Synthesis of (PVA-PVP: ZnO and Ag) Nanocomposite Films: Characterization and Antibacterial Application

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Abstract:

Polymer blend (PVA-PVP) and it's nanocomposites with constant ZnO and different ratios of Ag NPs films synthesized using solution cast technique. The obtained products were identified by X-ray diffraction (XRD), and field emission scanning electron microscope (FESEM). The development of more crystalline nanocomposite from the polymeric matrix was confirmed by XRD measurement, on the surface of the polymeric matrix. FESEM images revealed a good dispersion of ZnO and Ag NPs on the surface of the PVA-PVP films. The A.C electrical properties showed that the dielectric constant and dielectric loss for all films decreases with the increase of the electric field frequency, and that it's values increase with the increasing of the wt.% of Ag NPs. The antibacterial susceptibility test of synthesized NCs was made by agar disk diffusion method against two isolates of bacteria: gram - negative bacteria *Escherichia coli* and gram - positive bacteria *Staphylococcus aureus*. It results showed that the NCs films have a high antibacterial activity compared with antibiotic IMIPENEM 10mcg, best growth inhibition zone was observed with ratio 4wt.% of Ag (34.567±3.066) against *E. coli.*

Keywords: (PVA-PVP) films**,** ZnO and Ag NPs**,** A.C electrical properties, antibacterial activity.

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1. Introduction:

Several researchers have recently investigated PVA PVP polymer mixes with different nanofillers. Wound dressings, articular cartilage replacements, and membranes for high-energy electrochemical devices all employ PVA PVP mixes (Baraker and Lobo 2016; Ben Doudou *et al.* 2014; Kubo and Kadla 2003). The word

"nanotechnology" refers to the application of small quantities of material to processes such material separation, consolidation, and deformation by a single atom or molecule (Alkhayatt and Jaafer 2013). Polymer nanocomposite is a multicomponent system that contains minor elements (fillers) with a size of less than 100 nm in at least one dimension (Sadasivuni *et al*. 2016).As a new generation of antimicrobial agent, nano metal oxides have been shown to have antibacterial properties, and researchers have advised employing silver and zinc ions as excellent disinfectants against hospital pathogenic microorganisms (Reddy *et al*. 2007). Although scientists previously assumed that leftover metal ions may harm human health, tests revealed that the hazardous nature of ZnO NPs to different bacterial systems and human T cells is selective. (Blanc *et al.* 2005). These findings showed that ZnO nanoparticles might be effective as antibacterial nanomedicine agents in specific therapeutic dosage regimes (Reddy *et al*. 2007). The current work deals with the synthesis of nanocomposites (PVA-PVP/ ZnO and Ag) and the study of their structural and A.C electrical properties for antibacterial action.

2. Experimental part:

2.1 Materials

The polymers PVA (Molecular formula

$(CH_2CH(OH))_n$, Mol. wt. = 160,000 $g.mol^{-1}$) and PVP (Molecular formula $(C_6H_9NO)_n$, Mol. wt. = 60,000 $g.mol^{-1}$) were imported from Indi (Central Drug House, Ltd, Company). The additives nanomaterials were zinc oxide NPs ZnO (Mol. wt. = 81.408 $g.mol^{-1}$) is a white powder that is insoluble in water, and silver NPs Ag (20 nm - 30 nm) black powder that is poorly soluble in water and could be obtained from (Sky Spring Nanomaterials, lnc ,2935

West hollow Dr. Houston, TX 77082, Fax:281870-8002).

