Synthesis, and Study the Electrical Properties of Conductive (PVA:PANI)/CuI Blend Composite

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Abstract. PVA:PANI/CuI thin film composites were prepared by adding (CuI) nanoparticles to the blend of the poly vinyl alcohol and conductive polyaniline with various concentrations (0, 2, 4, 6, and 8% wt) using the casting method technique on glass substrate at room temperature. The type, concentration of charge carriers, and Hall mobility (μH) had estimated from Hall measurement and shown that the polymer thin films before additive of CuI nanoparticles were positive Hall coefficient (P-type). While the polymer thin films for all concentration of CuI nanoparticles have negative Hall coefficient (n-type) except of sample with concentration 6 %wt was remained positive Hall coefficient (P-type). In D.C measurement, increasing of temperature value leads to reduce the electrical resistance, also the D.C conductivity of the thin film composites rises with increasing additive concentration of CuI nanoparticles. The activation energy values for PVA:PANI polymer blend composites decreased when the concentration of CuI nanoparticles increased. Alternating electrical conductivity (σ_a.c) increases when the frequency of all samples increases. While the alternating electrical conductivity (σ_a.c) remains constant at very low frequency.

Keywords: PVA, PANI, CuI, composites, Hall Effect.

1. Introduction

Now-a-days polymer blends play a key role in various areas due to their relatively lightweight, simply preparation methods and varied resulting properties. The interest in studying polymer blends has been extensively improved because their important industrial applications. The improved characteristics blends are produced by blending various polymers to combine their properties for certain purposes [1-4]. Using polymers is a noticeable method in manufacturing of semiconductors because polymer matrices enable process ability due to solubility, control the growth, and morphology of the nanoparticles [5]. The using of PVA as a good host polymer for alkali metal salt particles is advantageous due to its good charge storage capacity, excellent thermo-stability, high dielectric strength, water solubility and chemical resistance, and its electrical and optical properties depends on the dopant. However, PVA has been gained an interest due to its non-carcinogenic, biodegradable, non-toxic, biocompatible qualities, reduction ability of the secondary alcohol groups and wonderful film-forming properties and optical transparency [6-9].

Polyaniline (PANI) is a polymer with semi-flexible construction. It also naturally exists as part of mixed copolymer with polycrylonitrile and polypyrrroles. PANI can be classified into three forms which fully oxidized pernigraniline, fully reduced leucoemeraldine base (LB), and half-oxidized emerald dine
base (EB) [10]. The best steady and conductive form of PANI is Emeraldine which is called (emeraldine salt) [11, 12].

The ability of PANI as conducting polymer and an ion-exchange resin has involved significant interest due to its worthy combination of properties, such low cost, easily synthesis, diverse structure, thermal and radiation stability, and conducting properties. This leads to utilize it in various fields, such as corrosion protection, micro-electronics, sensors and electrodes for batteries [13]. Polyaniline can be converted to conductive by doping, in which the polymer is partially reduced or oxidized [14]. Other benefits of polyaniline is that its ability to be both melt and solution which leads to the compound that can be easily mixed with conventional polymers that's advantage to formulate polyaniline products into required shapes. Additionally, products containing of polyaniline compound can be simply disposed of without environmental risks [15, 16].

This current work aims to study the electrical properties of thin films prepared from PVA/PANI polymer blend composites before and after adding different concentrations of (CuI) nanoparticles using casting method technique. Moreover, effect of (CuI) nanoparticles concentration on these properties due to its importance nowadays.

2. Experimental part

Microscope glass slides have been utilized as the substrate during the deposition process. The substrates were firstly cleaned in ethanol solution, subsequently ultrasonically washed with distilled water. The polymers blend thin films of polyvinyl alcohol (PVA)-polyaniline (PANI), and copper iodide(CuI) nanoparticles were synthesized by using casting method technique. (1 g) of PVA and PANI were used to prepare the films by dissolving them in (30 ml) of distilled water, the weight percent (50wt% PVA and 50wt%PANI). The solution was stirred to achieve homogeneous solution at the constant temperature 325°K for 12 hours. On the other hand, CuI nanoparticles were dissolved in double distilled water in the same condition, and added to polymer blend with concentrations (2, 4, 6, and 8) wt%. The resulting solutions were casted to glass slides to get thin films of PVA:PANI and PVA:PANI/CuI, after that left over it for about 72 hr. After drying, the thin films were kept in vacuum desiccators until use. The samples were prepared with thickness range (0.15–0.2) μm, which were measured by digital micrometer.

