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# Structure and Optical Characteristics of PVA Films Doped with Silver Nanoparticles

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## Abstract

Tests are conducted to ascertain the impact that the introduction of silver nanoparticles in the PVA matrix has on composite films. The samples are made up of extremely thin PVA films that have been infused with silver nanoparticles of various densities and concentrations. X-ray diffraction and the FTIR spectrum are used to examine the properties of structures. Sample reflectance and transmittance measurements are used to determine and explain the effect of doping concentration & nanoparticle doping on optical characteristics of PVA films. These features include, but are not limited to, the absorptivity, optical band gap of energy energies, difficult refractive index, complicated dielectric functions, optical imaging conductivity, and the relaxation time. Film refractive index change is examined and quantified using the Wemple-DiDomenico (WD) single oscillator model. The results show that when silver nanoparticles are incorporated into PVA, the amount of Bragg's planes in the polymer's structure increases, making the material considerably more crystalline. Bandgap energy was reduced due to the development of Ag-O bonds in the films. WD model calculations show that nanoparticles weaken PVA's anion strength as a dielectric medium.

**Keywords:** Polyvinyl Alcohol (PVA), Ag-Nanoparticles, X-ray Diffraction, FTIR Spectrum, Wemple-DiDomenico (WD)

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## 1. INTRODUCTION

Polyvinyl alcohol (PVA) films that have been doped with silver nanoparticles (also known as AgNPs) have been the subject of a significant amount of research because of the exceptional qualities they possess and the diverse range of possible uses for them. The concentration of AgNPs, the size distribution of the AgNPs, and the structure & optical qualities of the film are influenced by the processes employed during its fabrication.

***Optical Properties:*** The localised surface plasmon resonance (LSPR) of the AgNPs is thought to be responsible for the optical properties that are shown by PVA films that have been doped with AgNPs. The light-scattering and light-absorbing phenomena known as LSPR is caused when metal nanoparticles are subjected to electromagnetic radiation. This results in a certain frequency of oscillation for the electrons that are free in the metal nanoparticles. The position and intensity of the LSPR peak are affected by the size, shape, or concentration of the AgNPs.

When PVA films are doped with AgNPs, the location of the LSPR peak moves towards the longer wavelength, resulting in a red shift. This shift occurs regardless of the size or concentration of the AgNPs. This change is due to the increased interparticle distance, which weakens the coupling between nearby AgNPs and decreases the electron density at the surface of the nanoparticles. This shift occurred because the interparticle distance was increased. Due to the increased number of electrons that are oscillating, the intensity of the LSPR peak likewise rises as the size of the AgNPs and the concentration of the AgNPs increases.

Metal nanoparticles linked with polymers have attracted a lot of notice as of late [1–6]. This is mostly due to the wider application targets offered by hybrid materials such as these. Polymers, being dielectric materials, are often accepted as ideal host matrix for the encapsulating of metallic nanoparticles as silver, gold, copper, and so on [7-9]. This is because polymers are great hosts since they are dielectric materials. [45-46] Polymers are useful not just because of their capacity to maintain environmental and chemical stability but also because of their ability to serve as reducing agents and capping agents. At the same time, the properties of the host itself will be affected as a consequence of the presence of these nanoparticles that have been inserted inside the polymer matrix [1, 6, 10–13]. This may be attributed to the fact that the nanoparticles will modify the characteristics of the polymer matrix. Particularly intriguing as a candidate for a functional material are hybrids of polymers and metals, such as composites of polymers and silver nanoparticles [1, 14–18]. These composites include nanoparticles of silver, which provide them antimicrobial properties in addition to their optical, electrical, thermal, and mechanical advantages over polymers. There are several studies in the scientific literature that indicate efforts to synthesise metal nanoparticles based polymer nanocomposites. Some of these attempts were successful, while others were not. These tests show that the optical as well as electrical properties of the nanocomposites may be altered, which might be useful to be utilized in high - performing capacitors, conductivity inks, and a wide variety of other electrical parts [2, 19, 20, 41]. Polymer-metal nanomaterial combination, managing particle size, concentration, and dispersion within polymer matrices [2, 21–23], are main critical aspects sensors for use in opto-electronic devices, electrical equipment, optical instruments, biomedicine, and other fields, and other disciplines. The fact that they have so many potential uses is also important. Nanoparticles doped in polymer film have been demonstrated to have optical characteristics that are highly dependent on their size, shape, and concentration in addition to the medium in which they are embedded [24–26]. Polymers like PVA, PVP, or PMMA have been used to encase silver nanoparticles [1]. PVA is very stable at high temperatures, resistant to chemicals, strong under mechanical stress, water soluble, and somewhat conductive (depending on the presence of dopants), making it one of the best polymers for hosting silver nanoparticles [1, 28], and low toxicity. PVA is also considered to be polymers that host silver nanoparticles well are among the finest available. For these factors, it merits consideration as a host material. PVA has the ability to provide excellent protection against the aggregation of nanoparticles [1, 9].