2.2 Purification of PVA-PVP and its NCs Films of nanocomposites blend (PVA-PVP) with ZnO and different wt.% of Ag NPs have been prepared by a simple solution casting method. It is expected that the strong hydrogen bond forming capacity of PVA will interact with PVP and thus offers a new polymer designated as (PVA- PVP) with improved properties such as the control of PVA porosity and super-molecular structure (Abdelrazek *et al*. 2010; Baraker and Lobo 2016). 0.8g of PVA was dissolving in 60 ml of deionized water. The solution was prepared by mixing with a magnetic stirrer for 1hr at room temperature, then continue for another hour under ~80°C to get a good mix, afterwards, it was added 0.2g of PVP and Stir enough to get a homogeneous solution, then the solution casted into Petri dishe and solvent is allowed to vaporize slowly at room temperature conditions for 144 h. The synthesized dried film is taken off from the Petri dishes and kept in vacuum desiccators. NCs films from PVA- PVP/ 5wt.% ZnO and different (1, 2, 3 and 4 wt.%) of Ag, was obtained according to the following: firstly, used the solid-state method for mixing the ZnO and Ag NPs alone, which include dissolving it by ethanol solvent with continuous grinding in a crucible ceramic for 90 min, then dried at 60˚C for 4 hr before adding it to the polymer solution. Mixture of the polymers were continuing as in previous steps interspersed with the use of ultrasonic for 15 mints to prevent any agglomeration even get a homogeneous solution. The casting film kept at RT conditions for 144 h to dry. The uniform thickness was (120±5) μm measured by Digital Vernier Caliper.

2.3 Application of (PVA-PVP/ ZnO and Ag) nanocomposites for antibacterial activity

2.3.1 The preparation of the bacterium inoculum

Four- five isolated colonies were selected from an 24hrs culture and diluted in Mueller Hinton broth to a turbidity like to 0.5 McFarland turbidity standard. The antibacterial susceptibility test of synthesized nanocomposites was made by agar disk diffusion method.

2.3.2 Agar disk diffusion method:

Antibacterial activity of synthesized nanocomposites was performed by agar disk diffusion method. 20 ml of sterilized Mueller Hinton agar was placed in Petri dishes. After media solidification, 0.1 ml of each bacterial isolates were spread on the surface of media, the Petri dishes were left for 5 minutes, then 6 mm diameter disk from each NCs were placed in each Petri dish. The polymer blend pure was considered as negative control, the Petri dishes then incubated at 37°C for 24hrs. The zones of inhibition were measured and expressed as millimeter in diameter, the experiment was performed in triplicate.

4. Results and discussion

4.1 X-ray diffraction (XRD) studies XRD is a common and non-destructive technique for the study of material crystallographic structures. PVA-PVP polymer blend and its nanocomposite films with 5wt.% ZnO and different ratios of (1, 2, 3 and 4) wt.% Ag NPs were characterized by XRD technique as shown in Fig. (1). The XRD pattern of the pure polymer blend film had an obvious diffraction peak centered at around 2θ=19.4464°-20.090° Bragg reflection. This strong peak corresponds to the (101) reflection, demonstrating the existence of crystalline PVA aggregates. The (101) diffraction can be explained by the interference effect between PVA macromolecules in the direction of intermolecular H bonds, or due the orthorhombic reflection of PVA polymer. At higher angles (especially at about 41°), some diffused peak displayed on a broader region can be observed showing the diffraction of pure water in the amorphous zone (Teodorescu, Bercea, and

Morariu 2019). Thus, it can be concluded that PVA has a semicrystalline nature with domains of structural order and disorder. The 2θ values and planes for crystalline wurtzite hexagonal structure ZnO were respectively 31.9012° (100), 34.533° (002), 36.393° (101), 47.66° (102), 56.684° (110), 62.937° (103), and 68.313° (112), with lattice constant of a = 3.244A° and c=5.157 A° , which are in close agreement with the values mentioned in the literature(Panchal et al. 2020)(Jassim and Hashim 2021), and are coherent with the reported values (JCPDS Card No. 36–1451). Also, the 2θ values and planes for crystalline cubic phase Ag were respectively 38.371° (111), 44.458° (200), 64.735° (220), and 77.520° (311), with lattice constant of a = 4.065 A° , which are in close approval with the values mentioned in the research (Panchal *et al*. 2020), and are coherent with the reported values (JCPDS Card No. 04–0783). The nanocomposites related peaks on the XRD spectrum of the NCs films became sharper revealing that it had higher crystallinity. The wurtzite hexagonal structure ZnO peak (101) is dominate in (PVA-PVP/ 5wt.% ZnO) nanocomposite film, while in other nanocomposite films the dominate peak is (111) belonging to the cubic Ag structure. Very little shifted towards the larger angles is due to the micro strain generated in the chain polymer nanostructure by ZnO and Ag additives (Khan, Baek, and Kim 2016) . No extra impurity peaks are found as observed in XRD patterns, which means obtaining high purity films from the mixture of polymer and impurities. The XRD obtained data indicates the formation nanocomposite films more crystalline from the polymeric matrix.

