

Dielectric Performance of PVA/PPy Incorporating Copper Oxide Nanocomposite

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Abstract:- In this study, the films of PVA and CuO nanocomposite were synthesized using a simple solution casting technique. The produced films' optical and structural characteristics were thoroughly investigated. Copper oxide nanoparticles in 0.1–0.4 weight percent concentrations were implanted in the PVA film. Copper oxide nanoparticles were incorporated in polypyrrole and PVA host matrix to prepared films, as evidenced by X-ray diffraction (XRD) tests that revealed their existence in the PVA film without the emergence of extra impurity peaks. XRD tests verified the findings, which showed that the copper oxide nanoparticles belong to the monoclinic phase. The production of semicrystalline PVA polymer was reflected by the appearance of a peak at $2\theta = 19.4^\circ$. The produced nanoparticles had an average crystallite size of roughly 0.52 nm. FTIR analysis was also employed to confirm the vibrational bands of the films. The findings also demonstrated that when the concentration of CuO nanoparticles increased, the dielectric characteristics improved because of the creation of polarization and an increase in the density of states. Additionally, it was noted that the development of charge transfer complexes caused the optical conductivity of the composite films to increase as the concentration of nanoparticles.

Keywords:- CuO Nanoparticles, PVA, XRD, Dielectric, Conductivity.

I. INTRODUCTION

Because polymers have better optical and electrical qualities than traditional metals and alloys, materials experts from all around the world have recently been interested in them. The inclusion of nanoparticles is effectively facilitated by the polymer matrix, and the creation of nanocomposites increases the chemical and structural stability of the host polymeric material, hence improving its mechanical, optical, and electrical properties [1–10]. Because of their low cost, low density, great mechanical stability, and outstanding transparency, polymer nanocomposites are perfect hybrid materials for a variety of applications [11–15]. Because of their high electron affinity and ease of interaction with the surface groups of nanoparticles, polymers help create

homogeneous nanocomposites [16–20]. This work used polyvinyl alcohol (PVA) as a host matrix to include nanofillers. PVA's low density (1.36 g/cm³), high melting point (230 °C), and water solubility make it an excellent matrix for charge storage. It is suitable for a range of applications due to its strong dielectric strength [21–28]. PVA is also used in solar cells because of its long carbon chain and hydroxyl group, which encourage the creation of hydrogen bonds. Polymer nanocomposites make it simple to study band gap variations and the electrical structure of amorphous and semi-crystalline materials. A wide range of automotive and aerospace applications use thermoplastic polymers, like PP and PA, because of their superior mechanical qualities, ease of processing, and affordability. However, these polymers could not be employed as structural materials due to their limited energy absorption capacity and poor impact resistance [29–40]. It is well known that simple metal oxides, such as those of zinc, copper, magnesium, and cerium, can change the structural, optical, and electrical properties of polymers [41–50]. According to recent research, copper oxide (CuO) nanoparticles' superior photocatalytic qualities make them an appropriate nanofiller for polymer composites. It has been observed that the utilization of nanoparticles in nano-emulsions or as nano-fertilizers increases the availability of micronutrients to plants, especially in the seedling stage. This increase in nutrient availability encourages plant development and lessens the need for fertilizers that are hazardous to the environment and include chemicals. Even at low concentrations, copper oxide nanoparticles (CuO-NPs) have been shown to promote growth and dry biomass in a variety of plant species. In order to improve seed vigor and germination potential, this study postulates that applying CuO-NPs to *Lactuca sativa* seedlings will increase nutrient bioavailability to the roots and other plant components. [51–60]. CuO, a p-type semiconductor, is readily available and cost-effective, making it an ideal filler for nanocomposites. Its energy band gap ranges from 1.2 to 1.9 eV, and it possesses high dielectric permittivity and excellent insulating properties, making it suitable for various applications such as sensors, electrical, and optical devices [61–66]. Additionally, CuO demonstrates beneficial physical characteristics as photovoltaic, photoconductivity, spin dynamics, and superconductivity [67–73]. CuO nanoparticles have several

