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Evaluation of optical parameters and structural variations of UV irradiated (PEO/PVP)/Au polymer nanocomposites

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ABSTRACT

Gold nanoparticles (AuNPs) were successfully synthesized using *Chenopodium murale* (*C. murale*) leaf extract. Polymeric matrix of polyethylene oxide (PEO)/ polyvinyl pyrrolidone (PVP) doped with different concentrations of AuNPs were prepared via casting method. Fourier transform infrared spectroscopy (FT-IR) was used to retrace variations in the main structural building units within polymeric nanocomposites before and after exposing to different irradiation times of UV lamp type C. FT-IR analysis reveals an induced changes in chemical structure attributed to the doping level and irradiation times. Ultraviolet/visible optical absorption spectra (UV/vis.) confirm the presence of AuNPs in the nano scale as a consequence of observing band at 420 nm attributed to the surface plasmon resonance (SPR) of AuNPs. Optical parameters (i.e. optical energy gap E_g , refractive index n) for prepared polymeric nanocomposite before and after irradiation process were calculated and interpreted.

Keywords: UV irradiation; PEO, PVP, AuNPs; FT-IR; UV/Vis optical absorption.

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INTRODUCTION

The usage of metallic nanoparticles (NPs) as dopant to the polymeric matrix is due to the strong current interest in development of new materials for specific applications. Polymer nanocomposites (NCs) have been found successful in various applications such as non-linear optics, organic batteries microelectronics and sensors [1]. The obtained properties of NCs are usually simple combination of the properties of inorganic and organic components, although the appearance of novel characteristics can exist because of synergistic effect [1]. Thus, it is important from a fundamental and practical point of view, to understand the effects of embedding of NPs on the physical and chemical properties of the NC [2].

With the advent of nanotechnology and nanoscience, gold (Au) NPs have turned out to play an important role as they have the potential to behave as building blocks for putting nanotechnology to practical use. Nobel metal nanostructures, especially gold NPs, have recently received much attention due to their unique catalytic, optical and electrochemical properties that make them suitable materials for potential applications in various fields. Gold NPs have been found to play an important role in several catalytic, gas sensing processes and nanomedicine applications [1, 3, 4]. Nanocomposites prepared from metal nanoparticles, especially noble metals like Au, show a strong surface plasmon resonance (SPR) because of the collective oscillation of the valence electrons. The appearance of SPR makes Au NPs interesting candidates for potential applications in photovoltaic devices, imaging, optical filters, plasmonic devices, sensors and surface-enhanced spectroscopy [5, 6].

The blend between the polymers is a simple method to have new materials. The samples produced by blending of two or more polymers usually provide modified physical properties compared to the individual component of blend [7, 8]. Polyethylene oxide (PEO) is a semi-crystalline polymer which has both crystalline and amorphous phases at room temperature due to its high regularity of its structural unit. PEO is a linear polymer with etheric linkages and can solvate different types of inorganic salts. But, a high ordering of PEO structure restricts its conductivity so it must be coupled with amorphous polymer. PEO-based polymer electrolytes have been extensively studied as potential candidates for different electrochemical devices, such as fuel cells, batteries, supercapacitors, sensors, hybrid power sources, etc [9].

Polyvinyl pyrrolidone (PVP) is an amorphous polymer, which can allow faster ionic mobility compared with other semi-crystalline polymers having low scattering losses for different applications. Because of the existence of carbonyl group (C=O) in the PVP side chains, it produces a variety of complexes with different inorganic salts. Due to the PVP solubility in water which is a common solvent of PEO, so it is favorable to eliminate phase separation in the polymers of blend [10-12]. Also, PVP is a suitable capping agent for nanoparticles (NPs) due to the existence of both carbonyl group ($>C=O$) and $>N-$ that make anchoring for NPs and having long chain [13, 14]. The interaction/complexation of PEO/PVP blend with different inorganic salts has been studied by many authors [11, 12, 15-18]. However, to the best of our knowledge, there have been no reported studies to date on the preparation of PEO/PVP/Au nanocomposites followed by UV irradiation process.

Various physical properties for polymeric materials are modified and improved after subjecting to different irradiation techniques [19]. An irradiation process tends to damage polymers significantly by ionization and electronic excitation. It may lead to the creation of free radicals and can also cause formation of latent tracks in the polymers, intermolecular cross-linking, main chain scission, creation of triple bonds and unsaturated bonds. Free radicals are existed because of chemical changes initiated by ionizing radiation in the polymers. These may provide modifications such as formation of chemical bonds between different molecules; inter molecular cross-linking and irreversible cleavage of bonds (scission) in the main chain. The nature of the defects and the relative radiative sensitivity of different polymers depend on the properties such as the molecular weight and composition, on the mass and energy of the impinging ion and also on the environmental conditions during irradiation. Thus, the related physical properties of the polymers can be modified in a controlled way by easy to control parameters like the irradiation dose, irradiation time, energy and ion fluence [19, 20].

The main aim of this study is to investigate the structural and optical properties of PEO/PVP/Au nanocomposite films before and after exposing to UV light radiation at different times (0.5, 1, 2 and 4 h). The obtained samples are suitable in optical applications such as filters, optical coatings.

EXPERIMENTAL

Materials

PEO was supplied from (ACROS, New Jersey, USA with $M_w \approx 40,000$ gm/mol) and PVP was obtained from (SICO Research Laboratories Pvt. Ltd, Mumbai, India with $M_w \approx 72,000$ gm/mol). Both PEO and PVP polymers were used as basic polymeric materials. The used solvent was double distilled water.

