Electrical Studies on PVA/PVP Based Polymer Electrolyte Containing Different Concentrations of Au/Ag Nanoparticles

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Abstract: Prepared PVA/PVP polymer nanocomposite samples by casting method and was doped of Ag NPs and Au NPs, AC electrical possessions of PVA-PVP-Ag/Au NPs films was investigated by AC measurements were obtained by using phase sensitive LCR meter. The AC electrical conductivity, dielectric constant, dielectric loss are increased with the increasing of content of Ag/Au nanoparticles. Behavior AC conductivity of all samples was investigated over the frequency range 50 Hz–5 MHz in the temperature range 303–413 K. It propose that the hopping mechanism might be it has a role an important in the conduction process at high frequency. The dielectric properties and AC electrical conductivity are different with increasing of the frequency of practical electrical field. The dielectric constant (ε′) was decreased with increasing the frequency because direction dipoles of applied field electric and at high frequencies, decreasing of permittivity was nearly stable attribute to the dipoles orientation. Value higher of dielectric loss (ε″) was observed at low frequency because the mobile charge within blend PVA/PVP. An increases of loss tangent (tan δ) with increasing in nanoparticles content was expected because conductivity increases with increasing Au NPs/Ag NPs. Decreasing of tan δ with increasing frequency is attributed to the fact that the hopping frequency of carriers charge cannot follow any change of externally applied electric field.

Keywords: Ag NPs, Au NPs, Nanocomposite, AC electrical, Dielectric relaxation, SEM.
1. Introduction

Solid polymer electrolytes it was very important in many industrial applications, including in electric vehicles, energy cells and mobile phones. Nanoparticles of metal have good physical and chemical properties which make them important for applications such as electronics, optics, catalysis, electronics and biotechnology [1]. Gold nanoparticles (Au NPs) are of increasing interest in chemistry of materials because the broad versatility of chemical of the gold nanoparticles themselves and resulting colloidal matrix [2]. Silver nanoparticles (Ag NPs) have pulled the attention of researcher due to their suitable applications in the fields of electronic, material science and medicine [3].

Polyvinyl alcohol has been semicrystalline structure of exhibit the important features rather than of amorphous features one [4]. Poly (N-vinylpyrrolidone), deserves of the polymer conjugated because of its good stability of environmental, electrical conductivity can moderate, easy processability and rich physics in charges transports mechanisms. Polymer nanocomposite films are crossbred materials with different nanoparticles inorganic and integrated in a matrix of polymer. Metal nanoparticles such as gold (Au) or silver (Ag) significantly contributes with their characteristics optical properties. In order to confirmed the contribution to the overall optical properties of the crossbred materials, in generally it is called “optically effective additives” [5]. Conducting polymers have widely been investigated due to their increasing number of applications in transistors, rechargeable batteries, chemical sensors, diodes, microelectronics etc. [6].

A polymer/Ag NPs/Au NPs has multifunctional properties due to of interaction of nanoparticles with polymer matrices by hydrogen bonding. Thus, alignment of nanoparticles within polymer matrices has a predominating role about the electrical properties of two polymers/ nanoparticles. The principle challenges in nanocomposite materials and improve the electrical properties [7]. The addition of nanoparticles to polymer matrix is expected electrical properties is improve, due to of the distinguished electrical properties of Ag NPs/Au NPs are not only high efficiency conductors of electricity [8].

Polyvinyl alcohol and Poly (N-vinylpyrrolidone), are soluble water and miscible in all conditions. Structural, electrical and optical properties of PVA/PVP polymer blend can be suitably modified by the additional nanoparticles on their reactivity with the host matrix [9]. In this work, electrical properties of PVA/PVP blend (50/50) were investigated and their nanocomposite samples filled with different concentrations of Ag NPs/Au NPs to use the final product in solar cells, sensors and some technical application.

2. Materials and Methods

2.1. Materials
The polyvinyl alcohol from Merck, Germany has molecular weight 14,000 and the polyvinyl pyrrolidone molecular weight 40000 from Aldrich Chemical Co. Ltd., were used as a basic polymeric materials. The tetrachloroauric (III) acid trihydrate (HAuCl₄·3H₂O, 99.5% GR of analysis) was obtained from Merk, Germany. The silver nitrate (AgNO₃) was obtained from Sigma–Aldrich chemicals. The water deionized was used during the reactions as solvent. *Chenopodium murale* leaves was collected from Egypt. Quantity of PVA/PVP was equal of 50/50 by weight was added to doubly distilled water with stirring the solution at room tempertures to complete dissolution. The nanoparticles was dissolved in doubly distilled water and added to the solution of polymeric matrix with continuous stirring. The solution was poured onto cleaned Petri dishes and dried in oven at 50°C for 5 days to ensure removal of the solvent traceses as show in table 1.

