RESEARCH PAPER

Study the Thermal, Electrical, and Optical Properties for Nano Composite of PVA/PVP Blend Incorporated by Gold and Silver Nanoparticles via Laser Ablation

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ARTICLE INFO

Article History:
Received 20 March 2026
Accepted 13 May 2026
Published 01 July 2026

Keywords:
Laser ablation technique
Gold and silver Nanoparticles
Nanocomposite films
Physical properties
PVA/PVP blend

ABSTRACT

This analytical study of the functional properties of a PVA/PVP polymer blend incorporated with gold (Au) and silver (Ag) nanoparticles prepared via laser ablation technique revealed significant quantitative improvements in thermal, electrical, and optical properties. Thermally, thermal conductivity measurements showed a clear increase in samples containing nanoparticles. Sample silver with polymer blend (AgNPs/(PVA/PVP)) recorded the highest value of approximately 1.25×10^{-2} W/m·°K compared to the Sample pure polymer blend (PVA/PVP), which had a value of about 7.5×10^{-3} W/m·°K. Electrically, the results showed a substantial increase in the dielectric constant of the composite samples (Au, Ag and Au/Ag NPs with PVA/PVP polymer blend) at low frequencies. The electrical conductivity of the composite samples with polymer blend also increased with increased the applied field frequency, exceeding 2.4×10^{-4} S/m at high frequencies (5×10^{6} Hz) for sample Au/AgNPs/(PVA/PVP) and jumped from approximately 0.85×10^{-4} S/m for the pure polymer blend to about 2.5×10^{-4} S/m for sample AuNPs/(PVA/PVP, while it remained low for the pure sample. Optically, the optical transmittance of the composite samples decreased sharply in the visible region, dropping from about 90% for the pure sample to less than 10% at wavelengths around 240-340 nm for all samples. The absorption spectrum also showed a distinct absorption peak around 429 nm, indicating surface plasmon resonance. Furthermore, optical energy gap calculations showed a decrease from about 5.25 eV for the pure sample to approximately 4.5 eV for sample AgNPs/(PVA/PVP) and 4.95 eV for sample Au/AgNPs/(PVA/PVPSuch actual quantitative enhancements unequivocally illustrate the success of the laser process for producing advanced polymeric nanocomposites with enhanced capabilities, making them perfect candidates for use in flexible electronics, optical devices, and energy storage systems. Physical characteristics, PVA/PVP blend, Laser ablation technology, Gold and silver Nanoparticles, Nanocomposite films.

How to cite this article
Habeeb A., Abdallh S., Joban O., Hassan L., Hammoodi F. Study the Thermal, Electrical, and Optical Properties for Nano Composite of PVA/PVP Blend Incorporated by Gold and Silver Nanoparticles via Laser Ablation. J Nanostruct, 2026; 16(3):3405-3412. DOI: 10.22052/JNS.2026.03.033

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INTRODUCTION

The manufacture of polymers combined with nanoparticles is an important part of many medicinal and industrial applications, including photochemotherapy, photocatalysis and the electronics sector. Advanced composites can be developed by mixing PVA/PVP polymers with gold or silver nanoparticles that exploit the biological and optical properties of the materials as well as the stability and flexibility of the polymer to suit a wide range of application requirements [1,2]. The combination of (polyvinyl alcohol) PVA and (polyvinylpyrrolidone) PVP polymers is a promising polymeric system because of their high compatibility, mechanical flexibility and ability to generate homogenous thin films [3]. This blend in combination with laser ablated gold nanoparticles provides nanocomposites with increased characteristics.

