Original Article

Structural, optical, morphological and thermal properties of PEO/PVP blend containing different concentrations of biosynthesized Au nanoparticles

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\textbf{A B S T R A C T}

Casting technique was used for preparation of polyethylene oxide (PEO)/polyvinyl pyrrolidone (PVP) (70/30 wt.\%) films filled with different concentrations of gold nanoparticles (Au NPs). X-ray diffraction (XRD) pattern proved the semi-crystalline nature of the pristine and filled polymer blend. Fourier transform infrared (FT-IR) and Ultraviolet/Visible (UV/Vis.) analyses were used to retrace the structural and optical changes with increasing Au content. UV/Vis. analysis spectroscopy was utilized to calculate the optical properties such as optical energy gap $E_g$, refractive index $n$ and Urbach energy $E_u$ for blend/Au nanocomposite films. Scanning electron micrograph (SEM) suggested the dependence of morphological structure on filling level and the surface morphology changed from rough to smooth. Transmission electron microscope (TEM) micrographs showed that the size of Au NPs was increased with continuous filling in PEO/PVP. Thermogravimetric analysis (TGA) was performed to investigate the thermal stability for nanocomposite films.

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1. Introduction

Polyethylene oxide (PEO) is a linear and semi-crystalline polymer. Because PEO is a linear polymer, the regularity of structure unit permits a high crystallinity degree. The chemical structure of PEO contains of polar group –O– that can interact/associate with the cations of metal salt. Thus, PEO can solvate different types of salts. However, the reactivity is very low because of its structural unit has C–H, C–C, C–O bonds. Due to this, it is stabilized chemically and electrochemically. But, a high concentration of crystalline phase within PEO polymer confines the conductivity [1,2].

Polymer blending is one of the most favorable alternate choices of increase the amorphous content [3]. It is one of the most significant methods for the designing of new polymeric
materials and it is a valuable method for developing materials with a massive assortment of properties. The final product from blending process can be customized to the applications requirements, which cannot be accomplished alone by one polymer. Thus, polyvinyl pyrrolidone (PVP) has been selected as a partner for PEO to set up the polymer blend system because it is a conjugated polymer with high content of amorphous phase which can allow quicker ionic mobility compared to other semi-crystalline polymers. The existence of carbonyl group (C=O) lends marked Lewis base character to the side chains of PVP, resulting in the formation of a variety of complexes with different inorganic salts. Also, PVP have a great importance among the conjugated polymers because of its simple processability and moderate electrical conductivity.

Metal nanoparticle–polymer composites have gained significant research interest in recent years. With the embedding of nano-sized inorganic particles within the polymeric matrix, the new nanocomposite material shows unexpected properties that extremely differ from that of conventional materials [4]. These nanocomposites exhibit unique optical, electrical, or mechanical properties making them valuable for applications in different areas such as photo-imaging and patterning, optics, as antimicrobial coatings and sensor design [5]. Recently, nanoparticles (NPs) attract a great attention in many fields of physics, chemistry, medicine, material science, and photonics, because of their unique chemical and physical properties [6]. NPs generally refer to a type of material with a large surface-to-volume proportion and other charming properties deduce from the “quantum size effect” [7].

Among the metal NPs, Au NPs are of great importance due to their ability to interact with light efficiently by dint of surface plasmon resonance (SPR). SPR is the collective oscillations of the conduction electrons in the metal when the wavelength for incident light is much larger than the size of nanoparticle [8,9]. Also, it has catalytic activity due to high surface area to bulk atoms ratio. Thus, Au NPs surely have the potential to be the building blocks of future plasmonic and photonic devices as the nanotechnology field matures [10].

In this study, new series of stable densely dispersed Au NPs were obtained using an entirely green synthesis approach. In this approach, the natural non-toxic ingredients extracted from the leaf of Chenopodium murale (C. murale) were used, instead of common hazardous chemicals. After that, we study the structural, optical, morphological and thermal properties of polymer blend PEO/PVP (70/30 wt.%) and its nanocomposite samples filled with different concentrations of Au NPs.

2. Experimental

2.1. Materials

All the chemicals and solvent used in this study were of analytical grade. Both PEO (Mw = 40,000 g/mol, ACROS, New Jersey, USA) and PVP (Mw ≈ 72,000 g/mol, SICO Research Laboratories Pvt. Ltd, Mumbai, India) were used as basic polymeric materials. The C. murale leaf was obtained from the Mansoura District, Dakahlia governorate, Egypt during December 2015. Tetrachloroauric (III) acid trihydrate (HAuCl4 3H2O, 99.5% GR for analysis) was obtained from Merk, Germany. Double distilled water was used as a solvent.

