Structural and optical studies on sliver nitrate doped polymer blend and effect on some pathogenic bacteria

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In this paper, we report the effect of poly (vinyl alcohol) (PVA)/poly (vinyl pyrrolidone) (PVP) blend with different concentration (10, 20, 30 and 40) wt % of $AgNO_3$ preparation using the casting method . We conducted the characterization of Ag nanoparticles using Fourier transform infrared spectroscopy (FTIR) and (UV-VIS) spectroscopy. We specifically investigated the nanoparticles using UV-Vis spectroscopy in the spectral range of 200–900 nm. We established the energy gap of indirect permitted transitions and observed a decrease in their values as the concentration of nanoparticles increased. This study prepared a nanopolymer composite solution consisting of PVA-PVP-$AgNO_3$. We tested the sensitivity of the bacteria *S. aureus, S. epidermidis, E. coli, P. aeruginosa,* and *C. albicans* to this solution. Practical results have shown that the nanopolymer composite solution is highly effective in eliminating and restricting the growth of these bacteria.

Keywords: Polymer blend; $AgNO_3$; FTIR; UV-VIS; antimicrobial properties.

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1. Introduction

Nanotechnology makes (1–100) nanometer materials, devices, and structures. Initial nanotechnology applications included nanosensors [1-3]. Nanosensors have a low operating temperature, work at room temperature, are stable in performance, have fast reaction and recovery times, and are very selective and sensitive [4,5]. These are some of the most important qualities that make gas detection systems more effective. The wide variety of uses for polymers has contributed to their rising popularity. One way to make a material work better is to mix it with other types of polymers or inorganic materials; this process creates new composite systems that are better than the parent mixture [6]. One strategy to create new materials with a range of qualities is to blend various polymers. The characteristics of the original polymers and the blend composition primarily determine these features [7]. Polyvinyl alcohol (PVA), a polymer with a partially crystalline structure, has been extensively investigated by researchers due to its multiple fascinating physical features. The presence of hydroxyl (OH) groups and the creation of hydrogen bonds with other polymers or metals are responsible for these features. Polyvinylpyrrolidone (PVP) is a vinyl polymer that contains flat and strongly polar side groups formed via peptide bonding [8]. The combination of silver nanoparticles with polymers has garnered significant attention due to the expanded range of applications offered by these hybrid materials [9]. Due to their unique properties, silver nanoparticles and polymer composites are potential useful materials for optics, electronics, and mechanics. Several research studies have used silver nanoparticles to make polymer nanocomposites. Researchers have investigated these nanocomposites for high-performance capacitors, conductive inks, and other electronics [10,11]. Due to their physical and chemical properties, silver nanoparticles are popular. Polyvinyl alcohol, PVP, and PMMA have all been blended together. Dopants affect polyvinyl alcohol's thermostability, chemical resistance, mechanical strength, water solubility, and moderate electrical conductivity. These features make PVA a suitable host medium for metals, especially silver nanoparticles. Many consider PVA one of the best polymers for hosting silver nanoparticles [12]. A number of studies have lately examined the combination of PVA and PVP polymers with various nanofillers. Wound dressings, articular cartilage replacements, and membranes for high-energy electrochemical devices use mixtures of polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) [13,14]. Nanotechnology is the use of small amounts of material to carry out activities at the atomic or molecular level, such as material separation, consolidation, and deformation [15]. A polymer nanocomposite is a complex system made up of fillers, which are tiny components with dimensions smaller than 100 nm in at least one direction [16]. Nanometal oxides, a novel type of antimicrobial agent, have demonstrated potent antibacterial characteristics. Researchers recommend using silver and zinc ions as highly effective disinfectants against pathogenic germs found in hospitals [17]. The present study focuses on synthesizing nanocomposites (PVA-PVP/$AgNO_3$) and evaluating their antibacterial and antifungal properties.

2. Experimental section

2.1. Materials

The polymers PVA (Molecular formula $(CH_2\ CH(OH))_n$, Mol. wt. = (23000-13000) g. mol^{-1} and PVP (Molecular formula $(C_6\ H_9\ NO)_n$, Mol. wt. = 40,000 g.mol^{-1} (Central Drug House, Ltd, Company). The additions include silver nitrate ($AgNO_3$), a dark powder that is very soluble in water.