Gold nanoparticles are well known for their unique optical characteristics such as surface plasmon resonance as well as their high electrical conductivity and improved thermal stability [4]. There are many studies in this field that combined polymers and metals such as gold and silver nanoparticles, where [5] used the casting method to prepare PEO/PVP films filled with Au NPs. The structural, optical and thermal properties were studied using several techniques and it was found that the optical energy gap, refractive index and Urbach energy differ with the gold concentration.In the field of energy storage, [6] studied the preparation of flexible and insulating nanocomposites (PNCs) from a mixture of PVA/PVP with multi-walled carbon nanotubes (MWCNTs) and gold nanoparticles manufactured in an environmentally friendly way. The results showed electrical insulation stability, capacitance stability and a decrease in the optical energy gap.Also in the field of energy storage, a study [7] demonstrate that the preparation of quaternary compounds of nickel nanoparticles (NiO NPs) with PVA solution and PVP solution with (3-4-ethylenedioxythiophene) by casting method, and through the results it was shown that the addition of nickel oxide nanoparticles increased the dielectric constant and electrical conductivity, which led to improving the storage properties. The improvement of the structural, optical and electrical properties of a mixture of materials (PVA/PVP/Zinc manganite nanocomposites) was studied by [8] and the study identify that the addition of the metal led to an improvement in the energy storage properties.

Laser ablation is an important and environmentally friendly method for preparing nanoparticles and compounds, controlling their size and shape, and creating materials and compounds with improved optical properties and composition [9]. In this study we investigate the thermal, electrical and optical properties of the resulting nanocomposite. The study will also focus on the effect of gold and silver nanoparticle concentration and the laser-based synthesis method on these properties, contributing to a deeper understanding of their applications in optical devices, sensors, or flexible electronics.

Calculations of physical properties

The measured parameters were used to calculate the thermal, electrical and optical properties of the prepared films according to the following standard relations.

Thermal conductivity

The thermal conductivity (*K*) of the samples was determined from the measured heat flow and temperature gradient using the onedimensional Fourier law of heat conduction:

$$K = Q \cdot L / A.\Delta T \quad (1)$$

where *Q* is the rate of heat transfer (W), *L* is the sample thickness (m), *A* is the crosssectional area (m²) and ΔT is the temperature difference across the sample (K).

Dielectric properties

The dielectric constant (ε') was calculated from the capacitance measured by an LCR meter:

$$\varepsilon' = C \cdot d / \varepsilon^{o} \cdot A \quad (2)$$

where *C* is the capacitance (F), *d* the sample thickness (m), *A* the electrode area (m²) and ε^{o} = 8.85×10^{-12} F/m is the permittivity of free space.

The dielectric loss factor (ε'') was obtained from the measured loss tangent:

$$\varepsilon'' = \varepsilon' \cdot \tan \quad (3)$$

AC electrical conductivity

The frequencydependent electrical conductivity (σ_{ac}) was derived from the dielectric loss:

$$\sigma_{ac} = \varepsilon^{o}\ \varepsilon''\ \omega = 2\pi f\ \varepsilon^{o}\ \varepsilon'' \quad (4)$$

where $\omega = 2\pi f$ is the angular frequency and f the frequency of the applied electric field (Hz).

Optical properties

The optical transmittance (T%) and absorbance (A_λ) were directly measured using a UV-Vis spectrophotometer in the wavelength range of 190–1100 nm. The relationship between transmittance and absorbance is given by:

$$A_\lambda = 2 - \log_{10}(T\%) \quad (5)$$

The absorption coefficient (α) at a given wavelength was computed from the absorbance using the following relation:

$$\alpha = 2.303\ A_\lambda/d \quad (6)$$

where d is the film thickness (m). The factor 2.303 arises from the conversion of natural to common logarithm.

For direct allowed transitions, the optical band gap (Eg) was determined using the Tauc relation:

$$(\alpha h\nu)^2 = B\,(h\nu - E_g) \quad (7)$$

Here $h\nu$ is the incident photon energy (eV) and B is a constant. The value of Eg was obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of the curve to the energy axis $(\alpha h\nu)^2 = 0$.

MATERIALS AND METHODS

A First sample pure polymer blend of (PVA/PVP) was prepared using the casting method, employing specially designed molds that were cleaned thoroughly to remove dust and debris. The molds were then placed on a leveled surface. The weight ratio of the pure blend was (PVA: 1.2 g, PVP: 0.8 g) dissolved in 20 ml of distilled water, and the mixture was stirred using a magnetic stirrer for 1 hour at a temperature of 80°C.