2.2. Preparation of samples

Preparation of C. murale extract and biosynthesis of Au NPs were explained in detail in our paper [10]. Solution cast method was used to prepare the polymer blend sample and its nanocomposite samples. A quantity of PEO/PVP (70/30 wt.%) was added to double distilled with stirring continuously at room temperature to complete dissolution. Appropriate amounts of Au NPs (0.06, 0.12, 0.24, 0.48 and 0.72 wt.%) were added to the polymeric blend solution with continuous stirring for 24 h. These solutions were poured into polypropylene dishes and dried in oven for 4 days at 40 °C where the common solvent was allowed to evaporate slowly. After drying process, the free-standing polymer films at the bottom of dishes were peeled and put in highly evacuated desiccators to avoid any moisture absorption. The thickness of prepared samples was in the range of 0.07–0.09 mm.

2.3. Measurements

XRD analysis were done through DIANO corporation-USA equipped using Cu Kα radiation (λ=1.540 Å, the tube operated at 30 kV, the Bragg’s angle (2θ) in the range of 5–80°). FT-IR absorption spectra were obtained for the prepared films using the single beam Fourier transform-infrared spectrometer (Nicolet iS10, USA) in the spectral range of 4000–400 cm−1 at room temperature. UV/Vis. absorption spectra were measured utilizing spectrophotometer (V-570 UV/VIS/NIR, JASCO, Japan) in the wavelength range of 200–1000 nm. The shape, size and distribution of Au NPs were analyzed using Transmis- sion electron microscope (JEOL-JEM-1011, Japan). SEM (JEOL JSM 6510 LV, USA) was used to study the morphological properties of nanocomposite films. TGA curves for the studied samples were recorded using (NETZSCH, STA 409CD, Germany) in temperature range from room temperature to 700 °C and the heating rate was 10 °C/min in the existence of nitrogen as inert atmosphere.

3. Results and discussion

3.1. X-ray diffraction analysis XRD

Fig. 1a represents the X-ray spectra for pure PEO and PVP. PEO shows a maximum intensity peak at 23°, following maximum peak at 19° and more less intense peak at 26.91°, which are assigned to (112), (120) and (222) planes [11] [PCPDF Filenos.49-2200 and 49-2201] respectively. Several low intense peaks were also found around 14.40°, 20.74°, 27.01°, 29.24°, 36.11° and 45.40°, which are correlated with those of [PCPDF Filenos.49-2200 and 49-2201]. PVP exhibits two broad peaks at around 13° and 21°, which are referred to the amorphous nature of PVP [3,12].

The spectrum of pure blend film shows well-defined two diffraction peaks at 19° and 23° as shown in Fig. 1b, which confirms the semicrystalline nature of blend. These notes corroborate that the present polymer blend system exhibits both
amorphous and crystalline regions. XRD analysis of blend sample filled with Au NPs shows two diffraction peaks at 2θ = 19° and 23°, which their intensities slightly changed and irregularly increased with increasing Au NPs amount up to 0.12 wt.% of Au NPs. At concentration of Au NPs 0.12 wt.%, the intensity of both diffraction peaks has a maximum value indicating the more organized distribution of the Au NPs in the polymeric matrix. With increasing the content of Au NPs, there is a dramatic decrease in the intensity of main diffraction peaks. This implies an increase in the amorphous regions, indicates the distribution of the Au NPs in the polymeric matrix became random and causes a decrease in the degree of crystallinity. This observation indicates that complexation between the nanofiller and the polymers existed in the amorphous regions [13]. This is because of the interaction between the blend and Au NPs that results in a decrease in intermolecular interaction between the chains of polymer blend and make the coordination interaction between the Au NPs and ether (C–O–C) group of PEO and/or carbonyl (C=O) group of PVP of polymer blend, which will be confirmed by FT-IR analysis.