2.2. Synthesis of PVA-PVP/ Ag NO_3 Nanoparticles

We used the casting method to make a pure (PVA/PVP) polymer hybrid film and PVA/PVP with (10, 20, 30, and 40) wt% of $AgNO_3$ using certain glass molds. Using a magnetic stirrer at 80°C for (2) hour and a certain weight ratio of $AgNO_3$ polymer is added to distilled water, this makes a clean (PVA/PVP) polymer film. This makes a smooth solution that is put into a special glass mold and left on a soft surface until the solvent evaporates. After that, you get a pure (PVA/PVP) polymer film and a (PVA/PVP/$AgNO_3$) film.

2.3. Bioactivity test

Isolates of *Staphylococcus aureus and Staphylococcus* epidermidis were grown on Blood agar. Isolates of *Escherichia coli and Pseudomonas aeruginosa* were grown on MacConkey agar, and an isolate of *Candida albicans* was grown on Sabouraud dextrose agar.

MacFarland turbidity standard

We used the solution from the company (Biomeriex) to calibrate the number of bacterial cells. This solution yields an estimated count of around 1.5×10^8 cells/mm.

1- Muller Hinton agar

We made the medium by dissolving 38 grams in 1 liter of distilled water. The autoclave sterilized it for 15 minutes at 121°C and 15 pounds of pressure. Once cooled, we placed the medium on sterile plates and refrigerated it until it was ready for use.

2- Determination the Antimicrobial activity of PVA/PVP/$AgNO_3$ by agar well diffusion method

We dissolved 38 grams of the medium in a liter of distilled water. For fifteen minutes at 121 degrees Celsius and fifteen pounds of pressure, the autoclave sterilized it. Once the mixture cooled, we transferred it to clean plates and refrigerated it until we needed it. Next, we punched holes into the culture medium using a sterile cork borer. (100 μl) of the substance was added to each hole using a micropipette, and the effectiveness of each concentration was assessed by measuring the diameter of the inhibitory zone surrounding each hole.

2.4. Characterization techniques

The measurements of the nanocomposite film include the structural, optical properties of the prepared film, FTIR test, in order to record the (FTIR) spectra of the (IR Affnty-1CE (FTIR) spectrophotometer, Shimadzu, Japanese company) was used, the UV- visible absorption spectra's were measured using Shimadzu UV-1800 spectrophotometer, covering a range from (190-1100) nm.

3. Results and discussion

3.1. FTIR analysis

Fourier transform infrared spectroscopy is a powerful analytical tool for examining both inorganic and organic substances. You can think of an infrared spectrum as a sample' s fingerprint, with the absorption peaks representing the vibrational frequencies of the bonds between atoms. With a lower frequency and longer wavelength, infrared radiation occupies the space between microwave and visible wavelengths in the electromagnetic spectrum [18,19]. Fourier transform infrared spectroscopy (FTIR), which varies with their formulation, can analyze the band structure of materials. It has the potential to show how different components, like ions, cations, and polymers, interact with one another [19]. The FTIR spectrum of a pure mixed and gel electrolyte at (10, 20, 30, and 40) wt% of $AgNO_3$ is shown in Fig. 1. The FTIR spectrum of an $AgNO_3$-complexed system shows that the polymer mix has fully dissolved and complexed $AgNO_3$. This is shown by

TABLE I. Values of the wavenumbers of the absorption bands of the composite films of pure (PVA/PVP) with different concentration of $AgNO_3$.

Assignments	wavenumbers of the absorption bands				
	Concentrations				
	0	10	20	30	40
OH Stretching/vibration	3746	3741	3756	3751	3751
C-H stretching	2940	2924	2935	2953	2953
CH2 asymmetric stretching	2298	2313	2319	2313	2313
CH2 wagging and C=C stretching	1508	1529	1529	1529	1513
-C=N pyridine ring / stretching	1277	1282	1282	1282	1282
C-C Stretching vibration	1087	1108	1108	1108	1108
C-H out of phase bending	686	621	631	641	646
Ag O	538	554	543	554	548