Gold and silver colloidal nanoparticles were synthesized separately via pulsed laser ablation in liquid using an Nd:YAG laser (wavelength 1064 nm, pulse duration 10 ns), were introduced into the pure polymer blend. A second sample AuNPs/(PVA/PVP) was prepared by adding 20 ml of gold colloid to the pure blend under laser ablation with an energy of 750 mJ, 3000 pulses, a frequency of 1 Hz, and a height of 7 cm. Under the same conditions, a third sample AgNPs/(PVA/PVP) was prepared using silver colloid. Thus, two composite samples were obtained from the pure blend mixed with silver and gold colloids respectively.

For the fourth sample Au/AgNPs/(PVA/PVP), 10 ml of silver colloid and 10 ml of gold colloid were mixed with 40 ml of the pure polymer blend (PVA/PVP) blend to form a polymeric nanocomposite solution. Thermal, electrical and optical properties

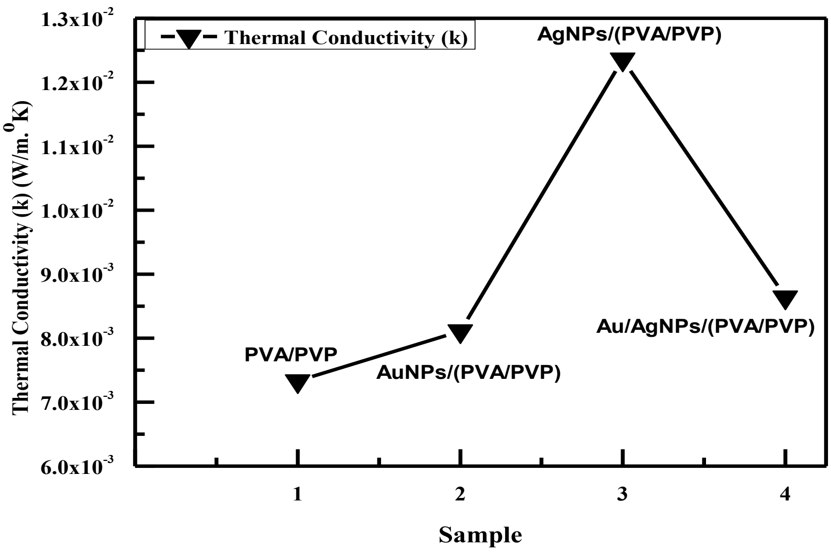

Fig. 1. Thermal conductivity.

were performed on all the prepared samples.

RESULTS AND DISSECTIONS

Thermal properties

Fig. 1 shows a noticeable increase in the thermal conductivity of the samples containing nanoparticles (Au, Ag and Au/AgNPs/(PVA/PVP)) compared to the pure sample (PVA/PVP). The improvement is mainly due to the efficient participation of metallic nanoparticles (gold and silver) that have very high thermal conductivity. These nanoparticles behave as good nano-bridges in polymer matrix (PVA/PVP) and useful in transmission of thermal energy (phonons) and lowering of total thermal resistance of composite material. The work of Alqarni, M. A.et.al (2024) [10] supports this which showed that addition of metallic nanoparticles such as silver into PVP polymer drastically increases the thermal conductivity due to the formation of a heat conducting network. Sample Au/AgNPs/(PVA/PVP) is expected to show the highest value due to a synergistic effect of both metals and an increased density of heat conduction paths.

Electrical properties

The composite samples (Au, Ag and Au/AgNPs/(PVA/PVP)) exhibit a significant improvement of the dielectric constant values at low frequencies (Fig. 2). The explanation is the Maxwell-Wagner-Sillars (MWS) interfacial polarization mechanism. The high polarization and the improved dielectric constant are ascribed to the accumulation of electrical charges at the interfaces between the insulating polymer matrix and the conductive nanoparticles. This conclusion is in agreement with the study of Singh et al. (2019) on PVA/PVP films doped with nanoparticles, where the substantial improvement of dielectric constant at low frequencies was mainly due to the dominance of interfacial polarization. The constant decreases with increasing frequency, since the charges cannot follow the rapid changes of the electric field.