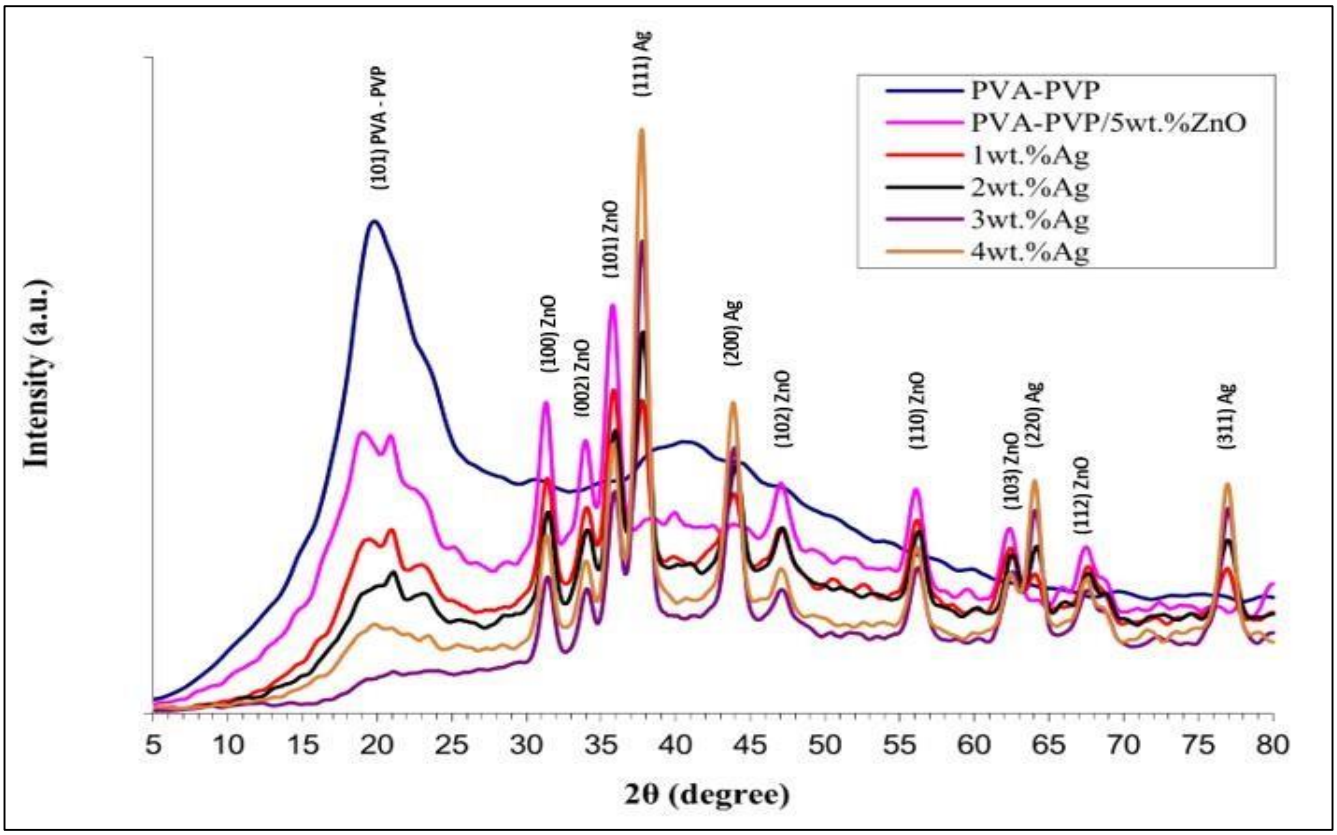

Fig.1 : XRD patterns of PVA-PVP and it's NCs with ZnO and different wt.% of Ag NPs.

4.2 Field Emission Scanning Electron Microscope (FESEM)

Surface morphological features of PVA-PVP polymeric blend and its NCs with ZnO and different ratios (1wt. %, 2wt.%, 3wt. %, and 4wt.%) of Ag NPs were identified using FESEM at a magnification of 200 kx. The addition of ZnO NPs showed agglomeration of small and close packed group of elliptical particles with slightly varying sizes, as the dense structure is formed due to evaporation of water as showed in figure (2, b). Silver addition at different ratios results in hampering the formation. PVA-PVP / ZnO with different (1,2, and 3) wt.% of Ag NCs showed reduction in the agglomeration as showed in figures (2, c, d and e), but in 4wt.% the NCs again showed agglomeration as showed in figure (2, f). Similar behaviour was reported in the research (Panchal *et al*. 2020).