The prime concern of this study is how the incorporation of silver nanoparticles might modify the structure and light-transmitting capabilities of the polymer. The nanoparticle doping is responsible for these variations. Using a process called laser ablation, silver nanoparticles were created. When carried out in a liquid, the laser ablation method results in the development of adequate metal nanoparticle samples. This, in turn, makes it simpler to analyse the photo physical and photochemical properties of the particles [29]. As compared to the process of preparing nanoparticles by chemical synthesis, the absence of uncontrolled by-products during the manufacturing of nanoparticles through the use of this approach is a distinctive and advantageous element [29, 30]. This method does not produce nanoparticles. It was observed that the optical properties of the crystal as well as its crystalline structure are subject to intriguing variations [42]. The nanoparticle dopant's surface plasmon resonance phenomena are accountable for the most noticeable of the essential adjustments in the host polymer's optical properties. Surface plasmon resonance is responsible for these alterations [27]. The range of 400-420 nm is where a surface plasmon resonance becomes most prominent for silver nanoparticles, has supplied irrefutable proof that the polymer in question incorporates silver nanoparticles into its structure. The effects of different silver nanoparticle concentrations on PVA films of constant thickness at room temperature are also investigated. Its behaviour is similar to that of PVA sheets doped with silver nanoparticles. This includes the response's reflectance and transmission as well as its dielectric relaxation time, dispersion refractive index, and dielectric constant [44].

Many fields are taking an interest in polymers made with inorganic compounds. Electrical, optical, and medical sensors are only a few of the many uses for doped polymers [31]. When it comes to electronics, optics, and mechanical properties, composite polymers stand out [32-35]. Reflective materials, magneto-optical data storages, optoelectronic devices, and photovoltaic cells are only a few of the many places these substances find use [36-37]. Polymer reinforcement using carbon nanotubes, semiconductors, magnetic nanoparticles, and metals are only some examples of the innovative polymers that have been developed and used to improve the composite polymer's optical properties [42]. Polyvinyl alcohol (PVA) is one of the few high-quality water-soluble vinyl polymers. It's semi-crystalline, entirely biologically biodegradable, non-toxic, and biocompatible, and it can be used for a variety of purposes. In addition, the carbon backbone is hydroxyl-assembled, making it a useful source of hydrogen binding that can aid in the creation of polymer composites.

In conclusion, the concentration of AgNPs, the size distribution of AgNPs, as well as the technique used to create the AgNPs all have influence on the composition and transparency of PVA films that have been doped with AgNPs. The Long-Short-Path-Reflection (LSPR) phenomenon of AgNPs is responsible for the one-of-a-kind optical features of these films, which in turn makes them appealing for a variety of applications, including photovoltaics, optical devices, and sensors.