Also the loss factor is similar to the pattern of the dielectric constant with high values of loss factor at low frequencies (Fig. 3). This loss is the electrical energy released as heat in the material by the movement of free charges and leakage currents, particularly in the presence of conductive particles. The peak in the loss curve is an indication of the presence of interfacial polarization resonance at a certain frequency. This has also been observed by SK. S. Basha et al.

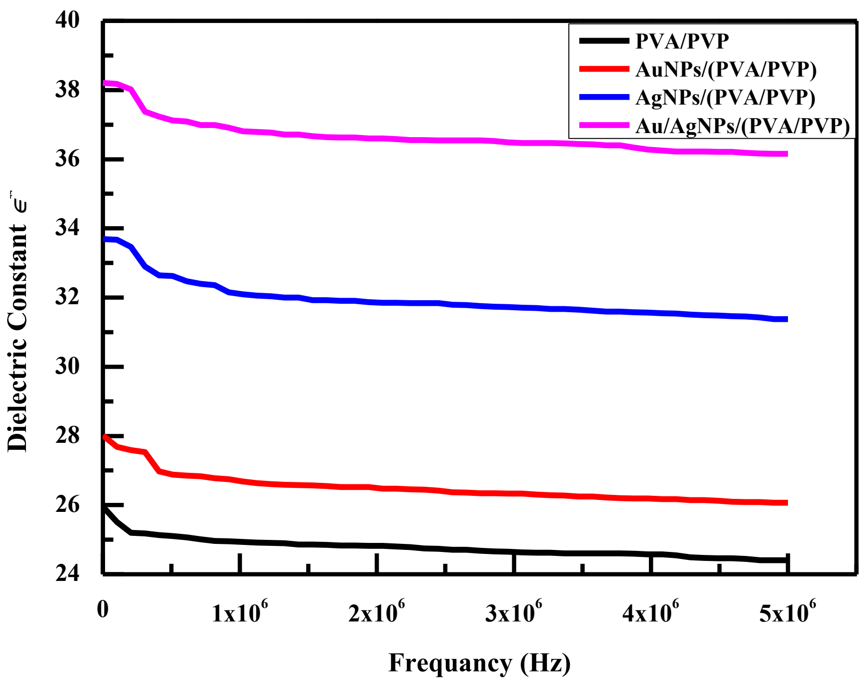

Fig. 2. Dielectric constant vs. frequency.

(2016) [11] in PVA/AgNPs composites.

The electrical conductivity of all samples rises with frequency and the composite samples are clearly better than the pure sample (Fig. 4). This common behavior of polymeric and nanocomposite materials is explained by the Quantum Mechanical Tunneling or Hopping Model of charge carriers between localized conductivity sites. The nanoparticles increase the number of these sites and decrease the distance between them, so that the baseline conductivity is increased and the hopping process is facilitated. This is verified by the research of El Sayed et al. (2015), showing that the conductivity of PVA/PVP/AgNPs composites obeys the power law ($\sigma AC(\omega) \propto A\omega^s$), which is characteristic of hopping conduction mechanisms.

Optical Properties

The optical transmittance in the visible region decreases significantly for the samples containing nanoparticles (Au, Ag and Au/AgNPs with (PVA/PVP)) (Fig. 5). This decrease is a direct result of two main phenomena: Surface Plasmon Resonance