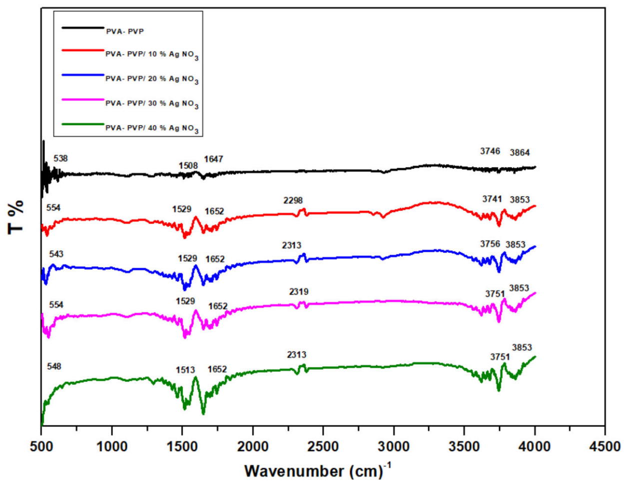

FIGURE 1. FTIR spectra of pure (PVA/PVP) with different concentration of $AgNO_3$

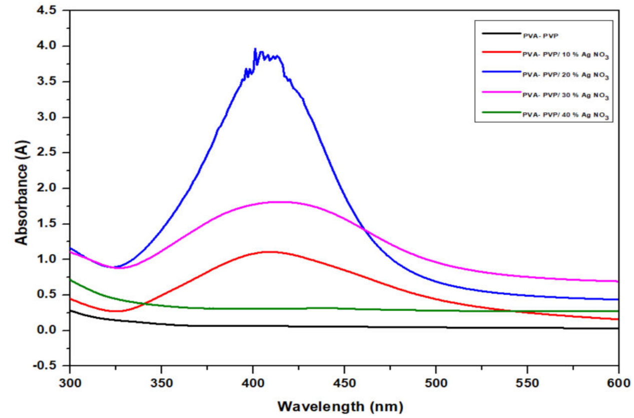

FIGURE 2. UV-VIS spectra of pure(PVA/PVP) with different concentration of $AgNO_3$.

the changing transmittance and band shifting. Changes in the infrared spectrum, like band moving and the addition or removal of an infrared spectrum band [20,21], can be linked to complexity. This project' s main goal was to change the FTIR band in order to learn more about how polymer mixes react and behave with various amounts of $AgNO_3$. Table I shows that the hydroxyl groups in the PVA-PVP mix moved a little (3746.5 cm^{-1}) when the amount of $AgNO_3$ went up. The absorption of the C=C bond didn' t change much at 1508 cm^{-1}. It is possible that hydrogen bonding interactions formed because the C-H stretching bond changed from (2940 cm^{-1}) to a smaller wavenumber of (2924 cm^{-1}) [22,23]. The fact that the PVA-PVP samples treated with $AgNO_3$ had a CH_2 signal suggests that not all of the vinyl groups went through reactions during the polymerization process [23,24].

3.2. UV-VIS analysis and energy gap calculation

In relation to their electrical structures, semiconductor materials' basic mechanism of light absorption or reflection is important. Figure 2 shows the absorption. The large absorption peak at 380 nm in the PVA/PVP nanoparticles confirms the results from the earlier studies, attributed to the optical transition of the initial excitonic state (Fig. 2). states that we obtain the formula for the transmittance (T) by dividing the incident light intensity (I) by the intensity of the light passing through the film (I_T/I) [25]:

$$T = \frac{I_T}{I}, \quad (1)$$

where T indicates the transmittance, I_T, represents the transmitted light intensity, and I represents the incident light intensity. The absorbance of the sample is defined as the negative log of the transmittance given by the relation [26]:

$$A = -\log_{10} T, \quad (2)$$

where A represents the absorbance of the sample. The reduction of Ag^+ into $AgNO_3$ under a PVA/PVP mix solution proceeded quickly. The change in hue of the solution from a colorless to a yellow color [27,28] revealed the formation of the nanoparticles in 1 h. $AgNO_3$ synthesis detection using UV-visible spectroscopy. We evaluated the effect of (0, 10, 20, 30, and 40) wt% of PVA/PVP blend solution on $AgNO_3$ synthesis using a UV-visible spectrophotometer, and Fig. 2 presents the results. Finally, we tracked the UV-Vis spectra of the reaction mixture at different time intervals to track the synthesis of $AgNO_3$ from its ions. Table II presents the results.