Preparation of PEO/PVP/Au nanocomposite films and irradiation process

The preparation mechanism for biosynthesized Au NPs was listed in details in our paper [4]. The films of polymer blend were prepared by solution cast technique. PEO /PVP quantity (70/30 wt.%) was dissolved in double distilled water separately and then the polymer blend solution was stirred continuously at room temperature until a homogenous viscous liquid was formed. Further, different concentrations of prepared Au NPs (0.3, 0.6, 1.2 and 2.40 mg) were added to the PEO/PVP polymer solution under continuous stirring for 24 hrs. Finally, viscous solutions were poured into polypropylene dishes and the common solvent was allowed to evaporate slowly at room temperature for two days to have free-standing polymer films at the bottom of dishes. The obtained films were stored in highly evacuated desiccators to avoid any moisture absorption. Film thickness in the range of 0.07–0.09 mm was obtained.

The light irradiation was performed using a UV lamp type (Phillips UV lamp, Koninklijke Philips Electronics N.V., Amsterdam, Netherlands) of wavelength of 254 nm. The thermal effects of the UV lamp were compensated by regulating the sample temperature to be fixed around $25 \pm 1^\circ\text{C}$.

Measurements

FT-IR absorption spectra were carried out for the prepared samples using Mattson 5000 FTIR spectrometer (Mattson Instruments, Inc., W1, USA) in the range of 4000 to 400 cm^{-1} at a resolution of 8 cm^{-1} at 25°C . Ultraviolet/visible (UV/Vis.) absorption spectra were measured in the wavelength range 200 – 1000 nm using spectrophotometer type (V-570 UV/VIS/NIR, JASCO, Japan).

RESULTS AND DISCUSSION

Fourier transform infrared analysis FT-IR

FT-IR spectroscopy has been confirmed to be a very strong technique to detect the intermolecular interaction between the polymer blend and its interaction with AuNPs. Fig. 1 shows the FT-IR spectra of pure PEO and PVP and pure blend PEO/PVP (70/30 wt.%) while Fig. 2 depicts FT-IR spectra for pure blend (PEO/PVP), (PEO/PVP) blend/ nanocomposites and its UV-irradiation at different times in the spectral range 4000 – 400 cm^{-1} .

FT-IR spectra for both PEO and PVP polymers are coincidence with those reported previously [10, 11, 15, 21]. From Fig. 1, PEO spectrum has sharp band at 2885 cm^{-1} is assigned to C-H asymmetric stretching of methylene group. CH_2 scissoring and CH_2 asymmetric bending are clearly observed at 1461 cm^{-1} and 1345 cm^{-1} , respectively. The relatively small band at 1240 cm^{-1} is due to CH_2 symmetric twisting. The absorption band located at 1110 cm^{-1} corresponds to C-O-C stretching mode. The bands at 956 and 840 cm^{-1} are due to CH_2 asymmetric rocking motion with some contribution from C-O stretching. The spectrum of pure PVP display a broad band at about 3425 cm^{-1} is corresponded to the stretching vibration of hydroxyl group (OH) of PVP and can be considered a source of Hydrogen bond in blending with PEO. The absorption band located at 2955 cm^{-1} correspond to CH_2 asymmetric stretching vibration. The vibrational band at about 1660 cm^{-1} corresponds to C=O stretching of PVP. Very small absorption band at about 1500 cm^{-1} is referred to the characteristic vibration of C=N (pyridine ring). C-H bending of CH_2 or OH bending is located at 1460 cm^{-1} while, the band at 1435 cm^{-1} is assigned to CH_2 scissoring vibrations. The vibrational band observed at 1290 cm^{-1} may be attributed to CH_2 twisting or wagging of PVP.

FT-IR absorption bands positions and their assignments for pure blend are listed in Table 1. The spectrum of pure blend shows both (C-O-C) group of PEO and (C=O) group of as shown in Fig. 1. This implies

that components of blend, PEO and PVP polymers, are miscible. With respect to the interaction nature between PEO/PVP, it's supposed that the quasi hydrogen-bonding exists because of the fact that the hydrogen atoms of PEO possess acidity and the oxygen atoms of carbonyl group of PVP offers electronegativity. A comparison of FT-IR spectra of pristine PEO and PVP with the pure blend spectrum clearly confirms the existence of the hydrogen bonding. The change in the intensity and decrease of broadness of C=O group of PVP exist when it blended with PEO. This observation can be explicated the effect of forming hydrogen bond between the carbonyl group of PVP and the methylene group of PEO. Also, intensities of the most absorption bands in the spectrum of pure blend sample such as OH, CH₂ and C-O-C stretching vibrations are changed irregularly compared to their values in individual polymers.

From the spectra of PEO/PVP/Au nanocomposites in Fig. 2, doping the polymeric matrix of PEO/PVP blend with Au NPs causes largely changes and effects on its functional groups. The intensity and broadness of Hydroxyl group increases after adding Au NPs. The broadness of both CH₂ stretching vibration at 2880 cm⁻¹ and C-O-C group at 1110 cm⁻¹ increase after doping associated with a decrease in its intensity. This means that there is a strong interaction between ether group of PEO in blend and Au NPs and results in a distortion in crystalline region in blend. Also, the intensity of absorption bands at 956 and 845 cm⁻¹ referring to the helical structure of PEO increases after adding Au NPs. The same behavior is also occurred for absorption band in region 1500-1200 cm⁻¹. Also, the broadness of carbonyl group of PVP is increased due to continuous doping. This observation confirms that there is a strong interaction between Au NPs and C=O. The pyrrolidinone adsorbs Au colloid surface preferably via the non-bonding electrons of C=O [14, 22].