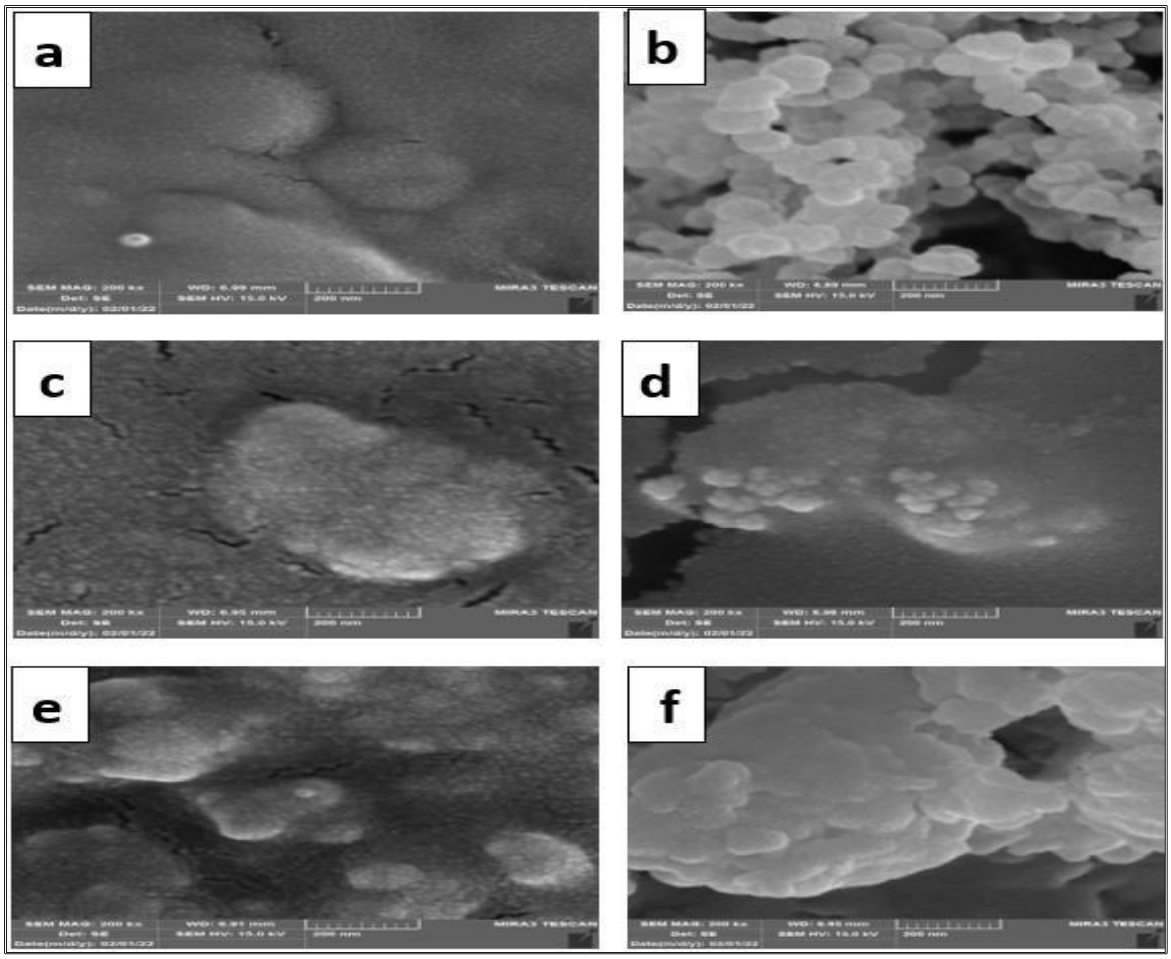

Fig.2: FESEM for, a. (PVA-PVP) blend, b. (PVA-PVP/ 5wt.% ZnO), c. 1wt.% Ag, d. 2wt.% Ag, e. 3wt.% Ag and f. 4wt.% Ag nanocomposite films.