uses, such as solar cells, batteries, and gas sensors. CuO is far less expensive than silver oxide and can be combined with polymers to create nanocomposites with the appropriate physical characteristics. In order to break down organic molecules, metal oxides such as ZnO, CuO, Fe₂O₃, TiO₂, and SnO₂ have recently been used as photocatalysts [74–80]. CuO-based photocatalysts' high adsorption coefficient, broad surface area, and chemical stability make them useful for treating wastewater and eliminating organic contaminants [81–86]. Farwa Mushtaq et al. [87] looked at the use of different polyvinyl alcohol-based adsorbents, including fibers, films, composite particles, and gels, to treat wastewater generated by the textile sector. PVA/CuO nanocomposite films' electrical and structural characteristics were documented by Jammula Koteswara Rao et al. [88]. The effects of zinc, copper, and graphene oxide nanofillers on the dielectric constant, dielectric loss, and AC conductivity characteristics of PVA-based composites were examined by Muhammad Aslam et al. [89]. The optical characteristics of mixed polyvinyl alcohol (PVA) nanocomposites were investigated by Omed Gh. Abdullah et al. [90]. The structural and thermal characteristics of pure ZnO, CuO, and nanofiller-doped PVA nanocomposite films were examined by Muhammad Aslam et al. [91]. CuO nanoparticles and PVA/CuO nanocomposites were synthesized and characterized by Alabur Manjunath et al. [92]. Using environmentally benign techniques, such as plant extracts like aloe vera, the authors of the current work created copper oxide nanoparticles and added them to the PVA matrix. The CuO nanoparticles had an average particle size of about 30 nm. The results of this study are innovative in comparison to earlier research since it presents green-synthesized CuO nanoparticles that are simple to manufacture in the lab. Along

with optical properties like direct band gap, optical dielectric constant, optical dielectric loss, and optical conductivity, the authors also examined the β -phase, functional groups, vibrational modes, and Raman spectral analysis. They also used a single oscillator model to estimate the optical dispersion parameters of pristine PVA and PVA/CuO nanocomposites.

II. EXPERIMENTAL

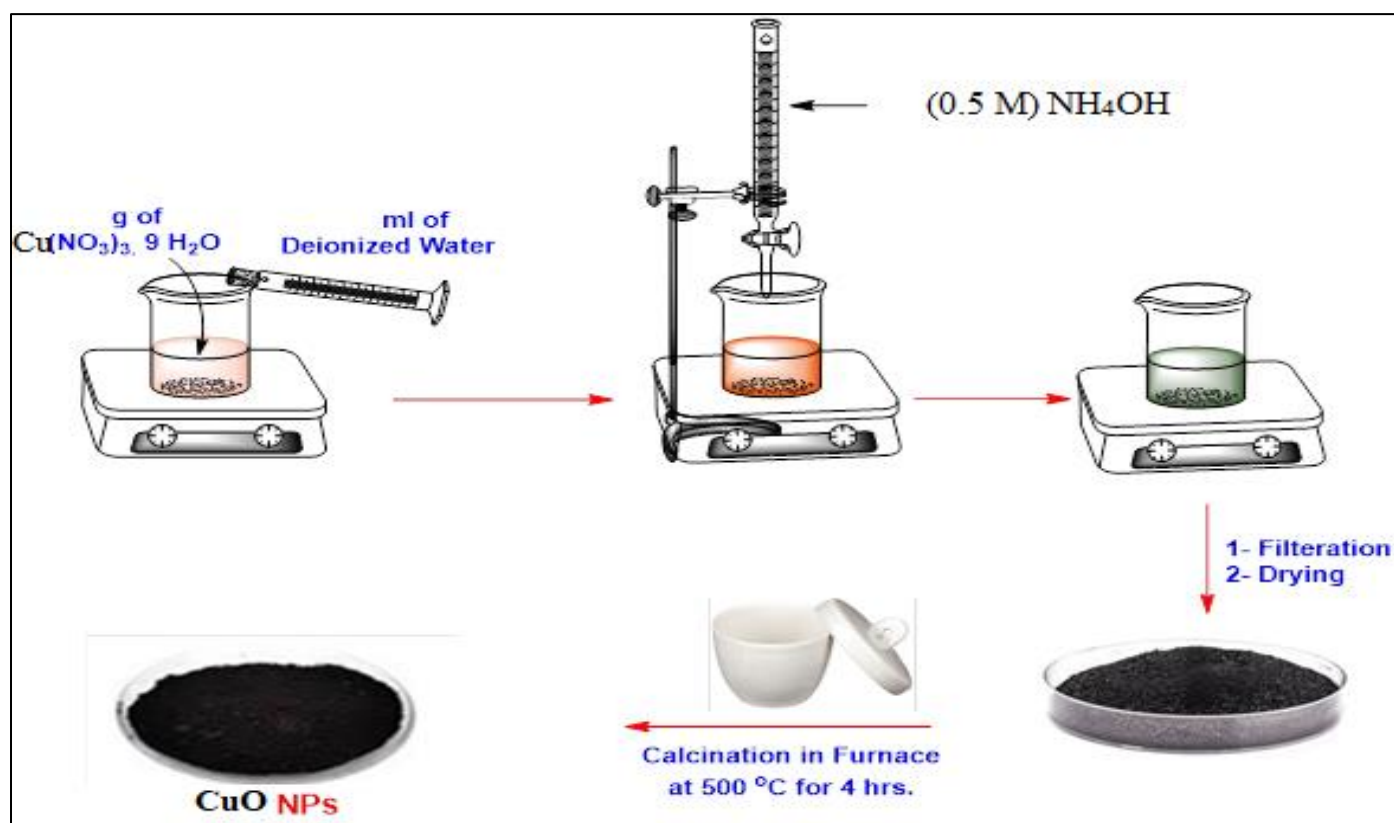
➤ Chemicals:

The study utilized solvents and chemicals obtained from different suppliers, including Riedel-de Haën, Sigma-Aldrich. These substances were used as received without undergoing any modification or purification.

