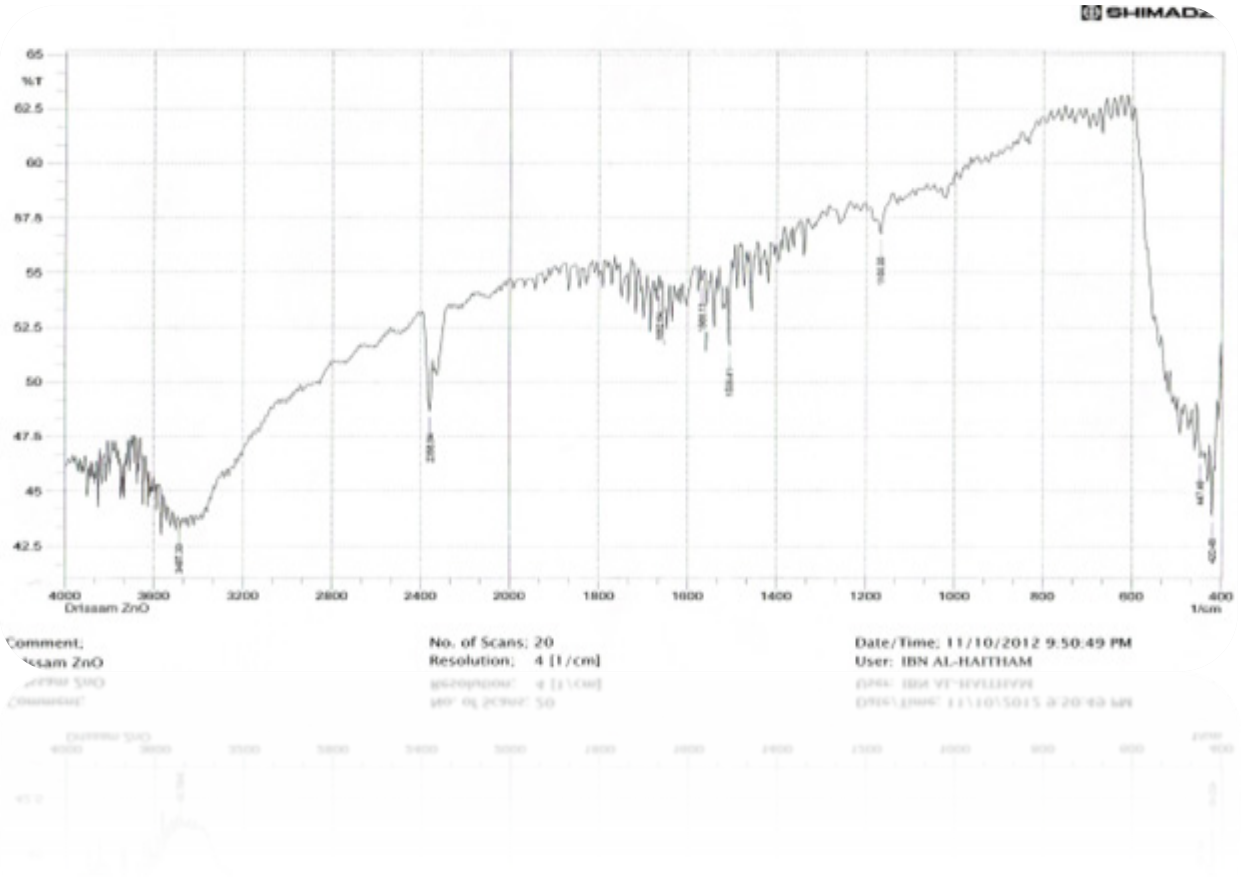


Figure 2. FTIR spectrum of ZnO nanoparticles

Evidence of carboxymethylation was provided by FT-IR spectroscopy. The spectrum of CPVA (Figure 1) not only shows the characteristic absorption bands for PVA, i.e. CH2 bending at 1416 cm-1, C–O stretching and O–H bending at 1079 cm-1, but also additional absorption bands at 1714 and 1620 cm-1, which are characteristic of the carboxymethyl group.