As UV-irradiation affects the polymeric nanocomposites and exposing time increases from 0.5 to 1 h, the intensity of OH group in the spectra of all nanocomposites is decreased, except for blend/1.2 mg Au NPs, and absorption band due to C-H asymmetric stretching of methylene group at 2880 cm⁻¹ is not slightly affected due to the irradiation process as shown in Fig.3, Fig. 4, Fig.5 and Fig. 6. But for blend/ 1.2 and 2.4 mg Au NPs, C-H asymmetric stretching is largely affected and its shape, broadness and intensity are changed according to the irradiation time as shown in Fig.5, and Fig. 6. As the irradiation time increases from 0.5 to 1 h, the shape of carbonyl group of nanocomposites becomes more organized associated with an increase in its intensity and a decrease in its broadness. The same behavior is also occurred for ether group of nanocomposite films. This means that there are structural rearrangements in the chain of PEO/PVP/Au nanocomposite in this exposing time of UV radiation.

With continuous increasing UV-irradiation time up to 4 h, the intensity of carbonyl group decreases and its broadness increases. The intensity of absorption bands in 1500-800 cm⁻¹ region is largely decreased. This is because of formation of chain scission/cross-linking through UV-irradiation at high exposing time intervals that leads to an increase in the amorphous region content within the polymeric matrix. These structural modifications and changes in the polymeric matrix of PEO/PVP after embedding Au NPs and moreover, exposure to UV light radiation, are in agreement with UV/Vis. analysis.

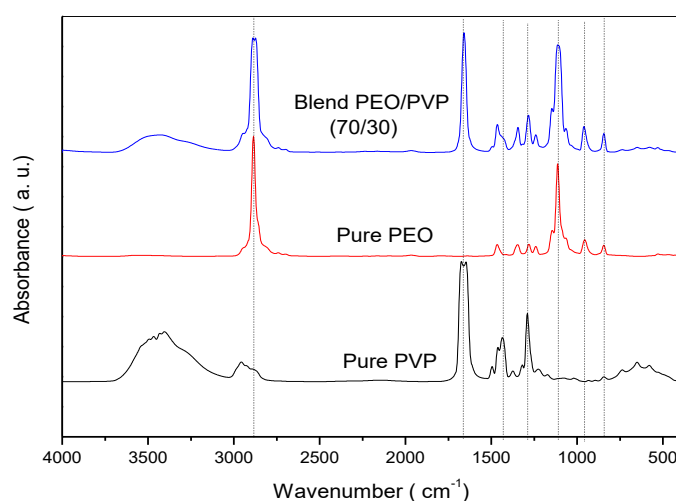


Figure 1: FT-IR spectra for pure PEO, pure PVP and pure blend PEO/PVP.

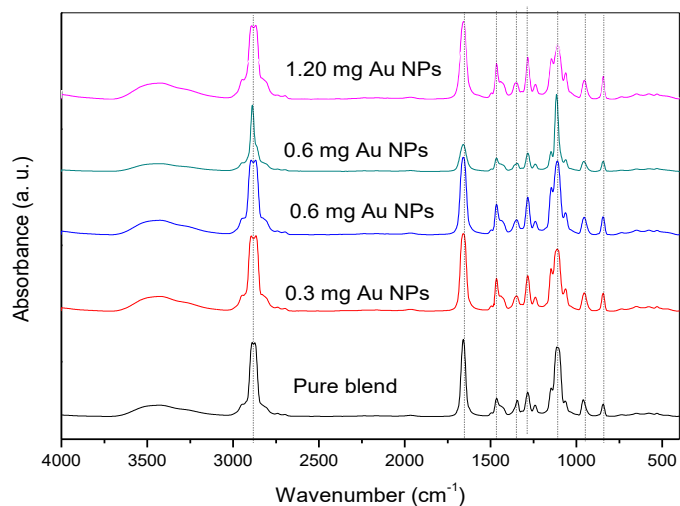


Figure 2: FT-IR spectra for pure blend and its nanocomposites with different concentrations of Au NPs (0.3, 0.6, 1.2 and 2.4 mg)

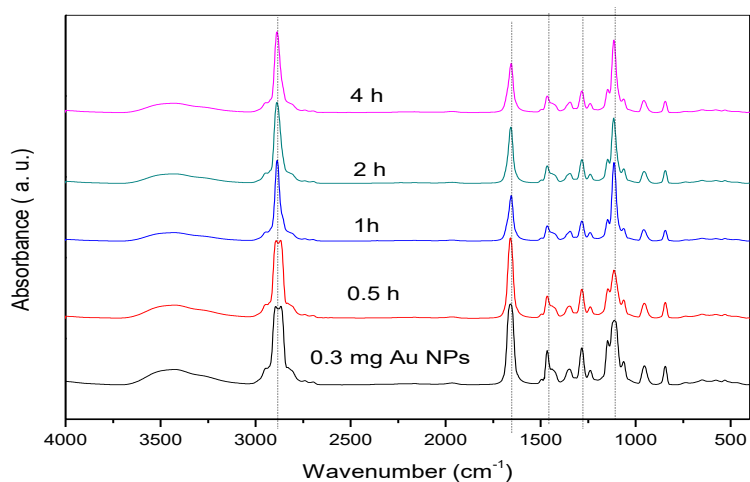


Figure 3: FT-IR spectra for blend/0.3 mg Au NPs before and after UV- irradiation at different time intervals (0.5, 1, 2 and 4 h).