4.3 A.C electrical properties of the casting samples

Dielectric constant, dielectric loss and A.C electrical conductivity for polymer blend and its NCs films were studied in the RT over the frequency range 10^2 -5×10^6 Hz. Figure (3) shows the dependence of dielectric constant on electric field frequency. Decreasing the dielectric constant with increasing frequency may be attributed to the tendencies of dipole in the samples for orienting themselves in the directions of the applied electrical fields and decreasing of space charge polarization. That means the space charge polarization becomes the more contributing type

of polarization at low frequencies. The maximum dielectric constant, are 1.21, 1.24, 1.27, 1.29, 1.32 and 1.35 for polymer blend and its NCs with 5wt.% ZnO and different wt.% (1,2,3, and 4) of Ag NPs at 100Hz, respectively. The magnitude of dielectric constant indicates the ability of the material to store energy from the applied electric field. These are similar to the results of researcher (Jassim and Hashim 2021).

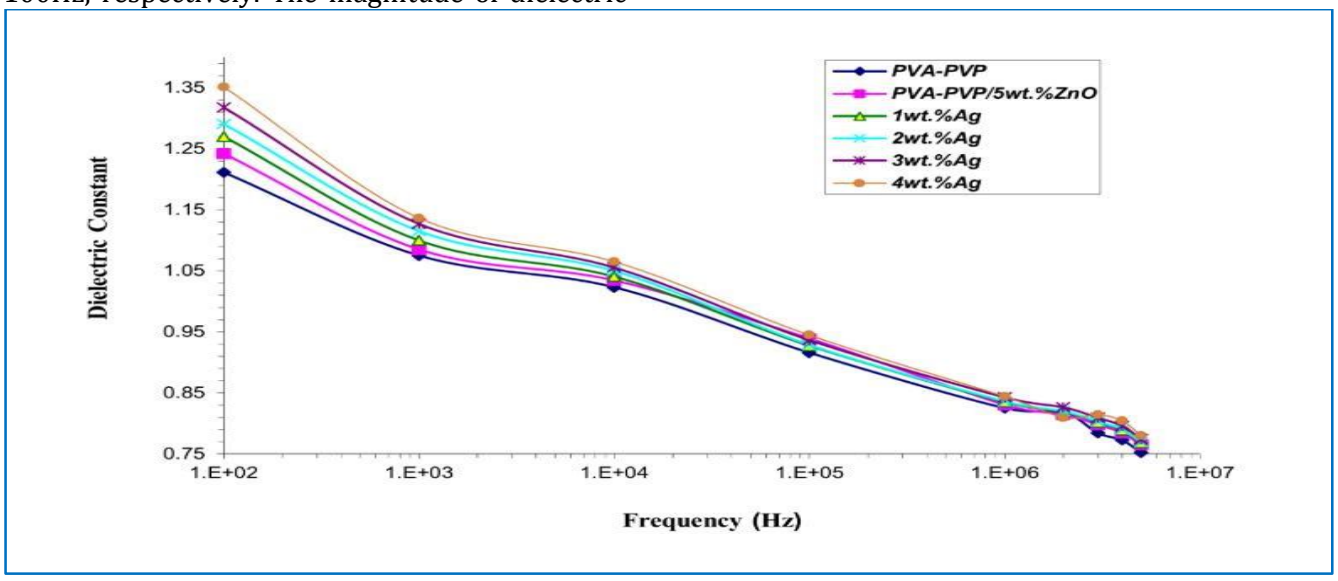

Fig.3: Dependence of dielectric constant of PVA-PVP on frequency and the additives NPs at RT.

The dielectric loss measures the lost electrical energy in the sample from the applied field which is transformed to thermal energy. The dependence of dielectric loss on electric field frequency range and the additives NPs (ZnO and Ag) for PVA-PVP blends at RT shown in figure (4). The maximum dielectric loss for pure polymer blend and its nanocomposites with 5wt.%ZnO and different (1, 2, 3, and 4) wt.% of Ag NPs at low frequency (100Hz), are 0.081, 0.090, 0.094, 0.099, 0.107 and 0.112 respectively, and decreases with increase the frequency of applied electric field. This behavior is attributed to a decrease of the space charge polarization contribution.