**Table 1:** Required amount of Ag and Au nanoparticles was aditional to polymer matrix

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mixed of (Ag-Au) NPs %</th>
<th>NPs Wt. %</th>
<th>NPs mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA/PVP</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ag₁₀₀Au₀</td>
<td>100 – 0</td>
<td>0.152</td>
<td>1.52</td>
</tr>
<tr>
<td>Ag₇₅Au₂₅</td>
<td>75 – 25</td>
<td>0.152</td>
<td>1.52</td>
</tr>
<tr>
<td>Ag₅₀Au₅₀</td>
<td>50 – 50</td>
<td>0.152</td>
<td>1.52</td>
</tr>
<tr>
<td>Ag₂₅Au₇₅</td>
<td>25 – 75</td>
<td>0.152</td>
<td>1.52</td>
</tr>
<tr>
<td>Ag₀Au₁₀₀</td>
<td>0 – 100</td>
<td>0.152</td>
<td>1.52</td>
</tr>
</tbody>
</table>

2.2. Synthesis of Ag NPs/Au NPs by *Chenopodium Murale* Extract

For the synthesis of gold nanoparticles was added 5-6 ml of the extracted *Chenopodium murale* was added to 100 ml of 4 mM of gold chloride (HAuCl₄·3H₂O) aqueous solution. The reaction was occur at room temperature. Change of the color was observed after 24 hr indicated the presence of gold nanoparticles in the solution and the solution was stored at 4°C. And for the synthesis of the silver nanoparticles, a certain volume of the *Chenopodium murale* extract of 4-5 ml was added to 100 ml AgNO₃ solution and the volume was adjusted with deionized water. The final concentration was 2.3 mM AgNO₃. The reduction process Ag⁺ to Ag⁰ nanoparticles was followed by the color change of the solution after 24 hr indicated the presence of silver nanoparticles in the solution, temperature and pH and time of reaction was constant and improve prepared nanoparticles by different technics such as UV/Vis., TEM and XRD where confirmed preparation of silver and gold nanoparticles

3. Results and Discussions
3.1. AC Conductivity

The AC conductivity of the samples with frequency at different temperature in the range 303–413 K and were calculated by:

\[ \sigma = \frac{L}{R A} \]  

where \( A \) is cross-sectional area of the electrode (cm\(^2\)), \( L \) is thickness (cm) of samples and \( R \) is the resistance bulk.

Electrical parameters (dielectric constant, dielectric loss and loss tangent (\( \tan \delta \))) and conductivity of PVA/PVP nanocomposite were obtained at a frequency range from 0.5 kHz–5 MHz and a temperature range from 303–413 K. The measurements were obtained from resistivity and capacitance (C). Was calculated of the permittivity by relation [10]:

\[ \varepsilon' = \frac{Cd}{\varepsilon_0 A} \]  

where \( C \) is the capacitance, \( d \) is the thickness of samples and \( A \) the area of electrode cross-sectional and \( \varepsilon_0 \) is permittivity of free space (\( \varepsilon_0 = 8.85 \times 10^{-12} \) F/m). The dielectric loss (\( \varepsilon'' \)) can be determined by [11]:

\[ \varepsilon'' = \frac{\sigma}{\omega \varepsilon_0} \]  

where \( \omega \) is the angular frequency and \( \sigma \) the conductivity. The variation of loss tangent (\( \tan \delta \)) with the frequency of the examined films at room temperatures. Was calculated the variation of loss tangent (\( \tan \delta \)) from an equation [12]:

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} \]  

where \( \varepsilon' \) is the real dielectric constant and \( \varepsilon'' \) is the imaginary dielectric constant.

3.1.1. Electrical studies

The AC electrical properties of pure PVA/PVP blend, PVA/PVP blend embedded of Au NPs/Ag NPs nanocomposite have been studied the measurements were loaded out in the parallel circuit mode. The temperature and frequency were performed to measurements in range of 303–413 K and 0.5 kHz–5 MHz, respectively.