3.2. FT-IR Characterization of ZnO

Figure 2 shows the FTIR spectra of the synthesized nanomaterials. The spectrum show Zn-O absorption band near 420.48 cm^{-1}. The peaks at 3487 and 2,358 cm^{-1} indicate the presence of –OH and C=O residues, probably due to atmospheric moisture and CO2 respectively.

3.3. Characterization of ZnO with X- Ray Diffraction (XRD)

The XRD spectra of ZnO nanoparticles are shown in Figure. 3. A series of characteristic peaks: 2.8112 (100), 2.5996 (002), 2.4702 (101), 1.9092 (102), 1.6239 (110), 1.4763 (103), 1.4060 (200), 1.3777 (112) and 1.3590 (201) are observed, and they are in accordance with the ZnO structure (International Center for Diffraction Data, JCPDS 5-0664). No peaks of impurity were observed, suggesting that the high purity ZnO was obtained. In addition, the peak is widened implying that the particle size is very small according to the Debye–Scherrer formula:

$$D = \frac{K\lambda}{B\cos\theta} \quad (7)$$

where K is the Scherrer constant taken as 0.94, λ the X-ray wavelength ($Cu_{K\alpha}$ = 0.15406 nm), B the peak width of half-maximum, and θ is the Bragg diffraction angle. The average crystallite size D is 41±1 nm calculated using the Debye–Scherrer formula.

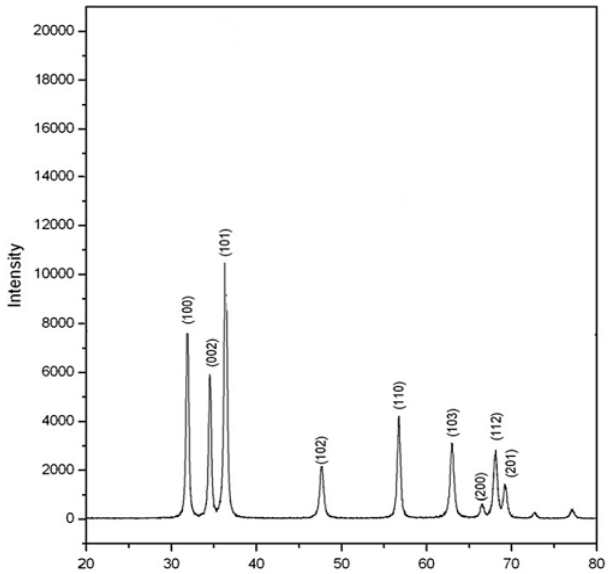


Figure 3. XRD pattern of ZnO nanoparticles powder

3.4. Atomic Force Microscopy

The Atomic Force Microscopy (AFM) image (Figure 4) represents ZnO nanoparticles. The particle size histogram was performed and shown as in Figure (4).

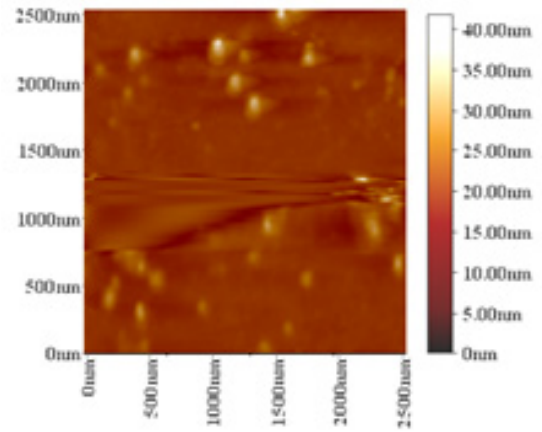


Figure 4. 2-D topographic AFM image of the synthesized ZnO nanoparticles (Scan size: 2500nm_2500 nm)

The particles which are to a large extent well-separated from one another throughout the field of the micrograph. Figure (5) show the maximum particle diameter; were less than (41.7 nm).