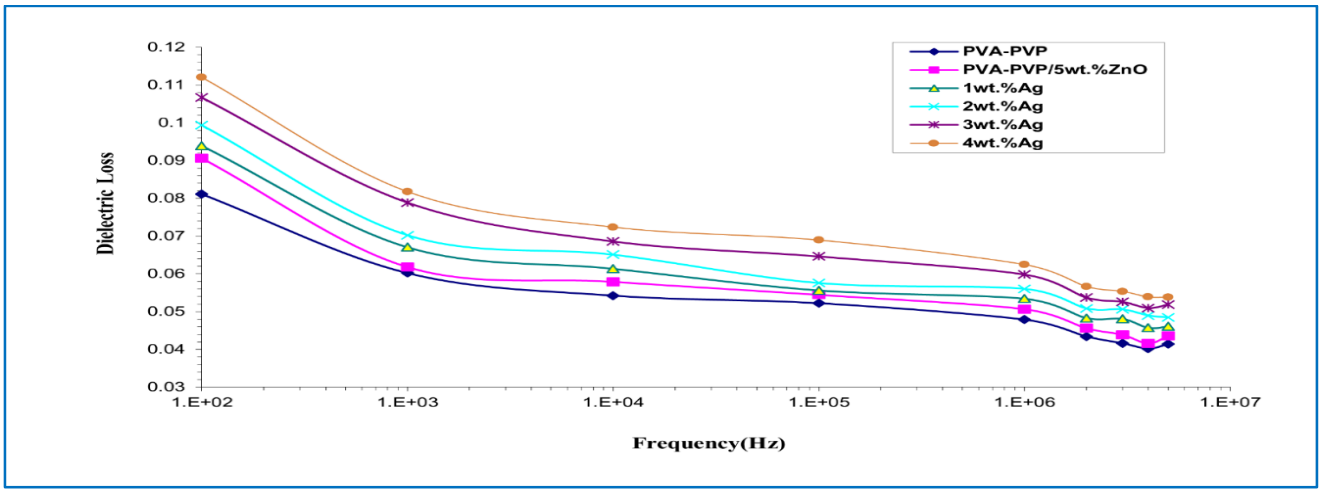

Fig.4: The dependence of dielectric loss of PVA-PVP blend on frequency and the additives NPs at RT.

The dependence of A.C electrical conductivity on electric field frequency range and the additives NPs (ZnO and Ag) for PVA-PVP blends at RT shown in figure (5). The A.C conductivity increases considerably with the increase of electric field frequency for all samples. This is attributed to the space charge polarization at low frequencies, and to the motion of charge carriers by hopping process (Abd-Alkareem 2016). Also, the conductivity increases with the increasing of the wt.% of Ag NPs. This behavior is due to the effect of the space charge as a result of the increase the charge carriers, due to the regular distribution in the polymer matrix. This is in agreement with the results reached by the researcher (Jassim and Hashim 2021).

4.4 Application of (PVA-PVP/ZnO and Ag) NCs for antibacterial activity

Nanoparticles are an attractive antibiotic choice because they have a broad spectrum antibacterial effect even at low concentrations (Herman and Herman 2014). PVA-PVP polymeric blend and its NCs with ZnO and different ratios wt.% (1,2,3 and 4) of Ag NPs were used to study antibacterial activity towards two bacterial strains *Escherichia coli and Staphylococcus aureus* (as showed in Fig.6), were investigated by agar disk diffusion method and the antibacterial sensitivity was measured by determining the diameter of zones of inhibition.