In current study, the kind of charge carriers, concentration (N_H) and Hall mobility (μ_H), have expected from Hall Effect measurements. The thin film electrical resistivity (ρ_{dc}) was calculated using the following equation [17]:

\[
ρ_{dc} = \frac{RA}{L} \quad (1)
\]

The electrical conductivity (σ_{dc}) of the membrane can be found according to the equation:

\[
σ_{dc} = \frac{1}{\rho_{dc}} = \frac{L}{R_{wt}} \quad (2)
\]

Where: A= wt, is area of the cross-section of the movement of charges, as for; R resistance, L: The distance between the poles, w: pole width and t: thin film thickness.

3. Results and Discussion

3.1 Hall Effect Measurement

The Hall parameter, concentration of the charge carriers, type of carriers, and the hole transfer are calculated from the Hall measurements. Table 1 shows the difference between N_H, μ_H and R_H for polymer blend composites at a different concentration of CuI nanoparticles.

Hall measurements indicated that the polymer blend composite (PVA:PANI) was P-type, but after adding of CuI nanoparticles at different concentrations the thin films of polymer blend composites become
n-type, this is consistent with the researcher [18]. The electrons represent the charge carriers, except for the concentration 6% from CuI nanoparticles was n-type. The reason for this may be the non-diffusion of CuI nanoparticles at adding to PVA:PANI polymer blend to prepare the thin films. The mixing process helps us at prepare of polymer blend composites diffused the copper atoms in the crystal structures [19].

Table 1. The values of $N_H$, $\mu_H$ and $R_H$ for polymer blend composites at different concentration of CuI nanoparticles.

| PVA:PANI/CuI samples | $R_H$ cm$^{-2}$/c | $N_H$ cm$^{-3} \times 10^{12}$ | $\sigma_{dc}$ (\(\Omega \) cm)$^{-1}$ | $\mu_H$ cm$^2$/v.sec | Type |
|----------------------|------------------|-----------------------------|-----------------------------|------------------|------|
| CuI = 0%             | 5.807E+5         | 10.75                       | 2.926E-7                    | 1.699E-1         | p    |
| CuI = 2%             | -3.286E+6        | 1.9                         | 6.302E-7                    | 2.071E+0         | n    |
| CuI = 4%             | -1.659E+6        | 3.762                       | 2.419E-8                    | 4.014E-2         | n    |
| CuI = 6%             | 5.958E+3         | 10.48                       | 9.546E-6                    | 5.688E-4         | p    |
| CuI = 8%             | -3.483E+6        | 1.792                       | 1.394E-5                    | 4.855E+2         | n    |

3.2. D.C Electrical Conductivity ($\sigma_{dc}$)

Figure 1 shows the change in the electrical conductivity for PVA:PANI polymer blend composites with adding the CuI nanoparticles, this values from Table 2. CuI nanoparticles were added in different concentrations of (2, 4, 6, and 8) wt% at a temperature equal to 30°C.

The Figure 1 shows that the electrical conductivity increased with increasing the CuI nanoparticles concentration and this increase was due to rearrangement of CuI nanoparticles throughout the polymer blend composite [20]. This may be caused a decrease in the values of the optical energy gap with an increase of CuI nanoparticles ratio for thin films due to increase the density of local cases within the gap. That was due to movement of the charge carriers between nearby energy levels within the energy gap, and make of need less energy to navigate an electrical conduction, these results are correspond to the researcher [21].

