Preparation and optical characterizations of PVA: Ag Nano composite

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Abstract. In this paper, a 3% of polyvinyl alcohol PVA polymer solution was prepared with distilled water. PVA:Ag Nanocomposites were prepared by adding different concentrations of silver (Ag) nanoparticles (3, 6 and 9) %. Pure as well as PVA:Ag nanocomposites films were prepared by drop casting method. The optical properties of PVA: Ag nanocomposite were studied using the absorption and transmittance spectrum measured at wavelength range (200-1000) nm. The optical parameters of the prepared PVA: Ag nanocomposite, such as absorption coefficient, refractive index, and extinction coefficient, as well as the real and imaginary part of the refractive index were calculated as a function of Ag NPs concentration. The results show that the absorption edge is red shifted towards long wavelengths after adding the silver nanoparticles as well as an increment in the optical parameters after adding the Ag nanoparticles. The energy gap was also calculated for all the prepared samples, which were decreased from 4 eV to 1.72 eV with the increase addition of Ag nanoparticles content (3 to 9) %.

Keywords: PVA polymer, nanocomposite, nanoparticles, optical properties

1. Introduction

“Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range (1 nm = 10–9 m)” [1]. Nanocomposites exhibited new technology besides business opportunities for all industry sectors, also it is environmentally friendly [1]. Generally, the nanocomposite class of organic/inorganic materials is a fast developing area for research. [2]. The combination of nanosized inorganic particles and polymer into a single material has fan-out a new zone in materials science that has extraordinary outcomes in the development of multifunctional substances[3]. The application of materials in nanoscale and nanocomposites which contain nanoparticles is an emanated area of nanoscience and the technology. The nanoparticles have an exceedingly surface: volume ratio. That so they usually show unique considerably and different chemical, physical, and biological properties comparing to their macro scaled counterparts [4]. Polyvinyl alcohol (PVA) is a polymer that has backbone of carbon chain attached with hydroxyl groups. PVA is not toxic, soluble in water synthetic polymer, which is used widely in the polymer blends because of its good chemical and physical properties, forming film with excellent characteristics,
emulsifying capability, and biodegradable, no carcinogenic and biocompatible qualities. These peerless characteristics enable PVA polymer in applicability in the pharmaceutical fields, surgical structures material, drug coating agents, and cosmetic industries [5]. It is well finder that polymers, which act as dielectric materials, are sterliney host matrices for encapsulated nanoparticles metal like gold, silver, copper, and so on, as well as they act both as reducing besides capping agents and provide stability environmentally and chemically. That embedded nanoparticles NPs inside the polymer matrix will affect the characteristics of the host itself. Particularly, the polymer and the metal hybrid like polymer: Ag nanoparticles composites is overgrown functional materials in several scopes like mechanical, optical, electrical, antimicrobial, and thermal properties [6].

2. Experimental Part

In this paper, the polymer solution was prepared by adding the polymer in powder form to distilled water, and the solution was placed on a magnetic stirrer device for two hours with a temperature of 30 °C. After the end of mixing, the solution was passed on filter paper to get rid of the sediments suspended in the solution and get a clear solution. Silver nanoparticles were added to the solution at different concentrations of 3, 6, and 9 % to study their effect on the optical properties of the polymer. PVA:Ag Films were prepared by drop casting method on glass substrate cleaned in three steps by using HCl, ethanol, acetone and ultrasound device. The optical properties of pure PVA and doped with Ag nanoparticles were studied by using the UV-VIS spectrophotometer in the range (200-1000) nm.

3. Results and Discussions

The optical absorption retrofitted useful information about band structure of solids, electronic, and phononic states. During the processes of optical absorption, the incident photon with certain energy excites an electron from the lower state to occupy a position in a higher energy state. By investigating the changes in transmitted radiation, the types of possible transitions for an electron can be concluded. The fundamental (main) absorption indicates to band-to-band (or to excitation) transitions. The main absorption shows by a fast elevation in absorption, which named as absorption edge which is used to determine the optical energy band gap [7].