TABLE II. The surface plasmon resonance values of pure (PVA/PVP) with different concentration of $AgNO_3$.

Surface plasmon resonance (SPR) (nm)	Samples
380	PVA/PVP
407	PVA/PVP/10 wt% Ag NO_3
414	PVA/PVP/20 wt% Ag NO_3
407	PVA/PVP/30 wt% Ag NO_3
380	PVA/PVP/40 wt% Ag NO_3

3.2.1. Energy gap

Figure 3 displays a straight line connecting the curve' s peak to the ultraviolet (UV) axis. This line shows the link between photon energy and $(\alpha hv)^{1/2}$ for PVAPVP-Ag NO_3. If αhv is equal to zero, it means that the allowed indirect transfer can happen. The numbers we got are shown in Table III. The numbers of the energy gaps go down as more nanoparticles are added. This is because more nanoparticles fill in the energy gap and make local levels. Electrons move from the valence band to the local levels during the shift in this case. This behavior is due to the different types of alloys and how the added Ag nanoparticles allow electricity to flow. As the added rate goes up, the polymer makes more routes for electrons to move from the valence band to the conduction band.

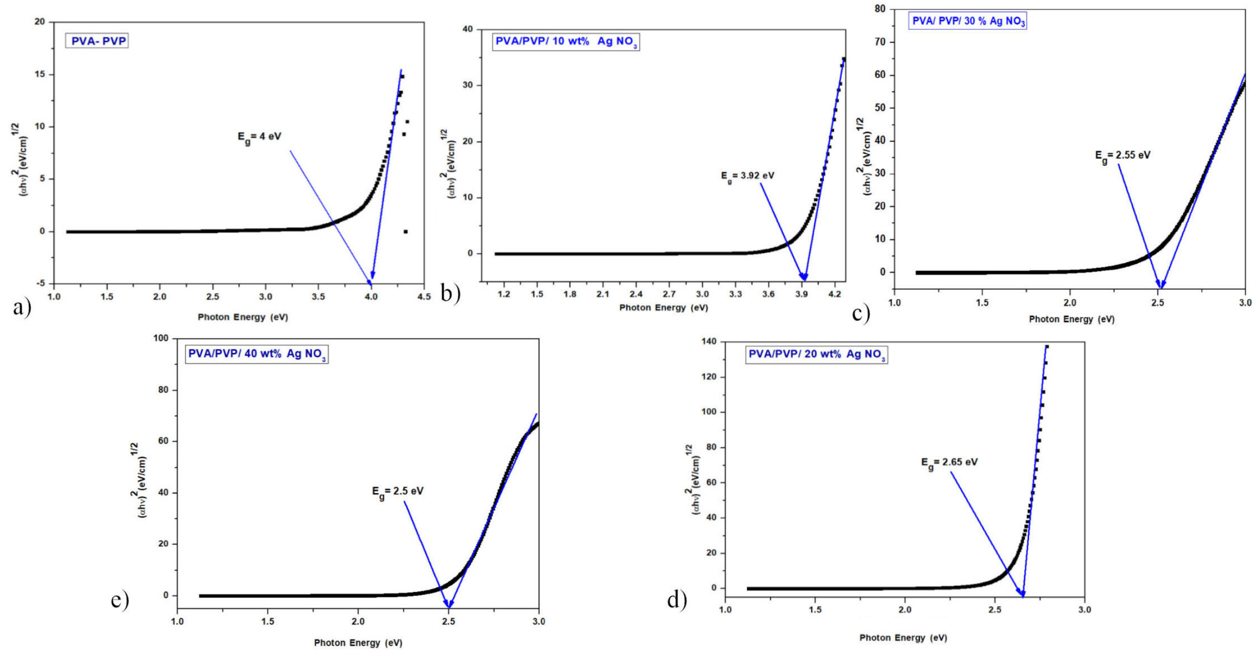

FIGURE 3. Direct band gap estimations of pure (PVA/PVP) with different concentration of $AgNO_3$

TABLE III. The energy gap values of pure (PVA/PVP) with different concentration of $AgNO_3$.