Figure 2 shows the change of Ln ($\sigma$) as a function of the inverted temperature (1000/T) for (PVA:PANI) polymer blend composites before and after addition of CuI nanoparticles with different concentrations. From this Figure, the Ln ($\sigma$) decreased as a value of the inverted temperature (1000/T) increased for different concentrations of CuI nanoparticles in polymer blend composites. As in the case of semiconductor materials, an increase in the temperature would lead to a decrease in the resistance of the polymer blend thin films, and thus the DC electrical conductivity was increased.
Figure 1. Electrical conductivity change ($\sigma_{d.c}$) at room temperature as a function of change in CuI nanoparticles concentration for thin films of (PVA:PANI/CuI) polymer blend composites (the values from Table (2)).

Figure 2. $\ln(\sigma)$ as a function of the thin films temperature for (PVA:PANI/CuI) polymer blend composites at different concentrations from CuI nanoparticles (the values from Table (2)).
3.3. The Activation Energy of Composites (\(E_a\))

Figure 3 shows the activation energy for thin films of PVA:PANI polymer blend composites before and after addition of CuI nanoparticles with different concentrations. This Figure shows that there were two values for activation energy, the electrical conduction occurred with two electronic transmission mechanisms at low and high temperatures. The first mechanism in the range of temperature (303-353 °K) in which the first activation energy \(E_{a1}\) was calculated, and the Conduction was done by hopping and tunneling between local levels within the forbidden energy gap. Adding different concentrations from CuI nanoparticles creates local energy levels in the forbidden energy gap, which was worked as traps for moving companies to move between these levels [22].

As for high temperature (\(T > 353 \text{ °K}\)), where the second activation energy (\(E_{a2}\)) was calculated. The conductivity occurs between the local levels above the valence band and under the conductive band or between the local and extended levels. The transfer was carried out by moving the carriers of the charges to levels up and down the kinetic edge through stimulation or thermal excitation.

![Figure 3. The activation energy for thin films of PVA:PANI polymer blend composites at different concentrations of CuI nanoparticles.](image)

Figure 3 shows that the activation energy values for PVA:PANI polymer blend composites decreased when the concentration of CuI increased. That was due to the increase of vector charges represented by the positive and negative ions at adding CuI nanoparticles to PVA:PANI polymer blend composites [23].
Table 2. the activation energy values \((E_a1, E_a2)\) and the electrical conductivity values \(\sigma_{d.c}\) when adding the CuI nanoparticles at different concentration.

| PVA:PANI/CuI Samples | \(E_{a1}\) (eV) at temperature range (303-353) °K | \(E_{a2}\) (eV) at temperature range (353-433) °K | \(\sigma_{d.c}\) (Ω\(^{-1}\).cm\(^{-1}\)) |
|-----------------------|-----------------------------------------------|-----------------------------------------------|------------------------|
| CuI = 0%              | 0.266                                         | 0.513                                         | 2.38E-05               |
| CuI = 2%              | 0.233                                         | 0.437                                         | 2.96E-05               |
| CuI = 4%              | 0.267                                         | 0.417                                         | 3.81E-05               |
| CuI = 6%              | 0.196                                         | 0.375                                         | 4.30E-05               |
| CuI = 8%              | 0.180                                         | 0.352                                         | 5.23E-05               |

By observing the Table 2 the inverse relationship between D.C electrical conductivity and activation energies \((E_a1 \text{ and } E_a2)\) is presented. In addition, it was noted that D.C electrical conductivity increased with activation energies decreased when the concentration of CuI nanoparticles increased in polymer blend composites. That may be due to the association of CuI atoms with atoms of the original material and compensatory to occupy the structural gaps within the polymer blend composites. This leads to the saturation of the bonds as well as reducing the size of the structural gaps. That may be due to change in the polymeric overlay chain due to the concentration of the CuI nanoparticles when added causing an increase in randomness and position levels. This is in turn caused create new-doped levels within the energy gap and thus reduced activation energy values and increased of D.C electrical conductivity [23].

The values of the activation energies \((E_a1 \text{ and } E_a2)\) decreased when the concentration of the added vaccination material increased, this results in line with the researcher's results [24].