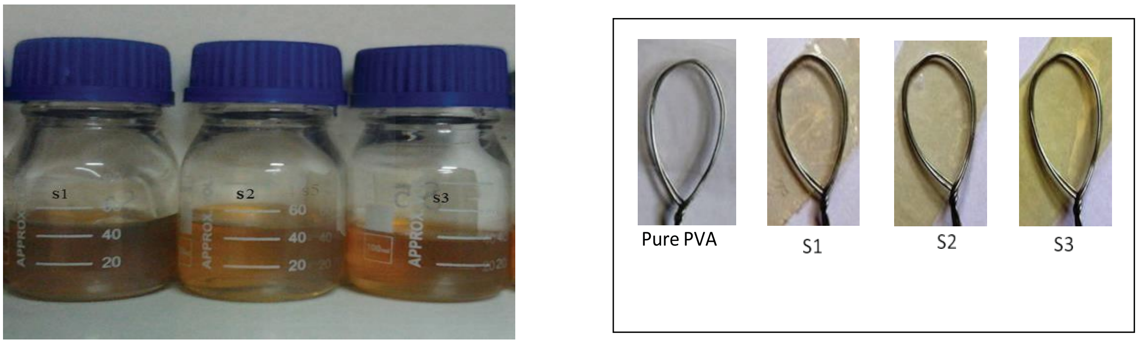
## 2. MATERIAL AND METHODS

- Pulse-width-modulated operation at 1064 nm using a Nd: YAG laser's fundamental harmonic width of 7 ns and a 10 Hz repetition rate, nanoparticles (NPs) were created by ablating a high purity silver mass in distilled water. This process was done utilising the fundamental harmonic of the laser.
- The surface of the silver mass that was located where water collects in the bottom of a bottle was brought into focus using a convex lens that had an aperture of 80 millimetres. The water level on the silver target was up 12 millimetres from its lowest point. Before the lens, the diameter of the laser beam was 2 millimetres, and after the lens, it was found that the diameter of the laser beam on the surface of the target was 30 micrometres. Twenty millilitres of water were kept within the ablation container, and the ablated silver target was hit with a total of five hundred laser pulses of varied strengths. For the whole of the production of samples 1–3, the laser pulse fluencies of 1.5, 2, and 3 J/cm2 were used in the appropriate sequence.
- We were able to calculate the mass of the ablated silver nanoparticles by weighing the dried target before and after the ablation procedure. Based on our findings, the mass of the ablated silver nanoparticles in samples S1, S2, and S3 was determined to be 3.7 x 10-4, 4 x 10-4, and 6.5 x 10-4 g, respectively.
- In order to produce PVA films, 1 gram of PVA powder was heated to 57 degrees Celsius and dissolved in 20 millilitres of distilled water. This process was carried out in a container. After continuously swirling the mixture for a total of two hours, a solution with a thick consistency was created. The Merck Corporation in Germany provided the PVA powder that was used in the experiment. After the completion of the desolation procedure, 8 millilitres of a suspension containing silver nanoparticles were added to 20 millilitres of an aqueous PVA solution. After this was done, the samples were air-dried at $24^{o}$C and 100% humidity for one day on a flat surface. The final product was three samples of homogenous PVA films that were doped with silver nanoparticles and had a thickness of 0.14 millimetres. PVA films S1 through S3 have each been doped with nanoparticles taken from sample 1, moving sequentially through the samples.
- All of the transmission electron micrographs were captured using a CM120 equipment from PHILIPS Co. Waveforms of X-ray diffraction (XRD) were compared between control and ion-implanted PVA films using Cu-K

radiation (= 1.544060 A) with a STOE-XRD diffract ometer. Specifically, we used a NEXUS 870 FT-IR to perform the required Fourier, transform infrared spectroscopy. To capture the materials' transmission and reflection spectra, Used was a Varian Cary-500 Scan UV-Vis-NIR spectrophotometer.

## 3. RESULTS

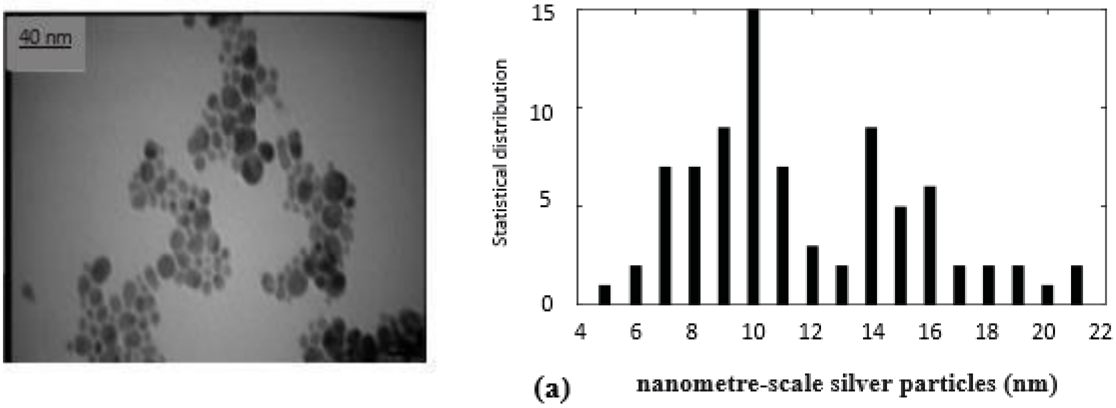
Figure 1a shows particles at the nanoscale, and Figure 1b shows layers of nanoparticles that have been doped with PVA and include Ag nanoparticle. PVA is a colourless polymer that becomes yellow when Ag nanoparticles are added. The colour of films has gotten darker as the concentration and size of doped nanoparticles have increased and decreased, respectively.