E_g (eV)	Samples
4	PVA/PVP
3.92	PVA/PVP/10 wt% Ag NO_3
2.65	PVA/PVP/20 wt% Ag NO_3
2.55	PVA/PVP/30 wt% Ag NO_3
2.5	PVA/PVP/40 wt% Ag NO_3

So, as the quantity of the additive goes up, the energy gap goes down [29,30]. Table III shows The energy gap values of pure (PVA/PVP) with different concentration of $AgNO_3$.

3.3. Bioactivity test

We used the Disc Diffusion Method to test the sensitivity of bacteria (*S. aureus, S. epidermidis, E. coli, P. aeruginosa, and C. albicans*) to a nanopolymer composite solution (PVA-PVP-$AgNO_3$) with varying volume ratios (10, 20, 30, and 40 wt%) of $AgNO_3$. In the study, it was found that the nanopolymer composite solution killed the germs very well. It got even better as the amount of silver nitrate in the solution raised. Nanoparticles are more effective because they can stick to the surface of bacterial cells better because they are small and have a lot of surface area. This makes them more poisonous to microorganisms. Which then changes how permeable the bacteria' s plasma membrane is, which finally ends with cell death. Nanopolymer composites and bacterial cells communicate with each other through an electromagnetic force. The charges on bacterial cells are negative, and the charges on nanometal oxides are positive Due to this attraction, the nanoparticles emit ions that interact with the thiol group (SH-group) of proteins responsible for transporting nutrients across the bacterial cell membrane. This interaction decreases the permeability of the membrane, ultimately leading to the death of the cell. Put simply, the mechanism prevents the replication of DNA, the expression of genetic genes, and the manufacture of essential enzymes for ATP synthesis. The lack of efficacy of the polymer composite (PVA-PVP-$AgNO_3$) leads to its potential to harm the surface of the cell membrane, which in turn disrupts the process of permeability and interferes with the electronic transmission

TABLE IV. The inhibition zone diameter (mm) of PVA/PVP at different concentrations of $AgNO_3$.

Samples	S. aureus	S. epidermidis	E. coli	P. aeruginosa	C. albicans	Toxicity
A/pure	0 mm	0 mm	0 mm	0 mm	0 mm	Slightly toxic
B/10 wt%	12 mm	0 mm	11 mm	15 mm	15 mm	Highly toxic
C /20wt%	12 mm	12 mm	11 mm	13 mm	13 mm	Highly toxic
D/30wt%	14 mm	0 mm	12 mm	14 mm	14 mm	Highly toxic
E/40wt%	15 mm	0 mm	12 mm	15 mm	13 mm	Highly toxic