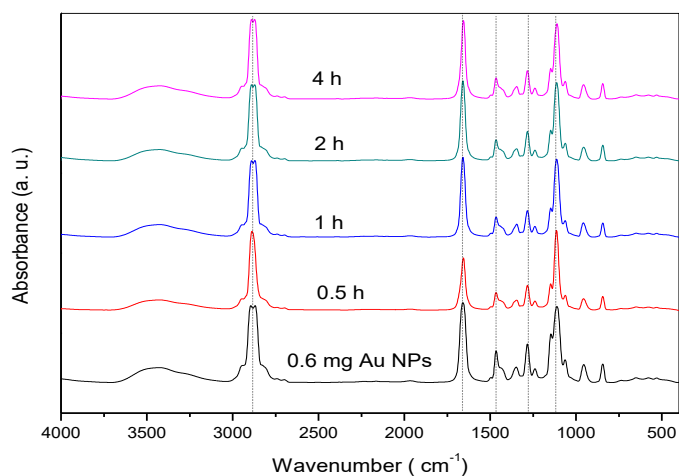


Figure 4: FT-IR spectra for blend/0.6 mg Au NPs before and after UV- irradiation at different time intervals (0.5, 1, 2 and 4 h).

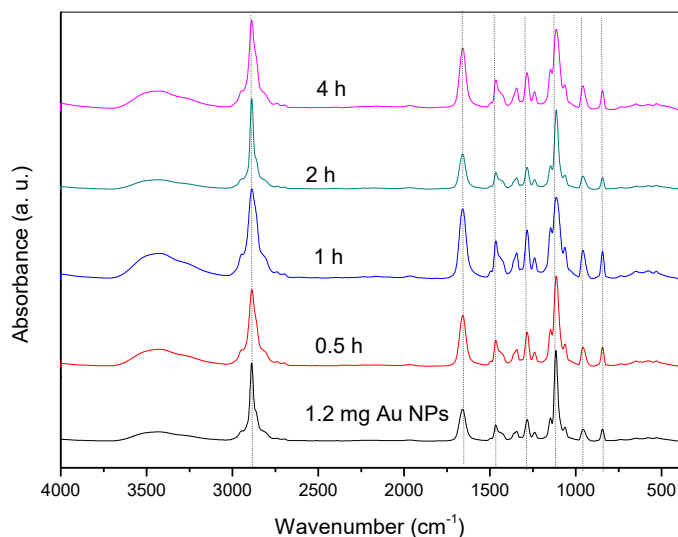


Figure 5: FT-IR spectra for blend/1.2 mg Au NPs before and after UV- irradiation at different time intervals (0.5, 1, 2 and 4 h).

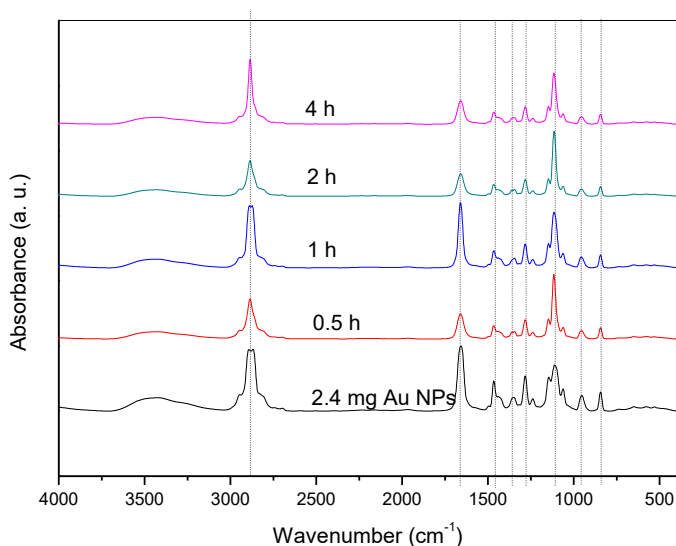


Figure 6: FT-IR spectra for blend/2.4 mg Au NPs before and after UV- irradiation at different time intervals (0.5, 1, 2 and 4 h).

Table 1: Assignments of the FT-IR characterization bands of pure PEO/PVP (70/30 wt.%) blend. Pure PEO/PVP blend

Wavenumber (cm ⁻¹)	Assignment	Ref.
3435	-OH stretching	[22]
2880	Asymmetric C-H stretching of CH ₂	[11, 23, 24]
1655	Symmetric & asymmetric of C=O	[11, 12, 21-23]
1465	CH ₂ scissoring	[11, 12, 23]
1345	CH ₂ asymmetric bending (Crystalline)	[11, 12, 23]
1285	CH ₂ wagging or twisting	[11, 12, 21, 23]
1240	CH ₂ symmetric twisting	[11, 12, 23]

1145	C-C stretching	[11, 23]
1110	Symmetric & asymmetric C-O-C stretching (Amorphous)	[11, 12, 23]
1068	-OH bending	[25]
960	C-O stretching with some CH ₂ asym. rocking	[11, 23]
845	CH ₂ rocking in PVP and with some C-O stretching in PEO	[11, 23]

Ultraviolet and visible analysis UV/Vis.

Figure 7 shows the UV/Vis. absorbance spectra for two basis polymers (PEO and PVP) and pure blend. The spectra show a sharp absorption edge which confirms its semicrystalline nature where it has nearly zero absorption in the wavelength region (300-1000 nm). Figure 8 displays UV/Vis. absorption spectra for pure blend (PEO/PVP) and its complexes with different contents of Au NPs. From Figure 8, the spectrum of pure blend shows absorption peak at 215 nm which may be attributed to $n \rightarrow \pi^*$ (R- band) because of containing single bond; so it would be thought to absorb radiation only in the far UV region. The spectrum of prepared Au NPs shows absorption peak in the visible region at $\lambda_{\max} = 531$ nm. The appearance of this peak is because of the surface plasmon resonance (SPR) of Au NPs [6, 26, 27]. The appearance of this band may be related to the formation of Au NPs by *C. murale* leaf extract.