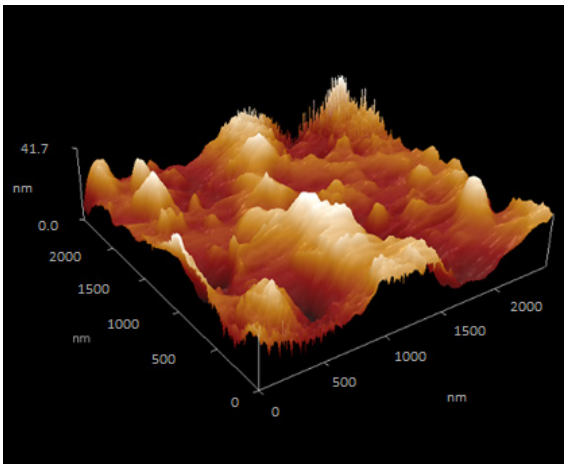


Figure 5. Represent the AFM 3-D image with maximum high (41.7 nm) of the nano ZnO particles (scan size: 2500_2500)

3.5. Dielectric Constant

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 [27].

In order to study the effect of different frequencies on different filler concentrations with the dependence of relaxation processes, effective permittivity was used Figure 6 and 7 show the real and imaginary part of the permittivity respectively obtained through Equations (1-3) and the electrical modulus was used. Figure 8 and 9 show the real and imaginary parts of the electrical modulus respectively obtained through Equations (4-6)[28] as a function of frequency. It can be seen from Figures 6 and 7 that the effective permittivity is increased for all polymer composites with decreasing frequency. Permittivity is a frequency dependent parameter in the (CPVA) polymer systems. The permittivity of (CPVA) system is governed by the number of orientable dipoles present in the system and their ability to orient under an applied electric field[29],[30]. 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 (CPVA) 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 (CPVA) system at higher frequencies. Similarly, the inherent permittivities in ZnO nanoparticles also decrease with increasing frequencies of the applied field[31],[32]. This combined decreasing effect of the permittivity for both (CPVA) and the filler particles result in a decrease in the effective permittivity of the (CPVA) composites when the frequency of the applied field increases. ZnO displays strong Ionic polarization due to Zn^{2+} and O^{2-} ions and therefore has a high value of static permittivity[32]. Therefore, in the range of frequencies under study, ZnO dielectric behaviors should have an influence on the resultant dielectric behaviors of (CPVA) composite. In figure 6 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 pure (CPVA) in frequency range more than $3{,}5x10^3$ Hz, but at frequencies less than $3.5x10^3$ Hz, there is a noticeable change in the permittivity slope. This observation of the steepness of the permittivity slope at frequencies lower than $3.5x10^3$ Hz is due to the influence of ZnO filler nanoparticles. Figure 7 show the variations of imaginary permittivity with respect to frequency, the steepness changes of the imaginary permittivity slop were observed at frequency less than $3.3x10^3$Hz. In Figure 8 it can be seen that M´ values increased with frequency. Nevertheless, the figure 9 peaks in M´´ values were developed at the same frequency range, indicating the appearance of a relaxation process. The maximum of M´´ increased when ZnO nanoparticles concentration amount increased, the frequency at the

maximum of the peak of M" show the (ω´) the relaxation frequency.

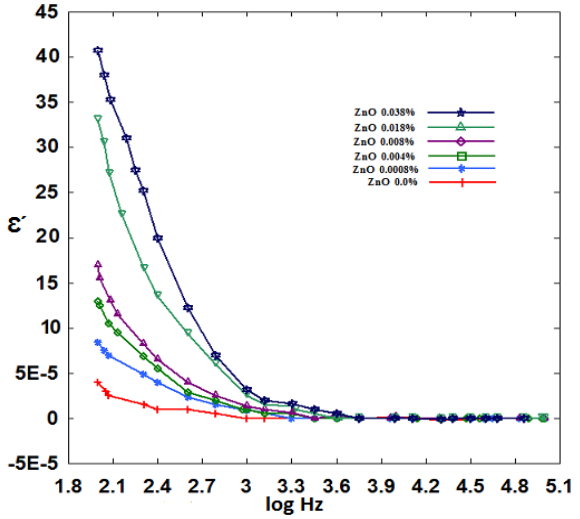


Figure 6. Variations of real permittivity with respect to frequency of polymer at different concentration ZnO nanoparticles composites