When a beam of light affecting the material surface, part of the incoming beam which that not reflected by the material will be transmitted or absorbed through the material. Lambert-Beer law clear that the fraction of light ray that is absorbed is a function of the thickness for the materials also the way that the photon interacts with materials structure [8].

\[ I = I_0 e^{-\alpha x} \]  

Whereby, (I) is the intensity of light beam that coming out of the material, (I_0) is the intensity of the incident light beam, (x) is the path where the photon moves, and (\alpha) is the absorption coefficient, which is a material characteristic.

Fig.1 shows the absorption spectrum of prepared films as a function of wavelength. The absorption increased with increasing the concentration of Ag nanoparticles. There is a relation between the position and shape of the spectral absorption peak with particle size and the morphology of the metal nanoparticles, so the spectral analysis will be the effective method to explain the spectral properties in metal nanoparticles [8]. The absorption peaks were between (392 and 477) nm where the maximum value was at 415 nm, which is the exemplary Plasmon Resonance Band (PRB) of AgNPs [9]. The peak and the location show that the ions of Ag⁺ in AgNO₃ solution were successfully reductive to AgNPs.
Fig. 1. Absorption spectrum as function of wavelength for pure and doped PVA

From Figure 1, one can see that the absorption increases generally with increasing the ratio of dopant. This increasing explained the existence of interaction between Ag nanoparticles with PVA and getting a new structures for PVA:Ag composites. The increasing in the ratio of Ag nanoparticles leads the edge of UV radiation absorption to zaps towards region of longer wavelength for all the samples especially for the concentration of 3 and 6% weight percentage of Ag[10].

The coefficient of proportionality in equation (1) is defined as absorbance coefficient, and it a measure to how strong samples absorbs light at a specific wavelength [11].

The absorption coefficient (α) can be determined by the equation [12]:

$$\alpha = \frac{2.303 \cdot A}{t}$$

Where (A) is absorbance and (t) is thickness. The absorption coefficient (α) of PVA: Ag films is important to determine the type of electronic transition, if (α>10^4) transition is direct where if (α≤10^4) transition is indirect [12]. Fig 2 shows the dependence of the absorption coefficient on wavelength for the samples before and after doping which shows increasing in absorption coefficient with increasing the concentration of Ag nano particles. Because the PVA polymer is a good insulating material and has low conductivity [13] hence the absorption coefficient is very low and the transition is indirect.

Fig. 2. Absorption coefficient as function of wavelength for pure and doped PVA.

The law of energy conservation state that lights ray is partially transmitted, absorbed and reflected as it shown in equation (3). Reflectance (R) can be calculated from the energy conservation law [14].
R + T + A = 1 ........................................(3)

Besides that the transmission is very low but the reflectivity is very high compared with absorption and transmission and this is shown by Fig. 3 and 4.

![Graph of transmittance as function of wavelength for pure and doped PVA](image1.png)

Fig. 3. Transmittance as function of wavelength for pure and doped PVA

The clear transparency of visible light is a particularly trait of the inorganic/polymer nanocomposite especially at dipped concentration, when the aggregation of NPs is constraining. The observation of irregularity in UV absorption spectrum by the nanocomposites of high loading Ag nanoparticles may be because of the elastic scattering of the arrival UV light upon the samples. This could be happened when the size of particles are smaller than wavelength $\lambda_{UV}$ (190-400 nm) [10].

![Graph of reflectivity as function of wavelength for pure and doped PVA](image2.png)

Fig. 4. reflectivity as function of wavelength for pure and doped PVA.

The most significant optical constant is the refractive index which depends on the wavelength of the electromagnetic wave. The electromagnetic wave lost some of its energy during the propagation throw a medium. Knowing that the real part $n$ is the refractive index and the imaginary part $K$ is the extinction coefficient [15]. Refractive index of an optical or dielectric medium ($N$) can be calculated by dividing the light velocity in vacuum $c$ on its velocity in the medium $v'$ ($N = c/v'$). Complex refractive index $N$, can be obtained by equation (4) [16].
N=n+ik………………………………………………(4)

Equation (5) can be used to calculate the refractive index n [17].

\[ n = \sqrt{\frac{4R-K^2}{(R-1)^2}} \left( \frac{R+1}{R-1} \right) \]  