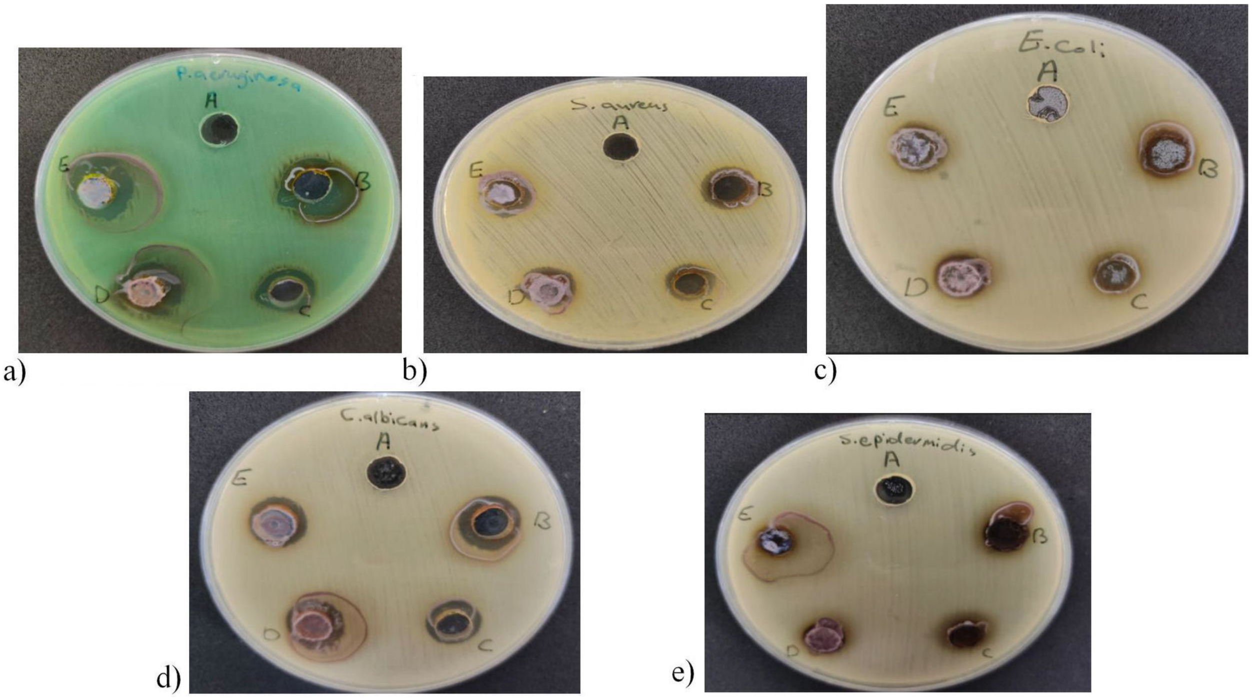

FIGURE 4. Inhibition zone (mm) of pure (PVA/PVP) at different concentrations of Ag NO_3.

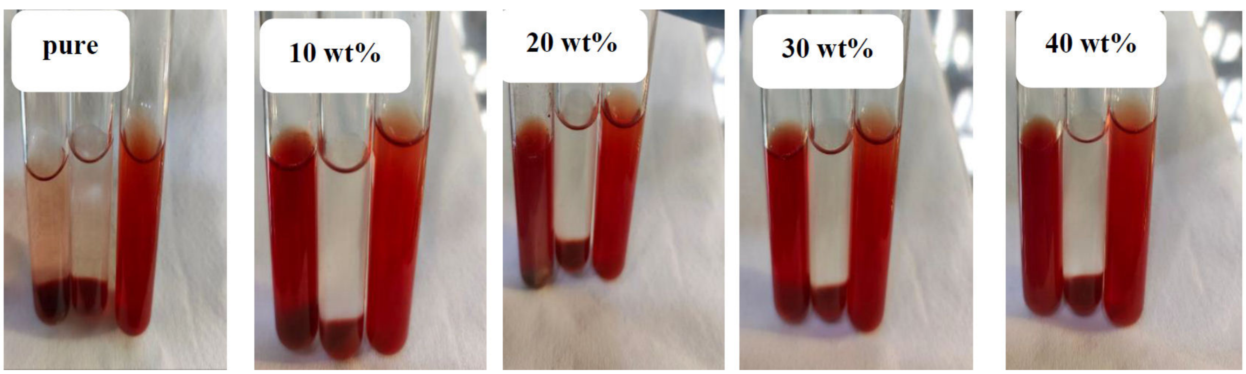

FIGURE 5. Toxicity of treatment with pure PVA/PVP with different concentrations of Ag NPs.

system of the bacterium [31,32]. Figure 4, and Table V shows the image of bioactivity test of the (PVA-PVP-$AgNO_3$) polymer composite on bacteria (*S. aureus, S. epidermidis, E. coli P. aeruginosa and C. albicans)* Fig. 5 shows samples with an increase (PVA/PVP-AgNO3) with varying volume ratios (10, 20, 30, and 40 wt%) respectively).

4. Conclusions

This study involved the synthesis and analysis of gel-polymer electrolytes. Through FTIR tests on the electrolytes, it was clear that the polymer blends (PVA-PVP) and $AgNO_3$ worked well together. The presence of $AgNO_3$ in electrolytes leads to changes in the intensity, shape, and position of stretching modes in polymer blends. Electronic transitions are defined as indirect transitions. The concentration of Ag nanoparticles has a direct effect on lowering the optical energy gap. The optical microscope analysis reveals a uniform distribution of PVA-PVP-$AgNO_3$.Scientists tested a mixture of PVA, PVP, and $AgNO_3$ on living things and found that it might be able to kill different types of bacteria, such as *S. aureus, S. epidermidis, E. coli, P. aeruginosa, and C. albicans.*

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