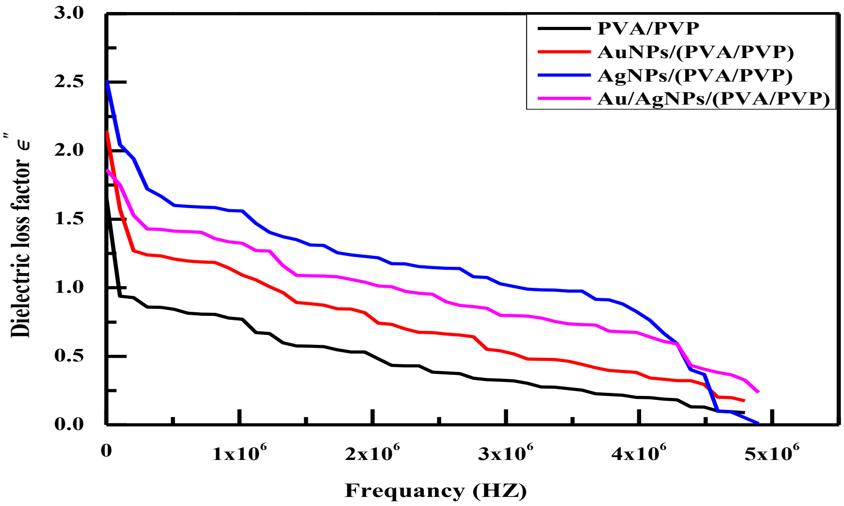

Fig. 3. Dielectric loss factor vs. frequency.

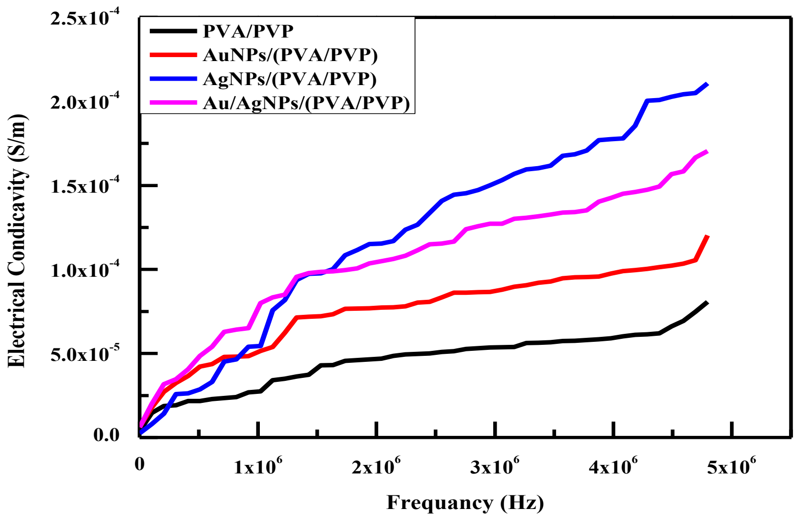

Fig. 4. Electrical conductivity vs. frequency.

(SPR) absorption and scattering. The gold and silver nanoparticles strongly absorb light at specific wavelengths (around 531 nm for gold and 428 nm for silver) due to the oscillation of surface electrons (plasmons). This effect was observed by Islam Shukri Elashmawi and Abdelrhman Anter Menazea et.al [12,13] who reported a sharp decrease in the transmittance of PVA/PVP films upon the addition of silver nanoparticles due to SPR.

The appearance of sharp and distinct absorption peaks in the curves for samples Au, Ag and Au/AgNPs with (PVA/PVP) at the aforementioned wavelengths is clear evidence of the formation of homogeneous and stable metallic nanoparticles within the polymer matrix (Fig. 6). This peak is the characteristic fingerprint of Surface Plasmon Resonance (SPR). This result confirms the findings of Mahmoud Fawzy Abd El-kader and Dhuha H. Al-Obaidi, Olfat A et.al[14,15] where a clear absorption peak appeared around 540 nm in PVA/AuNPs films, indicating successful preparation and the presence of nanoparticles[16,17].