➤ Procedures:

• Preparation of Copper Oxide Nanoparticles (CuO NPs)

A solution containing 1g of copper nitrate Cu(NO₃)₂(H₂O)₃ was prepared by dissolving it in 25 ml of distilled water. Subsequently, 3 ml of ethylene glycol (C₂H₆O₂) was added to the solution dropwise. Subsequently, the ammonia solution (0.5 M) NH₄OH was added at a frequency of one droplet per 30 seconds while stirring continuously at 60 °C. After adding three drops (24 ml) of the ammonia solution, a pH of 8 was obtained. The solution was then stirred for one hour and at 60 °C. Next, the solution underwent filtration to separate the desired substance, forming a precipitate. The precipitate was washed four times with distilled water and then air-dried. The solid was subsequently burned in a furnace at 500 °C. Scheme1.



Scheme (1): Schematic Diagram for the Preparation of CuO NPS

- *Preparation of Pyrrole Polymer*

(3 ml) of pyrrole was mixed with (20 ml) of HCl acid (0.5M) in an ice bath. The mixture was then dropped by (2M, 20 ml) ammonium persulfate (APS). The black precipitate formed was placed in the refrigerator for 24 h. The product was then filtered and washed several times until the solution became transparent (PH=7).

- *Preparation of Polyvinyl Alcohol (PVA)*

A (2% w/v) PVA solution was prepared by dissolving 2g of PVA in 100 ml of distilled water under continuous stirring for 3h at 80 °C.

- *Preparation of Dielectric Materials Film*

Separately, (0.01 g) of PPy was ultrasonicated with 5 mL of ethanol to obtain a homogeneous solution. Then it was mixed with (5 mL, 2%) of PVA solution under strong stirring for 2 h. After that, the mixture was poured into a glass mold. Finally, it was left for 36 h to dry at room temperature before

being taken for LCR measurement. The product was repeated with 0.01 g of CuO nanoparticles and after obtaining the result, several weights of it were taken (0.01, 0.02, 0.03, 0.04, 0.05) wt%) to find out which one is better.

III. RESULTS AND DISCUSSIONS

The FTIR of CuO is displayed in Figure 1. A peak at 3419 cm^{-1} wave number is associated with the O-H stretching of a hydroxyl group in the structure of copper oxide nanoparticles. A peak at 1612 cm^{-1} wave number is associated with the O-H bending of a hydroxyl group in the structure of a copper oxide nanoparticle. At 1376 cm^{-1} wave number, there is another peak connected to the C-O asymmetry in the copper oxide nanoparticle's structure. The C-O symmetry in the structure of the copper oxide nanoparticle is linked to the last peak, which is situated at wave number 1115 cm^{-1} . Finally, the peak is linked to the Cu-O bond and is situated at wave number 533 cm^{-1} . [93].