(a) (b)

**Figure 1: (a) A sample of silver nanoparticles in pure water and (b) Films made of polyvinyl alcohol (PVA) and silver-impregnated PVA**

Figure 2 displays TEM pictures of nanoparticles. Images depicting the space between brain regions. All of the manufactured nanoparticles are perfectly round and non-aggregated.



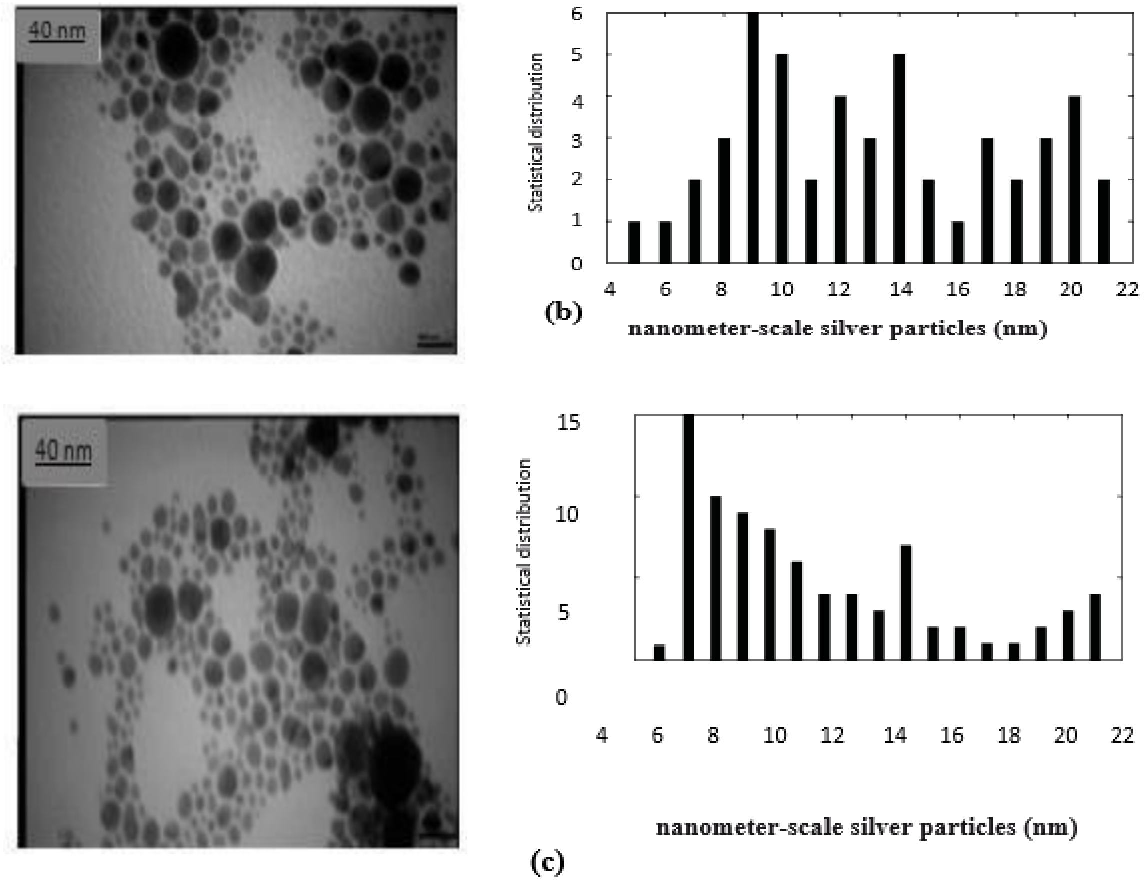


**Figure 2: TEM image shows size distribution of silver nanoparticles synthesised by laser ablation in ultrapure water. (a) S1, (b) S2, and (c) S3.**

- X-ray diffraction images of silver nanoparticles, untreated sheets of PVA, and AgNPs that have been coated with PVA. Strong intermolecular & intramolecular hydrogen banding may account for the peaks at 220 in a crystalline PVA polymer network [7, 38].
- FTIR spectra for pure PVA and PVA containing doped sheets are displayed in Figure 3 [39, 40]. In every spectrum, it is possible to make out the absorption maxima of pure PVA, which are located at 3580, 2974, 1740, 1540, 1445, and 845 cm-1. Changes in the samples' spectral characteristics can be observed in the range of 1100–500 $cm^{-1}$. The formation of new absorption bands and subtle shifts in the strengths of existing ones are among these modifications. In addition, these treatments cause the formation of new absorption bands.