3.4. A.C Electrical Conductivity \((\sigma_{a.c})\)
Alternating electrical conductivity \((\sigma_{a.c})\) measurements were made as a function of A.C field within the range of \((100 - 2\times10^5)\) Hz. Figure 4 represents the relationship between \(\ln(\sigma)\) as a function of the change in the frequency \(\ln(\omega)\) for thin films PVA:PANI polymer blend composites with different concentrations of CuI nanoparticles, and the effect of each concentration.

For all samples, Figure 4 shows that the conductivity of \((\sigma_{a.c})\) increased with increasing the frequency. This was due to the low-frequency, and polarization charge space as well as the movement of charge carriers mediated by hopes, there was little increase in electrical conductivity at high frequencies; this was due to the polarization charge space at low frequencies as well as the movement of the charge carriers by jumping processes. The increase in electrical conductivity was low at high frequencies. The reason for this was the electronic polarization and charge carriers that leave the hopping processes [25].
The electrical conductivity increased by increasing the CuI nanoparticles concentrations in polymer blend composites. This was due to increase in charge carriers, and the formation of a chain within the polymer composite [26]. The increase in A.C electrical conductivity with concentration leads to the increase of CuI nanoparticles within polymer blend composites is correspond to the results of researcher [27].

3.5. The Dielectric Constant ($\varepsilon_\infty$)

Figure 5 shows that adding CuI nanoparticles to polymer blend composites effects the dielectric constant at room temperature. The dielectric constant was decreased with the increase of CuI concentration within polymer blend composites. This decrease in dielectric constant can be explained by forming of a continuous CuI path inside PVA:PANI/CuI polymer blend composites [28].

In Figure 5, the value of dielectric constant is reduced with increasing the projected field frequency. The increase in frequencies was the result of a reduction in the polarization charge space (Internal polarization) relative to total polarization. Which was become a region or an area of polarized charges of the type that contributed to polarization in low frequencies. This contribution to polarization decreases with the increase of frequency that leads to a decrease in the value of the dielectric constant for all samples with increased field frequency. When the frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly. Therefore, their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation stopped, so $\varepsilon_\infty$ decreases at a higher frequency approaching a constant value due to the interfacial polarization.

This because the mass of the ion was greater than the mass of the electron. The response of electrons to higher frequencies in the field of vibrations of a lower electron mass is presented. That was why it makes
polarization a kind of electronic polarization, which is evident at higher frequencies. This makes the
dielectric constant fixed for all samples; these results were in accordance with what was published by the
researcher [29].

![Figure 5](image.png)

**Figure 5.** The relationship between the dielectric constant ($\varepsilon_1$) as a function of change in Ln ($\omega$).

### 3.6. Dielectric Loss ($\varepsilon_2$)

Figure 6 shows the isolation loss for thin films of PVA:PANI polymer blend composites as a function of
the frequency change before and after adding of CuI nanoparticles with different concentrations. This
Figure shows that the insulation loss decreased with the increase of frequency due to a decrease in the
polarization charge. It also shows that the value of the dielectric constant increased with increase of CuI
nanoparticle concentrations within polymer blend composites. This was because of the increase in the
mobile charge carriers within polymer blend composites, and this corresponds to what the researcher
published [27].

![Figure 6](image2.png)
4. Conclusion

PVA:PANI polymer blend composites were successfully prepared and using the CuI nanoparticles to add for polymer blend to prepare thin films by casting method. From the obtained results and discussion, one can conclude the following:

1- The electrical conductivity increased with raising the CuI nanoparticles concentration and this increase was due to rearrangement of CuI nanoparticles throughout the polymer blend composite.

2- Increasing the temperature would lead to decrease the resistance of the polymer blend thin films, and thus the DC electrical conductivity can be increase.

3- The activation energy for all polymer blend composites was decreased with increasing of concentration.

4- A.C electrical conductivity ($\sigma_{a.c}$)was increased with frequency increasing and CuI nanoparticles concentration.

5- Dielectric constant and dielectric loss decrease when increasing of frequency.

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