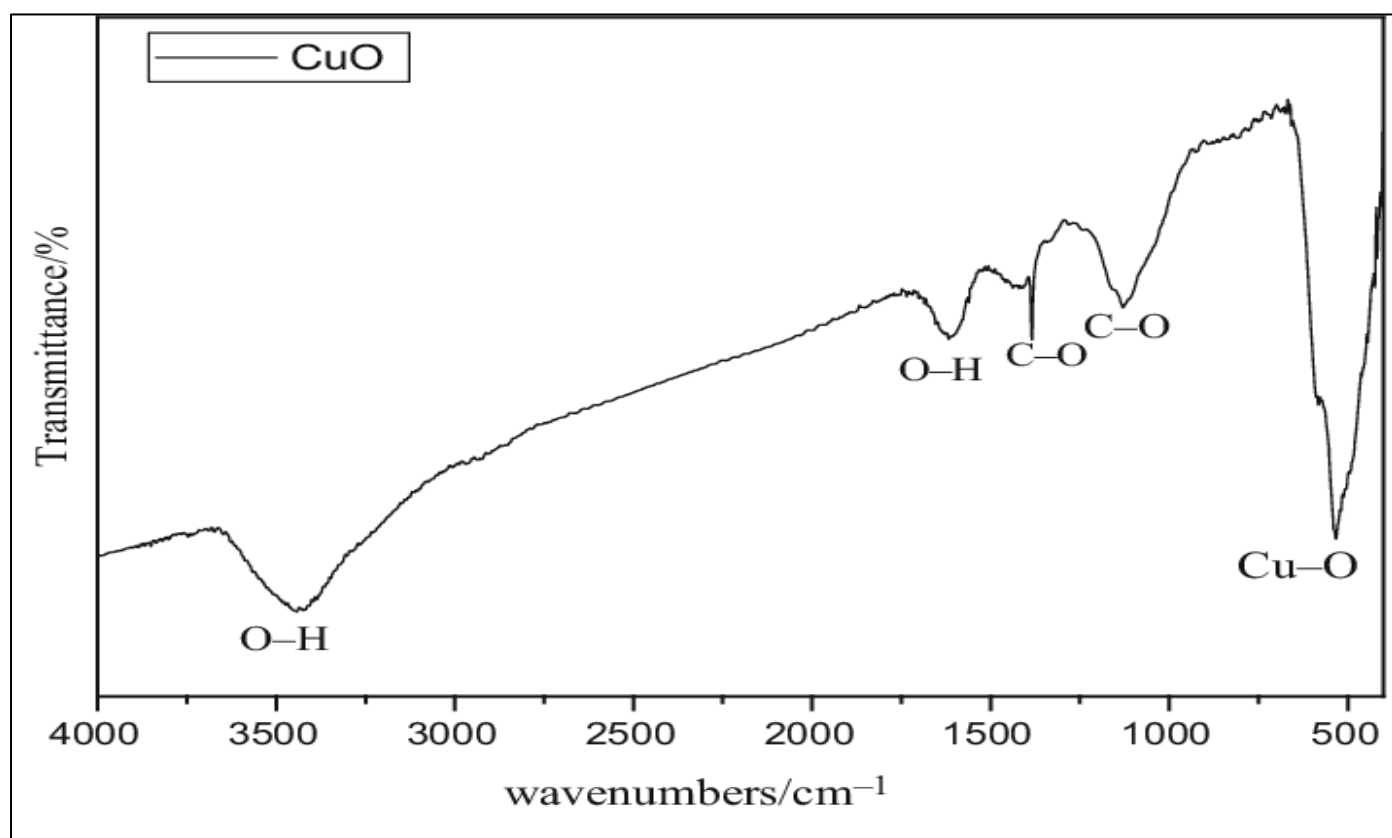


Fig 1 FTIR Spectrum of CuO after Calcination.

Figure 2 displays the XRD pattern of copper oxide nanoparticles produced using a straightforward chemical process. The synthesis of copper oxide with monoclinic symmetry with lattice constant $a = 4.683$, $b = 3.428$, and $c = 5.129\text{ Å}$ (JCPDS 80-1268) is confirmed by the appearance of XRD peaks at 2θ values of 32.53° , 35.63° , 38.74° , 48.83° , 53.56° , 58.36° , 61.51° , 65.85° , 66.42° , 68.11° , 72.34° , and

75.33° [94]. In the absence of any more addition, no extra peak resulting from the presence of any other phase was seen, indicating the creation of pure phase copper oxide nanoparticles. When Debye-Scherrer's formula was used to compute the average particle size of produced copper oxide nanoparticles, it was determined to be approximately 30 nm.