When Au NPs are added to the polymeric matrix of PEO/PVP, one can see that there is a strong increase in the absorbance in the UV/Vis. regions where the absorption coefficient of doped sample increases and its absorption edge moves toward longer wavelength. The red shift of the absorption edge in the doped PEO/PVP indicates the complexation between the AuNPs and the polymer blend. Also, it reflects the change in the optical energy gap, which arises because of the change in crystallinity within the polymer matrix [21, 28]. The dramatic enhancement in absorption are observed to be in coincidence with the color change of PEO/PVP sample which changes from transparent for pure film to pinkish-red for the nanocomposite sample. The position of SPR peak is red shifted to $\lambda_{\max} = 542.82$ nm as compared to Au NPs in colloidal solution. This red shift in the position of SPR peak may be because of wider size distribution of the NPs within the polymeric matrix.

As the exposing time of UV-irradiation process increased from 0.5 to 1 h, the intensity of SPR peak for all nanocomposites is largely decreased and its absorption edge for irradiated sample is shifted toward shorter wavelengths as shown in Figures 9, 10, 11 and 12. This observation may be understood that UV light cause structural rearrangements in the polymeric matrix where the chains of polymer acquire mobility on the experimental time scale. As the polymer chains relax, stresses are released and obtain ordered structure with high degree of crystallinity. This gives the ability for Au NPs to move again, allowing crystals to agglomerate and/or aggregate which in turn reduces the absorption band intensity [29]. On the other hand, the increased intensity of SPR peak is related to the increase of Au NPs concentration at high irradiation time intervals, for example blend/1.2 mg Au NPs/ 4 h, and its position is shifted to shorter wavelengths, to 534.71 nm, as in blend/2.4mg Au NPs/ 4 h, implying the formation of smaller particles due to its quantum size effect which is also confirmed by FT-IR analysis. This observation is due to cross-linking/chain scission within the polymeric matrix of PEO/PVP/Au nanocomposite. With increasing time intervals for UV-irradiation process, the individual macromolecules of PEO/PVP/Au nanocomposites are assumed to be cross-linked with each other, giving rise to a three dimensional network. The cross-linking of polymer molecules results in a significant increase in molecular mass. This in turn will increase the amount of polymer chains surrounding the nanoparticle. The more polymer chains there are, the more they prevent the growth and/or the aggregation of the Au NPs.

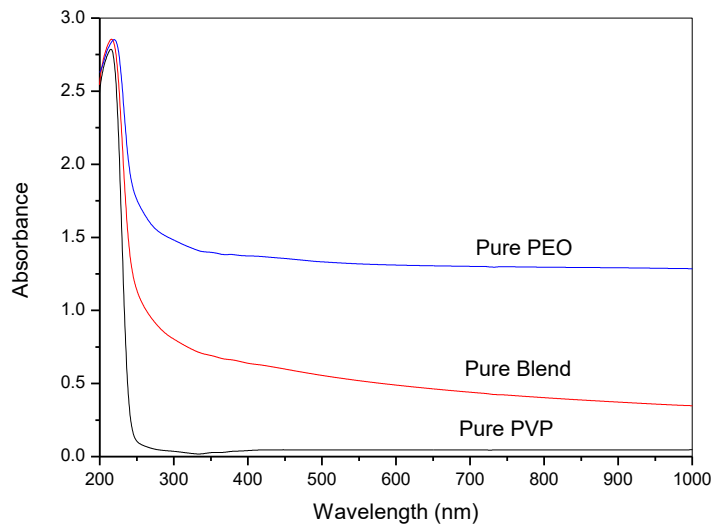


Figure 7: UV/Vis. spectra for pure PVP, pure PEO and pure blend PEO/PVP (70/30 wt.%)

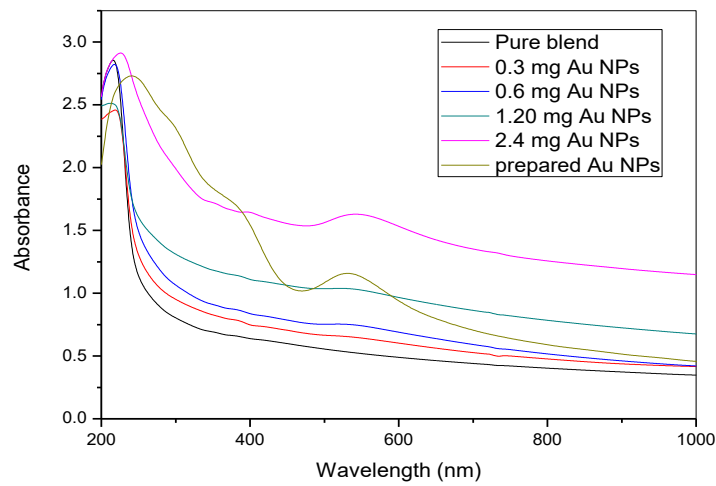


Figure 8: UV/Vis. spectra for pure blend, its complexes with different concentration of Au NPs and prepared Au NPs.