The AC electrical arising from the motion of the carrier charges through the polymer chains and nanoparticles. Parameters AC conductivity such as capacitance (C), Resistance (R), conductance (G) and dissipation factor dielectric loss tangent (\( \tan \delta \)) of the nanocomposite samples were measured. Figure (1-a) show the variation in the value of the AC conductivity of samples with a frequency at different temperature in the range 303–413 K and were calculated by using equation (1).

The variation of the AC electrical as a function of frequency. Figure (1-a) shows of AC conductivities of pure PVA/PVP blend samples were a behavior of dependence of the frequency as a function of frequency due to the polymer nature of an insulating material. In this figure, the AC conductivities was a small increase in the frequency range 50 Hz to \( 10^3 \) Hz and occur significantly improves in the range \( 10^3 \) Hz to 1 MHz after this frequencies conductivity value was constant and the
AC electrical increased with increasing temperature. Increases AC conductivity with the temperatures may be related to that the of could be related to that acquired more ions kinetic energy by thermally activated hopping of a carriers charge [12].

Figure 1: log sigma S cm$^{-1}$ and tan (δ) verses Log f (Hz) and ε' and ε'' for pure PVA/PVP blend

Figure (2-a) show of AC electrical conductivity for nanocomposite PVA/PVP/Ag NPs are observed, the conductivity changes with frequency and occur increase of conductivity at doped (Ag$_{100}$) NPs within polymer blend as show in Figure (2-a) and was observed that the nanocomposite shows higher AC conductivity at higher frequencies 4 MHz of the sample embedded of 50% mixed nanoparticles (Ag NPs/Au NPs) as show in Figure (3-a) and show enhancement of values of conductivity with increasing frequency at doped (Ag$_{50}$ Au$_{50}$).
Figure 2: log sigma S cm\(^{-1}\) and tan (\(\delta\)) verses Log f (Hz) and \(\varepsilon'\) and \(\varepsilon''\) for pure PVA/PVP/Ag\(_{100}\)
Au_{100} was show in Figure (4-a) we noticed more increase of value conductivity according of percolation theory \cite{10} because impurity and electronic contribution arise from the presences of small nanoparticles (Ag NPs, Au NPs) was additional to polymer matrix. At lower frequencies might be the charge carriers it is less number and which have high relaxations high time because energy higher barriers and respond in the low frequency regime. However, with high frequency the charge carriers showed higher conductivity at higher frequencies \cite{13}. The nanocomposite observed that exhibit increasing of AC conductivity due to an addition of Ag NPs/Au NPs to polymer matrix PVA/PVP blend, the value of conductivity was increased several orders (several order). Value conductivity of PVA/PVP nanocomposite may depend on the microscopic and the macroscopic conductivity. The microscopic conductivity depends on the doping level of the nanoparticle and length of the conjugation, whereas the macroscopic conductivity depends on the in homogeneities in nanocomposite.
**Figure 4**: log sigma S cm$^{-1}$ and tan (δ) verses Log f (Hz) and ε' and ε'' dash for pure PVA/PVP/Au$_{100}$

This type trend has been observed in the polymer conducting and may be attributed to the polarization of carrier charges and may be also because the existence of the interface nano-trapping states effectively interacting with a polaronic state [14], the values of Log(σ$_{ac}$) s cm$^{-1}$ with content of nanoparticles was recorded in table (2) . In general, in the semiconductor AC conductivity has been demonstrated in term of approach pairs. In this approach, in pairs consist two localized state between which the carrier electronic moves back and forth with a particular relaxation time. AC conductivity is a summation of the contribution from all pairs [15].
Table 2: Values of the Log ($\sigma_{ac}$) for pure PVA/PVP and blend doped different content of Ag and Au nanoparticles at constant temperature and frequency

<table>
<thead>
<tr>
<th>Samples</th>
<th>Log($\sigma_{ac}$) s cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA/PVP</td>
<td>-11.50</td>
</tr>
<tr>
<td>Ag$<em>{100}$ Au$</em>{00}$</td>
<td>-8.50</td>
</tr>
<tr>
<td>Ag$<em>{75}$ Au$</em>{25}$</td>
<td>-8.90</td>
</tr>
<tr>
<td>Ag$<em>{50}$ Au$</em>{50}$</td>
<td>-8.70</td>
</tr>
<tr>
<td>Ag$<em>{25}$ Au$</em>{75}$</td>
<td>-9.10</td>
</tr>
<tr>
<td>Au$<em>{100}$ Ag$</em>{00}$</td>
<td>-8.50</td>
</tr>
</tbody>
</table>