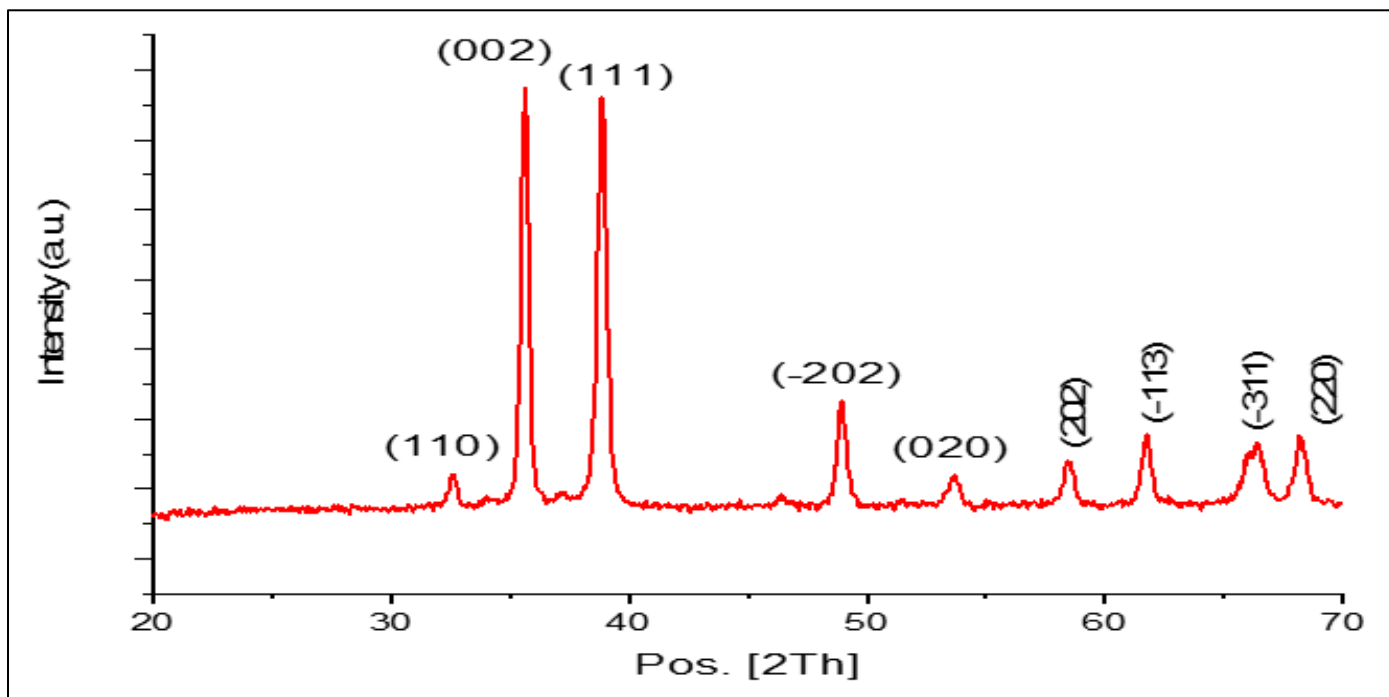


Fig 2 XRD of CuO Nanoparticles NPs

➤ *Scanning Electron Microscope (TEM):*

TEM examination was used to further establish the internal structure and to determine the particle size and shape accurately (Figure 3). The values for the average particle size

and interplanar spacing agreed closely with the XRD results. However, the crystalline character of the artificial copper oxide nanoparticles is confirmed by the SAED pattern.