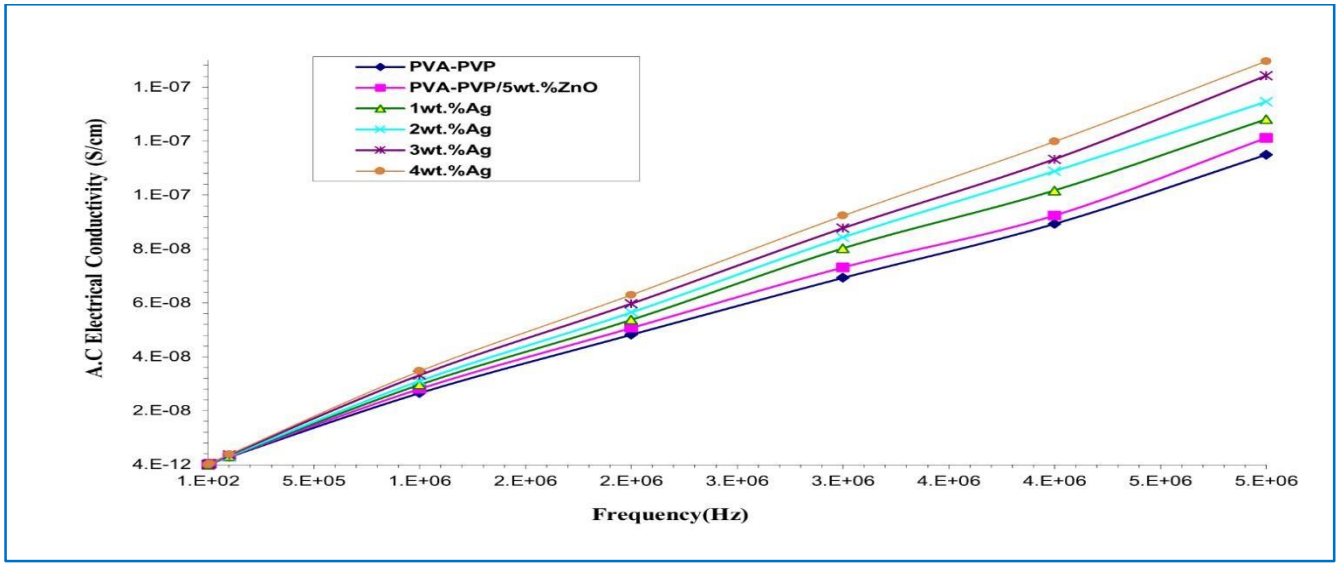

Fig.5: The dependence of A.C electrical conductivity of PVA-PVP blend on frequency and the additives NPs at RT.

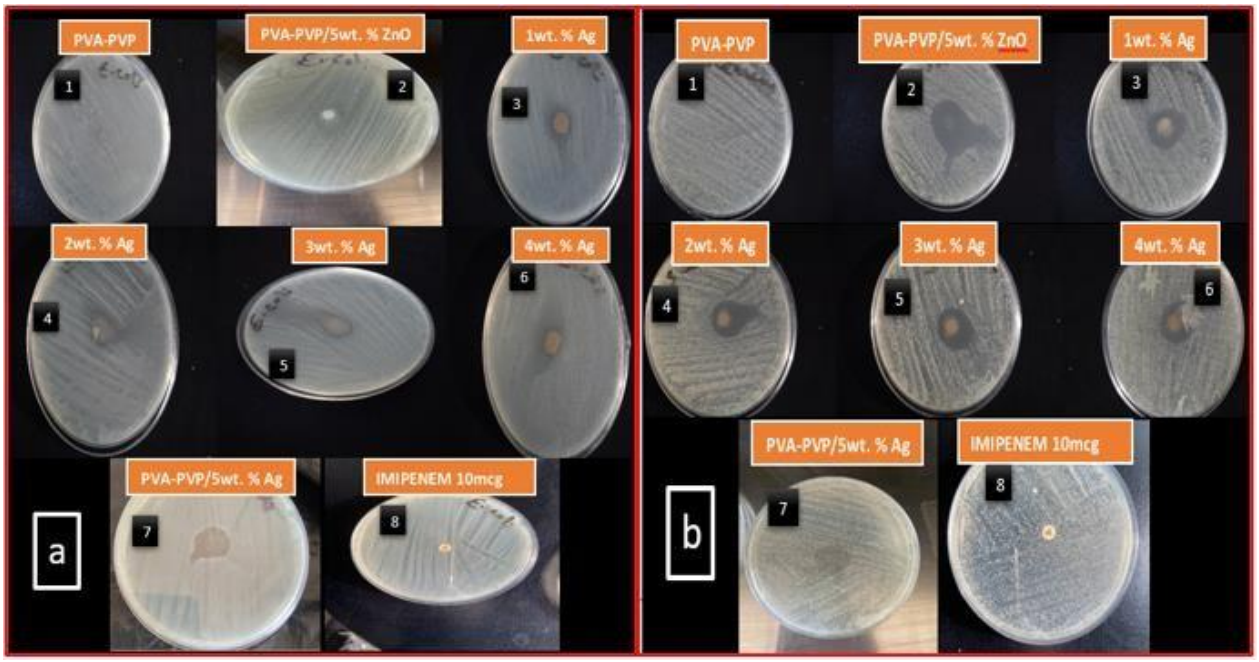

Fig.6: Images for inhibition zones of PVA-PVP with ZnO and different ratios of Ag nanocomposite films on (a) *E. coli* and (b) *S. aureus.*