3.1.2. Dielectric studies

Electrical parameters (dielectric constant, dielectric loss and loss tangent (tan $\delta$)) and conductivity of PVA/PVP nanocomposite were obtained at a frequency range from 50 Hz–5 MHz and a temperature range from 303–413 K. The measurements were obtained from resistivity and capacitance (C), the permittivity was calculated using equation (2) and dielectric loss ($\varepsilon''$) was determined by using equation (3). Figure (1-c) to Figures (4-c) shows the dielectric constant ($\varepsilon'$) depends on the frequency of pure blend PVA/PVP and blend doped different concentration of Ag NPs/Au NPs the dielectric constant was decreased with increases frequency and increases with increasing temperatures for all samples because direction of dipoles in polymer matrix to orient them in direction of the applied field.

The trend of permittivity decreasing seems at high frequencies, not sharp (stable nearly) as compared with lower frequency. This trend may be due to dipoles orientation, causing to rotate of dipoles at higher frequencies and at lower frequencies the permittivity value is high due to an interfacial effect of the samples and an effect of electrode [12][16]. Behind variation of the physics these can be shown depending on the fact that, in the materials polar the initial value of dielectric constant is high, but an increase of the frequency the value of dielectric constant decreasing [17]. Generally, the dielectric constant variations with the temperatures depend on the type of polymers. For examples in polar polymers the dielectric constant increases with increasing temperature while for the case of the nonpolar polymers the dielectric constant is independent on the temperature [18]. This may have corresponded to greater freedom movement of the chains molecular at high temperatures [19], causes increases the polarization is increased the dielectric constant with increasing the temperatures [20].

Variation of the dielectric loss ($\varepsilon''$) with the frequency is shown in Figure (1-d) to Figure (4-d). The type of variation is seen to be similar to that of the dielectric constant. Decreasing in the part of imaginary of dielectric constant is obviously more in comparison to the real of dielectric permittivity. The dielectric loss ($\varepsilon''$) gradually increases with increasing of content Ag NPs/Au NPs within the
polymeric matrix was indicated that the higher carrying of charges ability of loaded samples compared to pure PVA/PVP blend sample. Since the Ag, Au nanoparticles and charge carriers are bounded and needs more time for migration and accumulation at the interfaces.

The value larger of the dielectric loss (ε″) was shown at low the frequency because of movement of charge in the polymer matrix. The maximum value of the dielectric loss in the samples embedded of mixed (Ag NPs/Au NPs) was understood in the expression of the electrical conductivity.

In general, the mobile of the charge (polarons and or bipolarons) that belong to conducting polymer and increase free charges with increases nanoparticles reason influence low value of dielectric loss at high frequency [16]. Figure (1-b) to Figure (4-b) show the variations of the loss tangent (tan δ) with the frequency of examined films at room temperature and was calculated the loss tangent (tan δ) from equation (4).

The figure shows decreases of loss tangent (tan δ) for all samples with increases of the frequency. The high value of the loss tangent (tan δ) was observed at low frequency in all samples and increase the tan δ with increases of the nanoparticles concentration is expecting due to increases the conductivity with increases in Ag/Au nanoparticles within polymer matrix [11][12].

The decrease of the tan δ with increases of frequency corresponds to the fact that the hopping frequency of carriers charge cannot follow the change of external field applied of electric behind a limit of frequency certain [21] and may be because the decreases value of R with the temperatures. Generally, behavior of electrical conductivity for the films was discussion, and an increases of AC conductivity with increasing the frequency because a molecules start bridging gap separated two localized state [22].

The increase of the electrical conductivity with increasing of temperatures because increases in mobility of the segmental of a polymeric chains. AC conductivity an increase with the frequency and the temperatures because hopping carriers charge in the localized states and excitations the carrier charge in the conduction band to the states. At higher frequency behavior was observed that there no phases transitions in polymer matrix and proposed that there is no dynamic changes conformational. The electric field where applied at low frequencies, forces carrier charges to deviation over large distance, with temperatures increased, an inclination to retain nearly constant values is recorded [23]. The frequency of critical was found to be dependence on the conductive of size, distribution and fraction of nano-material and the temperature [24]. Term the hopping refer to displacement unexpected of carrier charges from position to another position neighbors site and generally includes both jumps over a potential barrier and quantum tunneling mechanical [25]. The conductivity affected by the temperature because the hopping of carrier charge in the localized state and the excitation of carrier charge to states in conduction band.
3.1.3. Dielectric properties

The Figures show plot of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) depend on the frequency at different temperatures of PVA/PVP doped of mixed nanoparticles. From these figures both value of dielectric constant and dielectric loss decreases monotonically with increase the frequency and it reach values constant at the higher frequency.