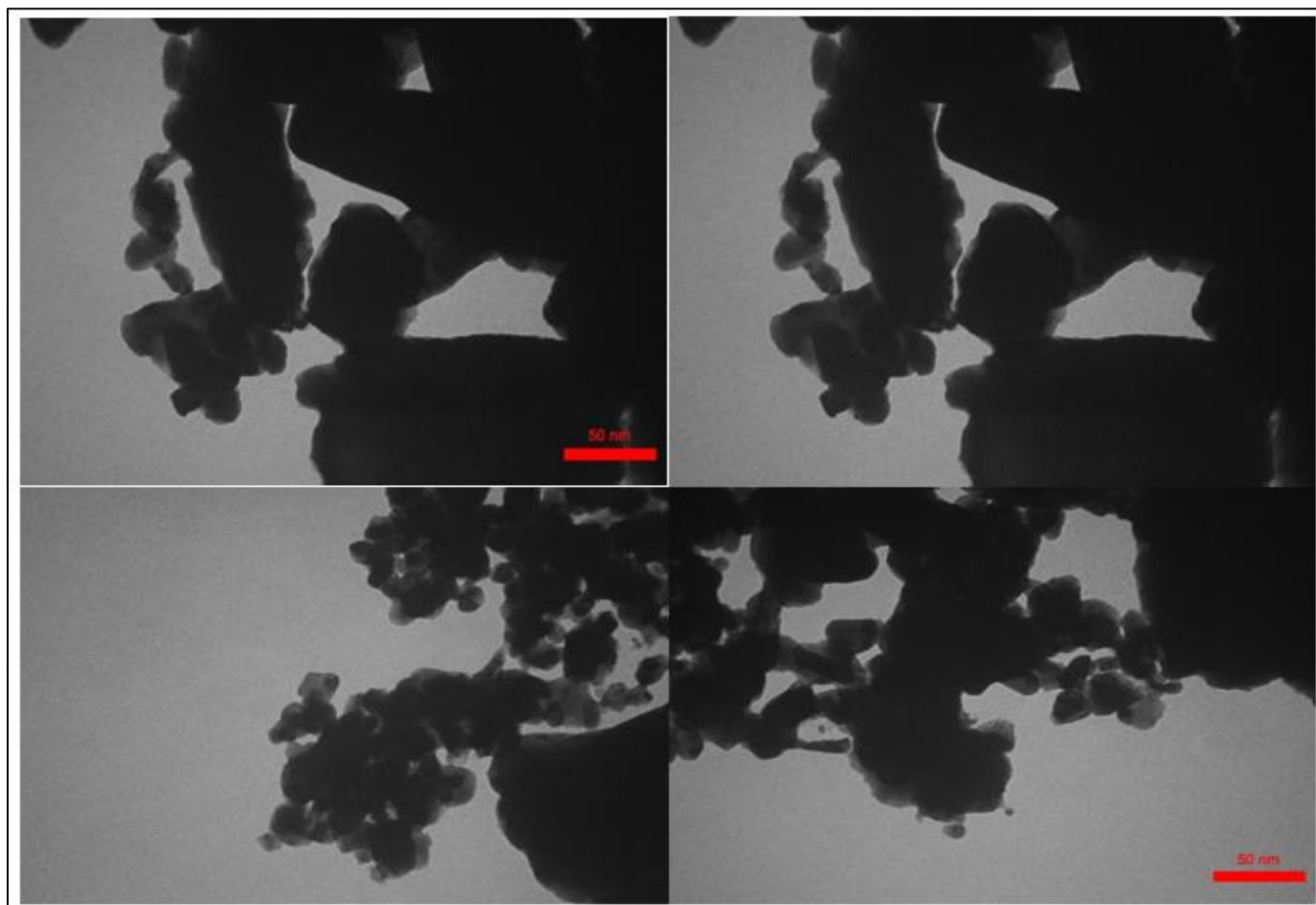


Fig 3 TEM of CuO Nanoparticles

➤ *Electrochemical Properties*• *Dielectric Constant*

Based on the connection, the dielectric constant was computed for pure PY, CuO, and Py-CuO membranes with weight ratios of 0.01–0.02, 0.03–0.04, and 0.05 weight percent at room temperature and in the frequency range of 50 Hz–5 MHz. Figure 4 shows that for all polymer composite membranes, the dielectric constant decreases slightly with increasing frequency. While dipolar groups in dielectric polymers can align themselves with the electric field at low frequencies, it is difficult for them to do so at large frequencies. At high frequencies, the time period is short and less than what molecules need to align themselves with the external field. In contrast to dipolar polarization, which takes a comparatively lengthy time in comparison to all

polarization, electronic polarization happens fairly quickly yet takes longer than ionic polarization. This could be the cause of the dielectric constant values decreasing as frequency increases, and the decrease in charge space polarization could also be a contributing factor. Additionally, the picture shows that the dielectric constant value at the same frequency rises as the weight percentage of the supporting material (CuO) grows. This increase in polarizability is often responsible for this dielectric constant value [95–98]. In addition to the heterogeneous system, which is caused by the accumulation of some vacuum charges in the interfaces, the presence of CuO also contributes to the increase in the dielectric constant value at the same frequency by increasing the weight ratio. This results in the formation of interfaces in the polymer mixture, which raises the number of dipoles per unit volume [99,100].

Table 1 The Relationship between Frequency and Dielectric Constant

Fr HZ	py	CuO	0.01	0.02	0.03	0.04	0.05
102089.8	50.05252	50.05252	70.15113	71.5118	60.75757	65.59096	122.119
510249	49.58257	49.58257	59.40509	68.74674	57.01162	62.12917	110.444
1.02E+06	49.42683	49.42683	57.10452	68.38881	56.96791	61.50348	107.515
1.53E+06	48.96234	48.96234	55.2739	67.26858	56.44877	60.87506	105.4931
2.04E+06	49.39951	49.39951	55.21925	67.21393	56.50342	60.90238	104.81
2.55E+06	49.1536	49.1536	54.3176	66.96803	56.17555	60.49254	104.2636
3.06E+06	49.78203	49.78203	54.18099	67.24126	56.58539	61.17561	104.81
3.57E+06	49.59077	49.59077	54.20831	67.56913	57.76027	61.03899	105.0559
4.08E+06	50.4651	50.4651	54.12634	67.48716	57.62365	60.82041	105.3565
4.59E+06	49.64541	49.64541	53.90776	67.78771	57.62365	60.90238	105.9029
5.00E+06	51.61265	51.61265	55.2739	69.48172	59.01711	61.83135	107.7609