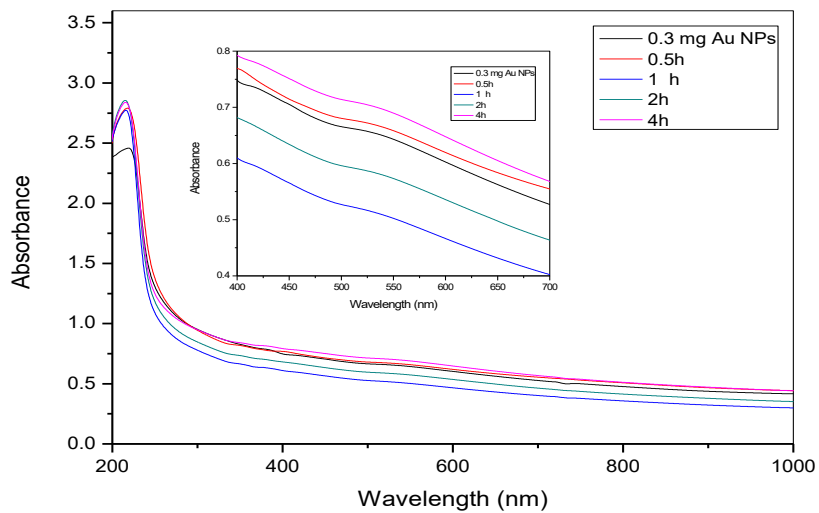


Figure 9: UV/Vis. spectra for blend/0.3 mg Au NPs before and after exposing to UV radiation at different time intervals (0.5, 1, 2, 4 h).

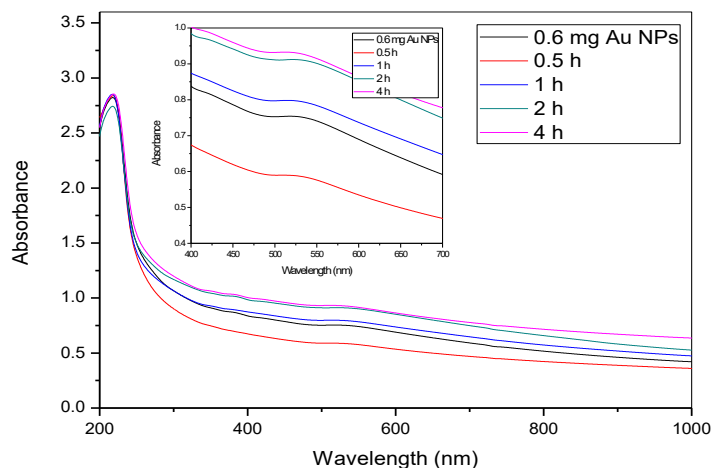


Figure 10: UV/Vis. spectra for blend/0.6 mg Au NPs before and after exposing to UV radiation at different time intervals (0.5, 1, 2, 4 h).

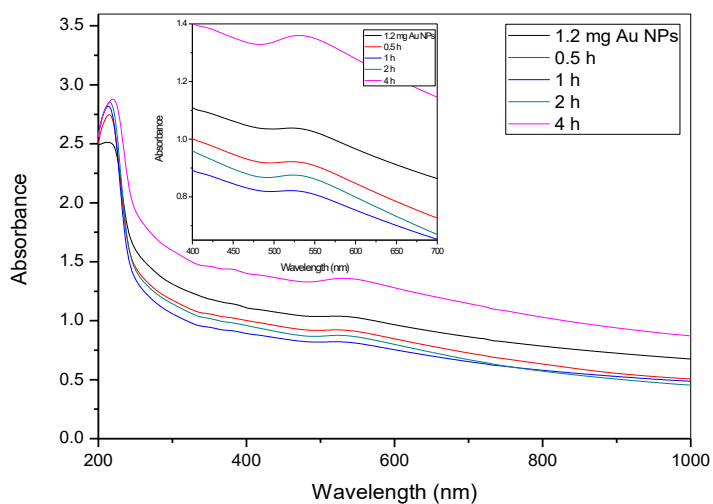


Figure 11: UV/Vis. spectra for blend/1.2 mg Au NPs before and after exposing to UV radiation at different time intervals (0.5, 1, 2, 4 h).

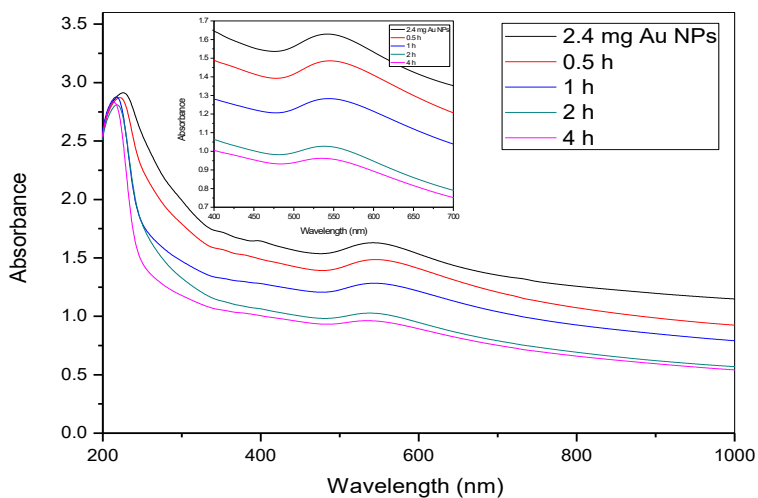


Figure 12: UV/Vis. spectra for blend/2.4 mg Au NPs before and after exposing to UV radiation at different time intervals (0.5, 1, 2, 4 h).