The optical absorption characteristic of PVA/PVP matrix and its nanocomposites with AuNPs, AgNPs and Au/AgNPs were studied using the Tauc plots of $(\alpha h\nu)2$ against photon energy, as displayed in Fig. 7. Well-defined linear patches near the absorption edge confirm that the optical transitions in all samples are of the direct permitted type. It is noticed that the absorption edge is significantly shifted towards lower photon energies due to the integration of metal nanoparticles, which indicates a lowering of the optical band gap compared to the neat PVA/PVP blend. This band gap narrowing can be ascribed to the creation of localized electronic states in the forbidden gap due to strong interfacial contacts between the polymer chains and metallic nanoparticles and to the increased structural disorder due to the dispersion of nanoparticles. Furthermore, different band gap reduction magnitudes obtained in the AuNPs-, AgNPs- and Au/AgNPs-loaded samples are related to the variations in the particle size, distribution and the electronic coupling with the host polymer matrix that influence the density of states and the probability of electronic transitions. These results illustrate the effectiveness of the embedding of noble metal nanoparticles in tailoring the optical characteristics of the polymer blend and improving its applicability for optoelectronic and photonic applications. This behavior is in agreement with

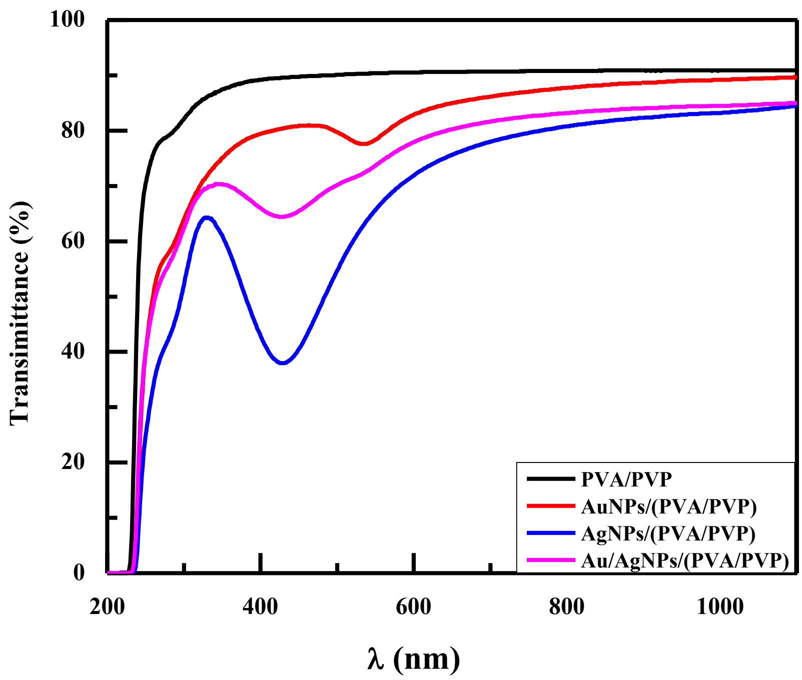

Fig. 5. Transmittance spectrum as a function of wavelength for pure and blended nanocomposites (PVA/PVP).

the Tauc model of direct transitions in amorphous materials and previous works on polymer composites reinforced with metallic nanoparticles of Islam Shukri Elashmawi and Abdelrhman Anter Menazea[12,13] that showed a similar reduction in the energy gap due to the introduction of internal energy levels and increase in the density of electronic states.