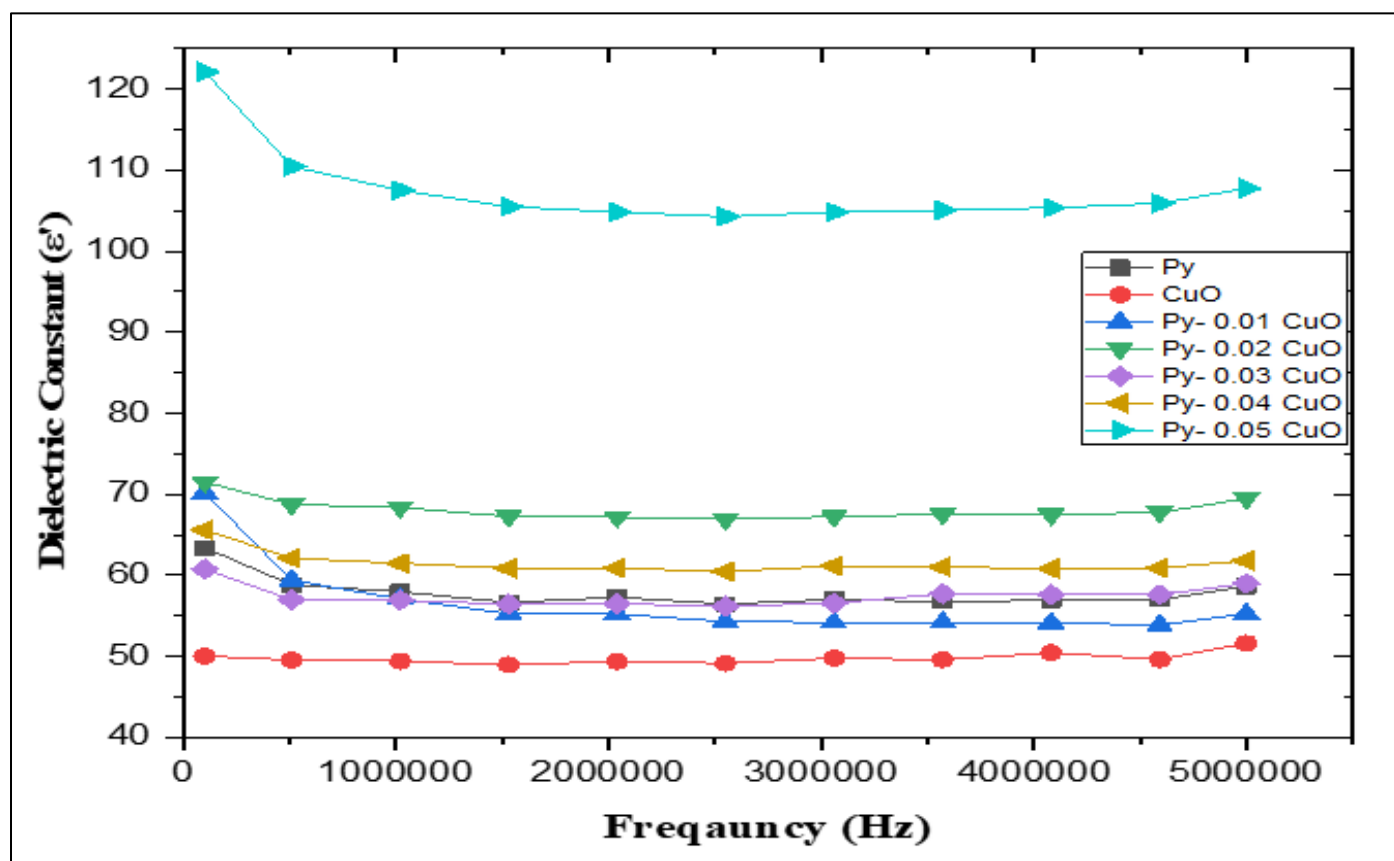


Fig 4 Dielectric Constant of CuO and CuO Doped Ppy

• Dissipation Factor

The dielectric loss factor is the ratio of the power loss in dielectric materials to the total power transferred through the dielectric, the energy dissipation in dielectric materials is directly proportional to the dielectric loss factor, so knowing the value of this factor is of great benefit in applications of polymer composite membranes, as the dielectric loss factor was calculated for pure PY, pure CuO and Py-CuO polymer composite membranes with weight ratios of (0.01, 0.02, 0.02, 0.03, 0.04, 0.05 wt%). The dielectric loss factor decreases with increasing frequency for all polymer blend membranes at room temperature and within the frequency range of 50 Hz to 5 MHz, as shown in Figure (5). It is also evident that the dielectric loss factor values are high at low frequencies and then start to decrease as the frequency of the applied electric field increases. This is because of the enhancement of charge carriers that occurs across the width of the electric charge

area, and the dielectric loss factor decreases at high frequencies until the electron energy equals the Fermi level. Another explanation for the frequency-dependent change in the dielectric loss factor is that the dipoles' energy is absorbed by the electric field in the system to overcome the resistance of the surrounding viscous materials during rotation. This absorbed energy decreases the amplitude of charge carriers moving between the boundaries as the frequency increases, meaning that the dipoles require more energy in the system to achieve relaxation, which results in a decrease in the dielectric loss factor. Additionally, the figure shows that as the weight percentage of the supporting material (CuO) grows, so does the dielectric loss factor value at the same frequency, and the percentage (0.05) of copper monoxide has the highest value, while the percentage (0.01) has the lowest. This is because the employing nanocrystals have more electrons, which raises the charge dipole and, in turn, increases electrical conductivity, which raises the value.