Optical Constants

Determination of optical energy gap E_g

The absorption spectrum measurement is the most direct method to investigate and give information about the band structure of materials. In the absorption process, an electron is excited from a lower to higher energy state by absorbing a photon of known energy. The changes in the transmitted radiation can determine the possible electron transitions types. The shift in absorption edge can be correlated with the optical band gap E_g by Tauc's expression as shown in the following equation [30];

$$\omega^2 A = (\hbar\omega - E_g)^2 \quad (1)$$

where, $A(\lambda)$ is the optical absorbance, λ the wavelength of incident beam, $\omega=2\pi\nu$ is the angular frequency of incident radiation and E_g the optical band gap, which may be deduced from the Tauc's plot of $(A^{1/2}/\lambda)$ versus $(1/\lambda)$, as shown in Figures 13 and 14 for pure blend and one irradiated sample (blend/2.4 mg Au NPs) as an example. The intersection of the extrapolated spectrum with the abscissa gives the gap wavelength λ_g from which the energy gap $E_g=hc/\lambda$ is derived, where h is Planck constant and c is the speed of light. The calculated E_g values of the films and are listed in Tables 2, 3, 4, 5 and 6. From these tables, it is obvious that, these energies values are decreased in general with increasing Au NPs content as compared with that of pure blend PEO/PVP. This indicates that the optical energy gaps are significantly influenced by the crystal structure. Assuming that E_g to be influenced by the induced states due to Au NPs doping of PEO/PVP blend, one may attribute the optical gap behavior to the change of the doping level (FL) mode. This indicates that the AuNPs significantly effect on the optical energy gap and there are charge transfer complexes arose between the polymer and Au NPs.

The increment of Au NPs content into polymer blend causes a resultant effect on the optical band gap. Au NPs is responsible for some defects formation in the doped films [31]. These defects create localized states in the gap of optical band. The localized states density is found to be proportional to the defects concentration [32]. The doping process may make the changes in the localized states to overlap. These overlaps give a proof for decreasing energy band gap when content of Au NPs is increased in the polymeric matrix [33, 34]. Also, this decrease can be explained by the increase in the disorder degree in the nano-composite films. The existence of the high content makes expanding of the localized energy levels [35].

As the exposure time for UV light on nanocomposite films increases, E_g is increased, for example from 3.72 eV for blend/2.4 mg Au NPs to 4.48 eV for blend/2.4 mg Au NPs/2 h. This observation is due to enhancing the degree of ordering/crystallinity of nanocomposite chains by irradiation process where the chains are relaxed and stresses are released as mentioned above in UV/Vis. analysis. Polymer ordering leads to a significant decrease in molecular mass. This in turn will decrease the polymer chains amount surrounding the NPs. The less polymer chains there are, the more they exhibit the aggregation of Au NPs [29].

With increasing the exposure time of UV-irradiation, the E_g values are gradually decreased, for example from 4.83 eV for blend/1.20 mg Au NPs/1 h to 4.53 eV for blend/1.2 mg Au NPs/4 h. This observation implies that more further irradiation causes the chains to be cross-linked with each other and resulting in a three dimensional network. Thus, this will increase the nucleation rate that leads to smaller particles formation where the intensity SPR peak increases [29]. Further irradiation causes the creation of unsaturated bonds, which are rich in charge carriers (delocalized electrons) [36].

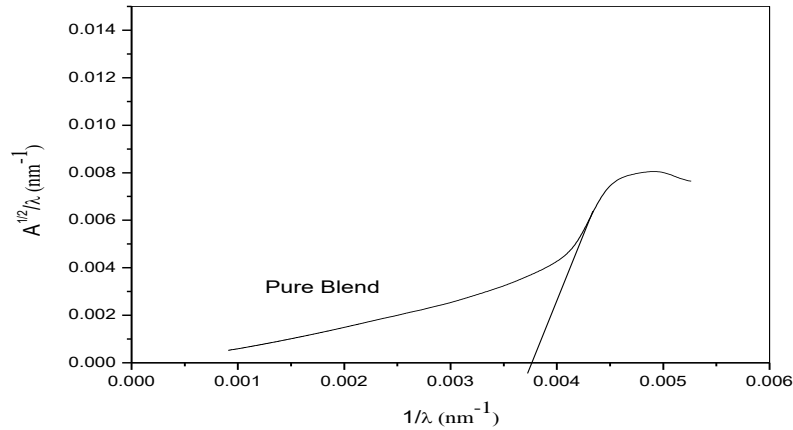


Figure 13: Tauc's plot ($A^{1/2}/\lambda$) versus ($1/\lambda$) for pure PEO/PVP blend.

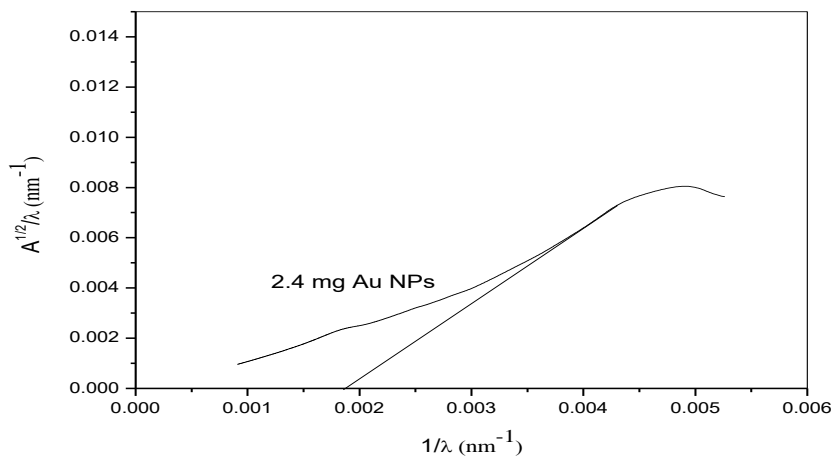


Figure 14: Tauc's plot ($A^{1/2}/\lambda$) versus ($1/\lambda$) for pure PEO/PVP blend.