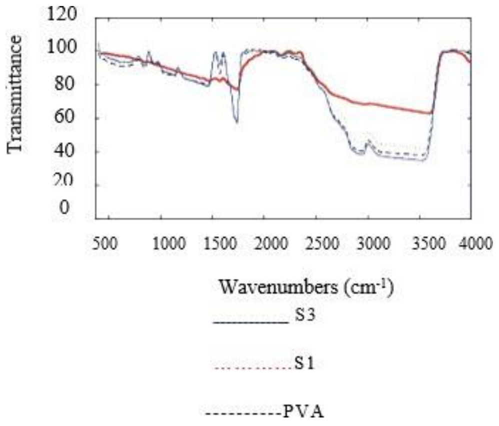


**Figure 3: FTIR spectrum of PVA polymer films containing Ag nanoparticles and PVA pure films**

- Figure 4 displays the pure PVA polymer sheets transmittance (T) or reflectance (R) versus wavelength against a black background. Pure PVA is a very transparent, odourless, and colourless polymer.

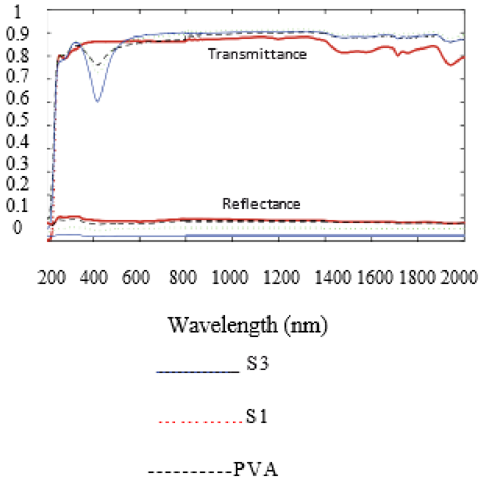


**Figure 4: Spectral illustration of optical transmittance with reflectance**

- Measuring the peaks of plasmon absorption within the absorption spectrum made it easier to find nanoparticles embedded inside polymer films, since this provided a window into their location. A larger absorption peak was seen in the UV region because the energy gap of the PVA polymer decreases with increasing density of Ag nanoparticles inside the structure of the films.
- Produced films used in a variety of applications must meet strict standards regarding their optical characteristics, such as a complex refractive index as well as a dielectric constant within a given wavelength range encompassing UV and near-infrared. Due to its close association with electronic dipole moment of ions as well as the local field inside the material [8, 9], the index of refraction is one of the fundamental characteristics of a substance.
- The degree of variation in the refractive index from one location to another may have a significant role in optical materials. It is crucial to the development of spectrum dispersion devices and the optical communication process [39]. The Wemple-DiDomenico concept of a singular oscillator has been utilized to examine the dispersion of a refractive index within the zone of normal dispersion [43].

$$1/n^2 - 1 = E_0/Ed - 1/E_0Ed\,(h\nu)^2$$

## CONCLUSION

Dispersion for a refractive index within the normal dispersal zone has been analyzed using the Wemple-DiDomenico concept of a single oscillator, ranging in size from 6–12 nm on average, and that the size of these nanoparticles decreases as the laser pulse fluence rises. Adding Ag nanoparticles to PVA causes a rise in the amount of crystal plane at certain angles, as seen by the X-ray diffraction spectrum. Silver is contained in the PVA polymer structure, as seen by the peaks in the FTIR spectra that correlate to molecules and chemical bonding. This may be deduced from the fact that the spectrum has peaks. The energy of the samples' optical bandgap decreases to a lower value as the quantity of silver nanoparticles in the samples increases. Both the refractive index and the dielectric constant go down when there is a higher concentration of silver nanoparticles. Because of the segregation effect, a higher dopant concentration resulted in a lower actual fraction of the optical conductivity. This was the case because increasing the dopant concentration decreased the amount of segregated dopant. PVA and doped PVA both had their refractive indices determined by using the Wemple-DiDomenico model, which allowed for the subsequent determination and explanation of their related dispersion parameters.

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