……………………………(5)

The complex dielectric function, \( \varepsilon \), consists of the real part \( \varepsilon_1 \) and imaginary part \( \varepsilon_2 \) as it shown in equation (6):

\[ \varepsilon = \varepsilon_1 - i \varepsilon_2 \]  

…………………………………………………..(6)

\( (n-ik)^2 = \varepsilon_1 - i \varepsilon_2 \)  

……………………………………(7)

\( \varepsilon_1 = n^2 - k^2 \)  

…………………………………………………..(8)

\( \varepsilon_2 = 2nk \)  

…………………………………………………..(9)

Fig.5. refractive index as function of wavelength for pure and doped PVA.

Fig.6. real part of refractive index as function of wavelength for pure and doped PVA.
Fig. 7. Imaginary part of refractive index as function of wavelength for pure and doped PVA.

The dependences of real and imaginary parts on the photon energy for all samples were clear in Figs. 6 and 7. Figs. 6 and 7 signifies that $\varepsilon_r > \varepsilon_i$ because the mainly depends on $n^2$ according to equation (8) and that is way because the extinction coefficient (K) was extremely small so it could be neglected. The imaginary part depending on extinction coefficient is due to the equation (9) because the value of the refractive index is very small [13]. The real and imaginary parts in Fig. 6 and 7 show that an increasing after doping, which indicates that the samples were not have similar structure. For this the change in the concentration of doping lead to change in chemical composition for polymer [12].

The optical conductivity of a material is the frequency response of the material when it is irradiated by light [18]. The optical conductivity ($\sigma_{\text{opt.}}$) is mainly based on the optical parameters such as optical absorbance, reflectance and absorption coefficient. The refractive index ($n$) with absorption coefficient ($\alpha$), were used to obtain the optical conductivity ($\sigma_{\text{opt.}}$), using the following relation [19]:

$$\sigma_{\text{opt.}} = \frac{\alpha n c}{4\pi} \quad \text{.............................................. (10)}$$

Fig. 8. optical conductivity as function of wavelength for pure and doped PVA.

The determination of optical energy band gap will be applied according to following equation [20]

$$\alpha E = B(E-E_g)^\gamma \quad \text{............................................. (11)}$$
Where \((B)\) is a constant, \((r)\) is an empirical index, and it is equal to 2, 3, 1/2 and 3/2 relied on the nature for electronic transition responsible of the absorption. The drawing for the value of product of absorption coefficient by the photon energy \((\alpha h\nu)^{1/2}\) via photon energy \((h\nu)\) at room temperature, induction for liner portion of this curve to a point \((\alpha h\nu)^{1/2}=0\) gave the value of the optical energy band gap to films of pure PVA and doped with Ag NPs which can be considered as an evidence for indirect transition. The value of energy gap are showed in table (1).

### Table (1) Energy gap values for pure and doped samples.

| Samples       | Energy gap (eV) |
|---------------|-----------------|
| Pure PVA      | 4               |
| PVA:Ag(3%)    | 2.11            |
| PVA:Ag(6%)    | 1.95            |
| PVA:Ag(9%)    | 1.75            |

The Ag doping is found to affect in strong manner on the optical energy gap of the polymer films, a decreases in the energy gap with increasing of Ag concentration maybe due to an increases in structural disorder of the polymer films and increases of the density of localized states in the band gap, which causes a shift optical energy gap to lower values of photon energy.

The absorption coefficient \((\alpha)\)and the extinction coefficient \((K)\) can be involved by[20].

\[
K = \frac{\alpha^2}{4\pi} \tag{11}
\]

The extinction coefficient \((k)\) behaves just like the absorption coefficient\((\alpha)\) because they are joined by previous relation(7). From Fig.5 observe that the increases in absorption coefficient cause increasing in extinction coefficient values.
4. Conclusion

The optical constants of PVA as (absorption, transmission, refractive index, absorption coefficient, reflectance, extinction coefficient, and real & imaginary dielectric constant) were changing with increasing of concentrations of Ag nano particles. The energy gap of PVA decreases with increasing of concentrations of Ag nano particles also the transition was indirect.

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