Table 2 Relationship between Dielectric Loss and Frequency

Fr HZ	py	CuO	0.01	0.02	0.03	0.04	0.05
102089.8	8.00525	0.84589	22.75703	4.2621	4.19835	3.8961	24.04523
510249	5.1194	1.55193	10.56817	3.32734	3.02162	3.55379	13.02134
1.02E+06	4.32544	1.85845	8.41721	3.13221	2.8313	3.29659	1.05E+01
1.53E+06	3.3147	1.038	6.8816	2.2535	2.09989	2.73938	9.13E+00
2.04E+06	2.76103	0.40508	6.02442	1.90215	1.72335	2.15594	8.16E+00
2.55E+06	2.94828	0.85036	5.70878	1.94207	1.70774	2.11119	7.93E+00
3.06E+06	2.69723	0.6621	5.81904	1.88276	1.53346	2.18397	7.53E+00
3.57E+06	2.43522	0.5455	4.85164	1.68923	1.91764	1.83727	7.56E+00
4.08E+06	2.16396	0.46933	4.64404	1.38349	1.33687	1.49618	7.41E+00
5.00E+06	0.90328	1.16128	3.21694	0.06253	0.51345	0.61213	6.41E+00

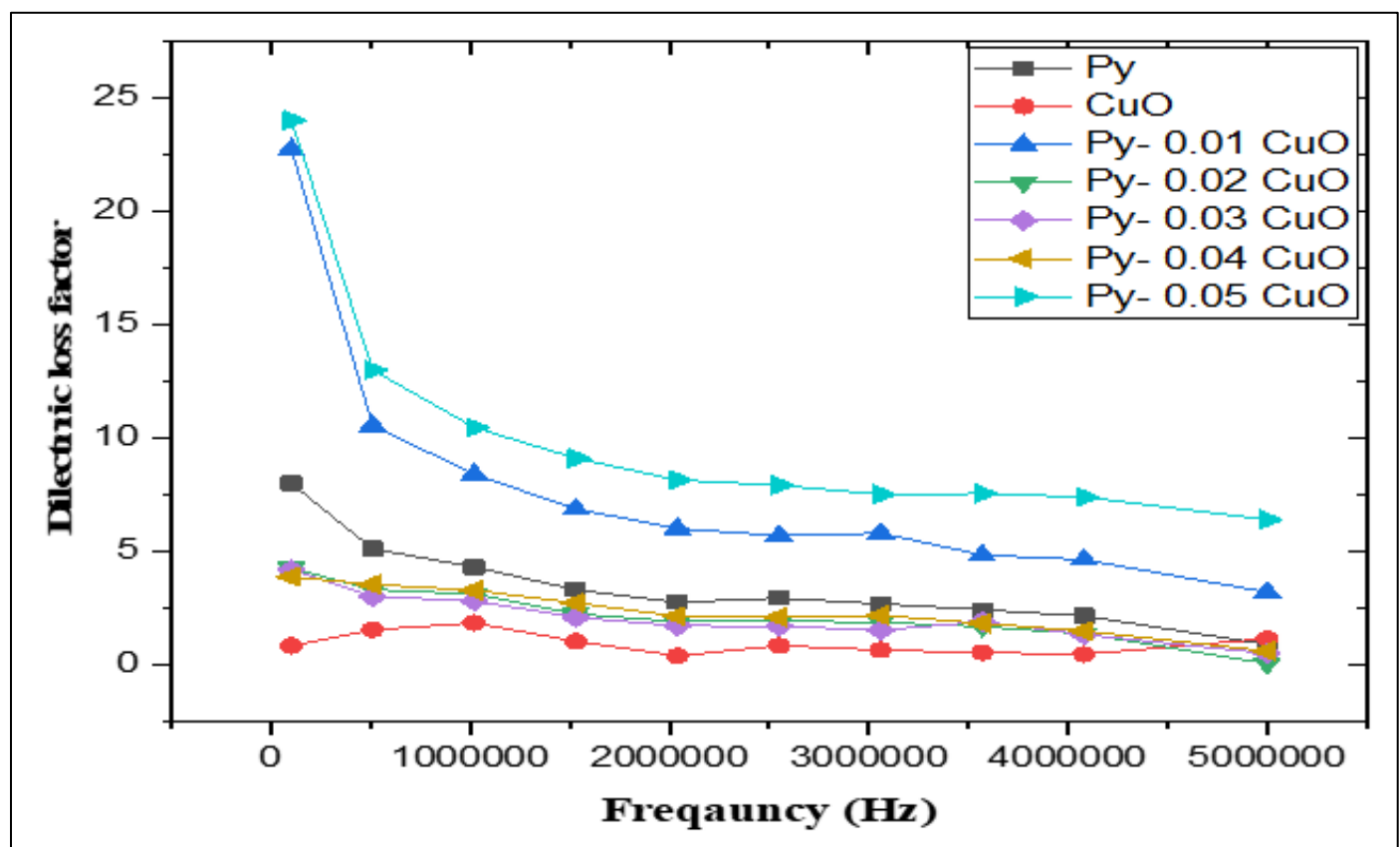


Fig 5 Dielectric Loss Constant of CuO and CuO Doped Ppy

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