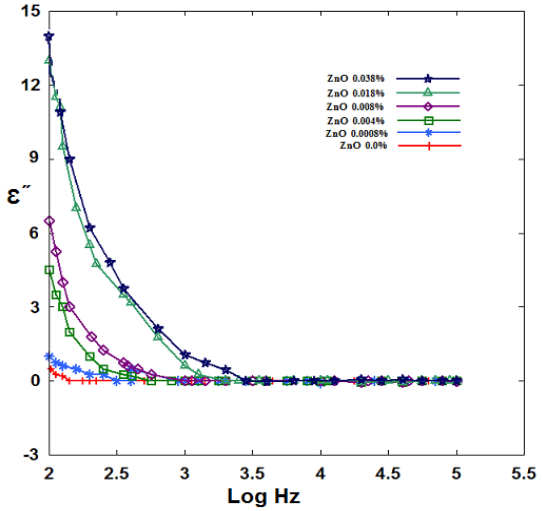


Figure 7. Variations of imaginary permittivity with respect to frequency of polymer at different concentration ZnO nanoparticles composites

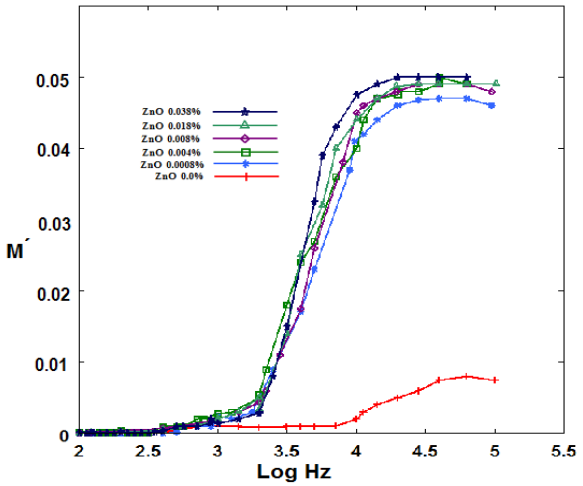


Figure 8. Variations of real electrical modulus of polymer at different concentration of ZnO nanoparticles composite

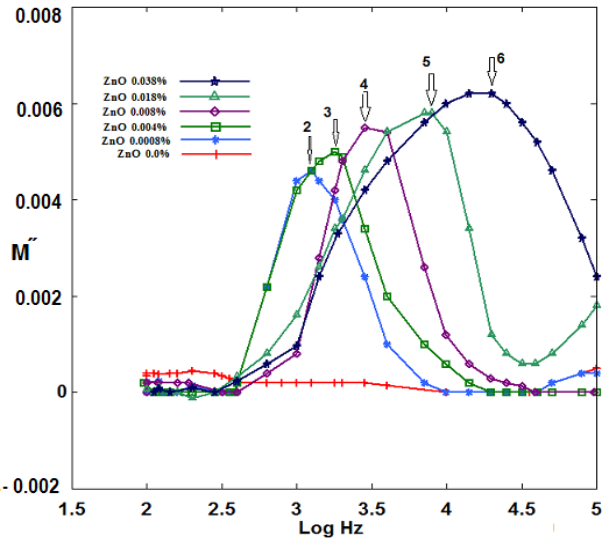


Figure 9. Variations of imaginary electrical modulus of polymer at different concentration of ZnO nanoparticles composite

Relaxations peaks were displaced to higher frequencies, since relaxation processes were influenced by the interfacial polarization effect which generated electric charge accumulation around the ZnO nanoparticles and the displacement of the peak as the particle content increased and this is identified with work of Tsangaris,G,et.al,[33].

4. Conclusions

In this study, the dielectric behavior of the polar (CPVA) /ZnO 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 CPVA matrix. Relaxation times become shorter as the composition of ZnO nanoparticles concentration is increased indicates high availability of free charges.

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