The study showed that synthesis NCs films have antibacterial effect against all tested bacteria, and at the same time the tested bacterial strains were not sensitive to the antibiotics (IMIPENEM 10mcg). Among the tested ratios of the synthesis pure PVA-PVP blend and its NCs with ZnO NPs and different wt.% of Ag NPs, best growth inhibition was observed with ratio 4wt.% of Ag (34.567±3.066) against *E. coli* (as tabulated in

Table 1).

Furthermore it, the results showed that inhibition zone of *E. coli* bacteria increased by adding different ratios wt.% of Ag NPs, while the inhibition zone of *S. aureus* bacteria decreased with adding different ratios wt.% of Ag NPs. In my opinion, the reason may be the different chemical components of the bacterial wall in the negative and positive bacteria, or it may be due to the acquired resistance of bacteria to antibiotics or other materials including the mixture of the material used in the work, so it is likely that the presence of Ag NPs with ZnO NPs is loaded on the pure polymer consisting of PVA-PVP reduces the inhibition activity of ZnO NPs for *S. aureus*, in contrast, their presence together increases the sensitivity of *E. coli* of NCs films.

Table (1): Inhibition zones of NCs films against different bacterial strains.

Zone of inhibition* (diameter, mm)		
Bioactive agent	***E. Coli*** **Mean±Sd**	***S. aureus*** **Mean±Sd**
PVA-PVP	0.000±0.000 a	0.000±0.000 a
5wt.% ZnO	22.100*±2.762* b	31.600*±8.062* e
5wt.% ZnO&1wt.% Ag	26.700*±2.931* bcd	26.567*±0.603* de
5wt.% ZnO&2wt.% Ag	30.500*±2.451* cd	25.133*±1.401* d
5wt.% ZnO&3wt.% Ag	33.633*±4.123* cd	23.633*±2.030* cd
5wt.% ZnO&4wt.% Ag	34.567±3.*066* d	19.000*±2.960* c
5wt.% Ag	26.290±9.*792* bc	0.000±0.000 a
Anti IMIPENEM 10mcg	6.000±0.000 a	6.000±0.000 b
The similar letters of the vital coefficients indicate that there is no significant difference p>0.05		

The bacterial inhibition zone in *E. coli* colonies show's a significant difference between the pure polymer blend and its NCs also there are significant differences between ZnO at 5wt.% and the different ratios wt.% (2, 3, and 4) of Ag. While there are no significant differences among the other ratios. The comparison between the pure polymer blend and its NCs for *S. aureus* showed significant differences (p≤ 0.05), also, there is a significant difference between ZnO at 5wt.% and the different ratios wt.% (2, 3, and 4) of Ag, significant differences was also found between 1wt.% of Ag and 4wt.% of Ag, finally there are significant differences between 2wt.% Ag and 4wt.% Ag. While there are no significant differences between the other materials ratios. It was also noted that there were significant differences between the antibiotic (IMIPENEM 10mcg) and the polymer with its NCs.

5. Conclusions

Polymer blend (PVA-PVP) and its nanocomposites with constant and different ratios of Ag NPs films synthesized using solution cast technique. The XRD analysis confirmed the formation nanocomposite films more crystalline from the polymeric matrix. FESEM images revealed a good dispersion of ZnO and Ag NPs on the surface of the PVA/PVP films. The AC electrical properties showed that the dielectric constant and dielectric loss for all different wt.% of Ag nanoparticles decreases with the increase of the electric field frequency. Increasing the content of NPs leads to an increase in the diameter of the inhibition zone for *Escherichia coli* and a decrease in the diameter of the inhibition zone for *S. aureus* for antibacterial application.

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