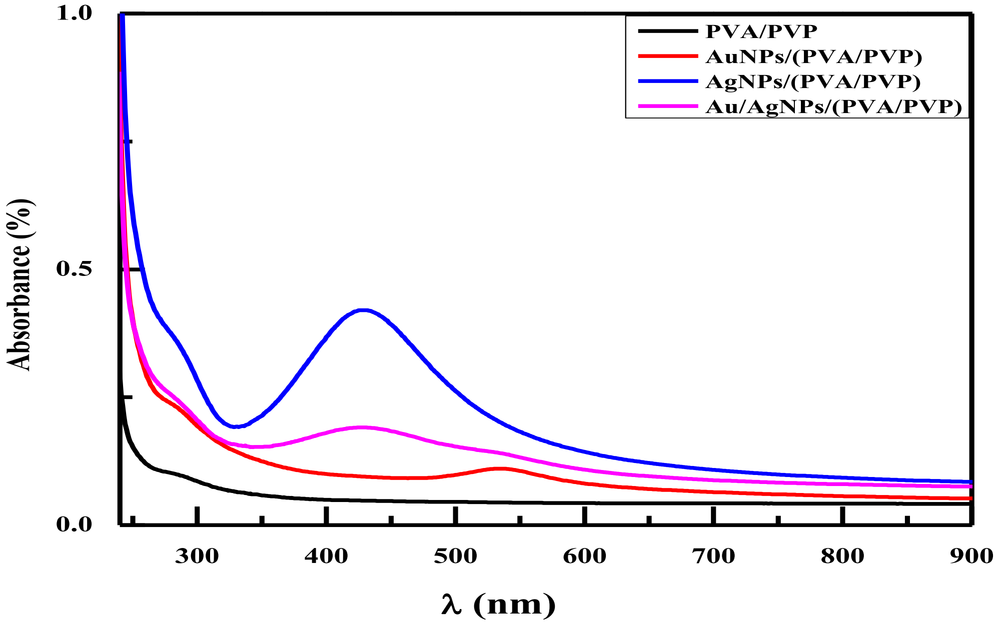

Fig. 6. Absorbance spectrum as a function of wavelength for pure and mixed Nano composites [PVA/PVP].

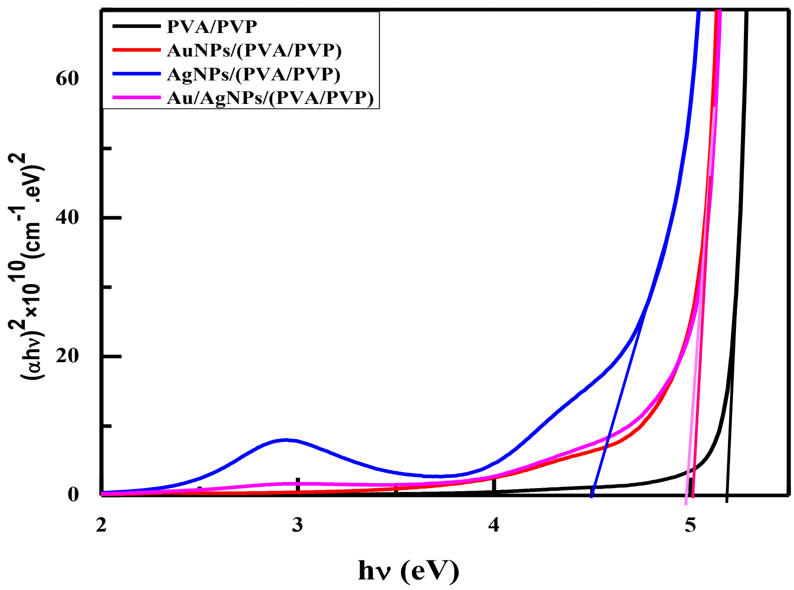

Fig. 7. Optical Band Gap Energy.

CONCLUSION

The thermal, electrical and optical properties of the nanocomposite films were greatly improved by the introduction of Au and Ag nanoparticles into PVA/PVP blend using laser ablation. The phonon transport through the metallic nanoparticles efficiently enhanced the thermal conductivity by ~67% (from 7.5×10−3 to 1.25×10−2 W/m•K). Dielectric experiments show interfacial polarization at low frequencies and AC conductivity up to 2.4x10-4 S/m at high frequencies controlled by hopping conduction. The optical transmittance went below 10% in the UV area, and the unique SPR peaks were seen at 429 nm (Ag) and 531 nm (Au). In the case of hybrid Au/Ag sample the direct optical band gap was reduced from 5.25 eV to 4.5 eV, which shows development of localized states. The present work demonstrates the potential of laser ablation technology as an excellent tool for the fabrication of multifunctional nanocomposites for optoelectronic and energy storage devices.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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