The polar materials have this behavior due to initial value of the dielectric constant and dielectric loss is high, but with the frequency is raised the value to drop begins, could be due to dipole are not able to follow the field difference at higher frequency.

Figures show the variance of $\tan \delta$ with the frequency at different temperature. From this figure it is clear that the $\tan \delta$ slightly increases with temperatures, and decrease with the frequency. The higher value of $\tan \delta$ that occurs at lower frequency because an accumulation of free charges at the interface between the samples and the electrode. At higher frequencies, the ionization polar because the accumulations of charges decrease leading to decrease in $\tan \delta$ value.

According to this model was suggested that tunneling mechanical model, $s$ was nearly equal 0.7 and shown independence and variation with temperatures. The barrier correlated hopping (CBH) model in this samples and characterize carriers charge hops between sites over the potential barrier separating them. According this model, value of exponent, $s$, it is predict to increases with decreasing temperatures tend toward unity as temperatures approach to zero Kelvin. From obtained experimentally results, the variation of frequency exponent, $s$, as a function of temperatures is shown in Figure (5-a,b). It is obviously that values of exponent, $s$, increasing with decreasing temperatures and approach 0.7 at 303 K. This result indicate that the correlated barrier hopping model (CBH) in the samples prepared [25].

**Figure (5-a, b):** Dependence of the frequency exponent, $s$, dependence on temperature for (a) pure PVA/PVP and b) PVA/PVP- doped Ag$_{50}$ Au$_{50}$.
3.2. Scanning Electron Microscopy (SEM)

SEM is almost used to study the surface morphology in the samples prepared and embedded by the different content of silver and gold nanoparticles. Figure (6) shows micrographs of SEM for the surface topography of pure PVA/PVP blend and blend doped of mixed nanoparticles (Ag/Au) at magnification 5000 times. Scanning electron micrograph suggests that the structure morphology depends on the doping level of Au NPs/Ag NPs. From Figure (6), the micrographs of pure PVA/PVP blend and blend doped of Au NPs/Ag NPs.

From figure 5, pure PVP/PVP has a smooth surface and occur homogeneously between tow polymer PVA/PVP and nanoparticles additional, after additional of Ag Ns and Au NPs to the PVA/PVP polymer blend was the change of surface morphology from smooth to roughness, as shown in Figure (6). A continuous injection of Ag NPs and Au NPs within the polymer matrix leads to appear small spots on the surface, where they are completely doping of Ag NPs/Au NPs and becomes more roughness.

The rough morphology surface of nanocomposite samples is clear indication of nanoparticles it is an increase in the degree of the amorphosity (disordering for polymer chains)/decreases of the degree of crystalline for PVA/PVP pure blend after additional of Ag NPs/Au NPs. This is because the increase of the cross-linking with polymer chains and Ag NPs/Au NPs and increasing of the disordering. On the other hand, this originates from random separation and Ag NPs and Au NPs distribution in the polymer matrix may be present topological disordered in the electrolyte, which make more amorphous phases.

Figure (6) shows bright spot the existence of spots indicated occur change on the morphology surface of a samples prepared and desperation of silver and gold nanoparticles within the polymer blend, interfaces of a polymer was increasing with increases the NPs content this means complexation/miscibility between PVA/PVP and Ag NPs/Au NPs.

The enhancement in porosity has been attributed to the enhancement of free ion formation and hence to the enhancement of ionic conductivity. The occurred changes at the surface of filled samples indicated confirmed the interaction between the nanoparticles and the polymer matrix.
4. Conclusion

Films of PVA/PVP containing Au/Ag NPs were prepared by casting technique. The AC conductivity was improved by increasing of both temperature and frequency revealing the presence of charge carriers transported through the defect sites in chains of polymeric matrices and charge carrier reinforcement. The AC conductivity was enhanced after adding of Ag/Au due to conductive network between NPs and the PVA/PVP. Both permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were decreased with
increasing of frequency according to direction of dipole steward applied electric field. A thigh frequencies, the decreasing trend of permittivity and dielectric loss seems nearly stable attributed to dipoles orientation. The decrease of tan δ with increasing frequency attributed to the fact that the hopping frequency of charge carriers cannot follow the changes of the externally applied electric field. An increases of tan δ with increasing in content is expected because the conductivity increases with increase NPs.

References

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