Refractive index (n)

The variation in refractive index 'n' as a function of E_g for pure blend and its nanocomposite without and with different exposing time intervals to UV- light has been calculated by the following relation [37]:

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_g}{20}} \tag{9}$$

The dependence of refractive index n on both Au NPs content and exposing time to UV radiation is listed in the last Tables. It is obvious that the refractive index value increases after the addition of Au NPs within the polymeric matrix of PEO/PVP and its value varies according to the irradiation time for irradiated samples. This increase in n of PEO/PVP/Au nanocomposites may be because of the formation of intermolecular hydrogen bonding between Au with the adjacent OH group of PEO/PVP blend which is confirmed by an increase in the intensity of OH in FT-IR analysis [36]. The high value of refractive index is an indication of high density of the film, which leads to a reduction of the inter-atomic spacing. As the time of UV-irradiation increases, PEO/PVP/Au nanocomposite films suffers from structural rearrangement leading to decrease in the number of non-bridging oxygen (NBO) bonds. Moreover, high UV-irradiation time intervals (4 h) of PEO/PVP/Au nanocomposite films enhances the number of inter-chain interactions, resulting in the change in molecular weight distribution, packing density etc., which results an improvement in n . This increase in refractive index extends the usability of these materials from anti reflection coating for solar cells to high refractive index lenses and has an application in optoelectronics field.

Table 2: Absorption edge (λ_g), optical energy gap E_g^T , refractive index n for pure PVP, pure PEO and blend PEO/PVP (70/30 wt.%)

Sample	Absorption edge λ_g (nm)	E_g^T (eV)	n
PVP	241.09	5.14	1.98
PEO	274.88	4.51	2.07
Blend PEO/PVP (70/30)	258.18	4.80	2.03

Table 3: Absorption edge λ_g , optical energy gap E_g^T , SPR position, absorbance at SPR position and refractive index n for 0.3 mg Au NPs sample before and after UV-irradiation at different times

Sample	Absorption edge λ_g (nm)	E_g^T (eV)	SPR position (nm)	Absorbance at SPR position	n
0.3 mg Au NPs	263.20	4.71	537.40	0.64	2.045
0.5 h	261.30	4.74	535.17	0.66	2.04
1 h	251.26	4.93	537.5	0.50	2.01
2 h	254.51	4.87	533.05	0.58	2.198
4 h	257.10	4.82	532.4	0.7	4.27

Table 3: Absorption edge λ_g , optical energy gap E_g^T , SPR position, absorbance at SPR position and refractive index n for 0.6 mg Au NPs sample before and after UV-irradiation at different times

Sample	Absorption edge λ_g (nm)	E_g^T (eV)	SPR position (nm)	Absorbance at SPR position	n
0.6 mg Au NPs	265.70	4.69	517.45	0.75	2.048
0.5 h	261.42	4.78	515.41	0.59	2.034
1 h	262.31	4.72	514.40	0.80	2.043
2 h	263.76	4.70	513.02	0.91	2.046
4 h	269.41	4.60	511.31	0.93	2.063

Table 4: Absorption edge λ_g , optical energy gap E_g^T , SPR position, absorbance at SPR position and refractive index n for 1.2 mg Au NPs sample before and after UV-irradiation at different times

Sample	Absorption edge λ_g (nm)	E_g^T (eV)	SPR position (nm)	Absorbance at SPR position	n
1.2 mg Au NPs	270.90	4.58	522.38	1.04	2.066
0.5 h	261.60	4.74	521.21	0.92	2.040
1 h	256.32	4.83	520.37	0.82	2.026
2 h	263.76	4.70	523.35	0.87	2.046
4 h	273.50	4.53	530.37	1.36	2.074

Table 5: Absorption edge λ_g , optical energy gap E_g^T , SPR position, absorbance at SPR position and refractive index n for 2.4 mg Au NPs sample before and after UV-irradiation at different times

Sample	Absorption edge λ_g (nm)	E_g^T (eV)	SPR position (nm)	Absorbance at SPR position	n
2.40 mg Au NPs	333.72	3.72	542.82	1.63	2.226
0.5 h	306.16	4.05	545.36	1.48	2.16
1 h	277.02	4.48	543.08	1.28	2.083
2 h	273.47	4.53	537.76	1.02	2.074
4 h	260.74	4.76	534.71	0.96	2.037

CONCLUSION

Different concentrations of Au NPs were successfully embedded within the polymeric matrix of PEO/PVP blend through casting method and exposed to UV light at different time intervals. FT-IR analysis confirmed miscibility between the blend components by showing the main polar groups of blend, C=O of PVP and C-O-C of PEO. These polar groups were largely affected due to both the addition of Au NPs and exposing to UV-radiation. The UV/Vis. spectra for nanocomposite films showed a shift for the absorption edge toward longer wavelengths and confirmed the existence of Au NPs within the polymeric matrix by showing SPR peak in the visible region. The position and intensity of SPR were changed according to the concentration of Au NPs and exposing time to UV light. The values of optical energy gap and refractive index were enhanced after the addition of Au NPs and were largely affected due to irradiation process. Such an improvement in the optical properties for nanocomposites will make these films a potential candidate in optoelectronic and electrochemical devices.

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