XRD analysis for the crystalline phases of pure Au NPs is shown in Fig. 1c. The Bragg reflection patterns appearing at 2θ = 38° (111), 42° (200), 64° (220) and 78° (311) are indexed for the face-centered cubic FCC structure of Au NPs [10,14,15], which is close to the reported data (JCPDS File No. 4-0784). It is clear that, there are no peaks referring to pure Au NPs in the spectra of prepared samples shown in Fig. 2 that indicates the complete dissolution of Au in the matrix of polymer blend [13,16]. But at high concentrations of Au NPs (0.48 and 0.72 wt.%), its diffraction patterns show a small sharp peak at 2θ = 38°. It is also observed that the position of the sharp peak is coincided with a peak at 2θ ≈ 38° in the X-ray scans of pure Au NPs. This confirmed the presence of Au crystallites within the polymeric matrix [17]. Also, a new peak at 2θ ≈ 31° for 0.72 wt.% sample is observed. This result confirms that more addition of Au NPs can occur structural changes in the polymeric network [18] for filled samples and this sharp peak might have arisen from scattering atomic planes of some crystalline patterns of the blend-Au complex. In other words, clear sharp peak at 2θ ≈ 31° arising from the crystalline phase with the polymeric matrix, because of increasing of Au content. These scattering angles may be accompanied with the (200) and (112) reflections, respectively [19].

According to Scherrer’s formula [20] \( D = \frac{K \lambda}{\beta \cos \theta} \) where \( k = 0.89 \) (shape factor in the case of spherical nanoparticles), \( \lambda = 1.540 \text{Å} \) (X-ray wavelength for Cu Kα), \( \beta \) is line broadening at half the maximum intensity (FWHM) in radians and \( \theta \) is the angle obtained from 2θ value corresponding to (111) planes in XRD analysis. The average dimensions of Au NPs for prepared samples (0.48 and 0.72 wt.%) at 2θ value 38° are estimated as 22.44 and 21.87 nm, respectively. The crystalline size of pure Au NPs the same angle is 17.60 nm. This means that the particle size is increased with increasing Au NPs content in polymer blend/Au nanocomposite which is confirmed by UV/Vis. analysis.

3.2. Fourier transform infrared analysis FT-IR

Fig. 2a presents FT-IR absorption spectra of pure PVP, pure PEO and pure blend while Fig. 2b shows the FT-IR absorption spectra for the nanocomposite samples. FT-IR absorption spectra and its assignments for all prepared films are listed in Tables 1 and 2 [2,3,13,21–26].

For spectrum of pure blend PEO/PVP, the co-existence of (C–O–C) of PEO and (C=O) of PVP implies that the components of blend are miscible. PEO has a strong tendency to make intramolecular hydrogen bonding with other species having groups with highly electronegative. Furthermore, polymers
having electronegative oxygen and ternary amide groups, such as PVP, are potentially good proton acceptors because of the basic functional groups nature. It will be expected that the interaction is the hydrogen bonds between C–H of CH₂ for PEO and C=O of PVP (Scheme 1). This conclusion is confirmed from shift of the C=O peak (1655 cm⁻¹) of the PVP associated with decrease its broadness matrix as well as the increase in the intensity and broadness of C–O–C peak (1110 cm⁻¹) of the PEO.

From Fig. 2b, the FT-IR spectra of PEO/PVP blend filled with Au NPs were roughly conforming to the pure PEO/PVP blend spectra. The effect of Au NPs on the vibrations modes was observed in terms of decrease in the broadening, intensity of the bands with Au NPs content and shifting for the bands to lower wavenumbers that result from the formation of co-ordination between Au and ether oxygen atoms of PEO and coordination between Au and the oxygen atom of carbonyl groups of PVP. The band intensity at 1110 cm⁻¹ decreases progressively and slightly shifts of its position to lower wavenumber with the increase of Au content. This is because of the coordination interaction of Au NPs with the ether units of PEO [25] (Scheme 2), which results in the interruption of crystallization, thereby, increase of fraction of amorphous content. In PVP, interaction mechanism between pyrrolidone ring of PVP and nanoparticles was discussed by our research group paper [22] in details (Scheme 3). The spectral perturbation of carbonyl band becomes extensive because of increase in the basicity of C=O group with the increased Au concentration, indicating that the carbonyl group is able to behave as a strong electron donor to interact with Au NPs [22,23]. These interactions result in the interruption of crystallization due to which the fraction of amorphous content
Table 1 – Assignments of the FT-IR characterization bands for pure PEO and pure PVP.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Pure PEO</th>
<th>Ref.</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Pure PVP</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1461</td>
<td>CH₂ scissoring</td>
<td>[2,3,20,24,25]</td>
<td></td>
<td>2955</td>
<td>CH₂ asymmetric stretching</td>
<td>[12,21,24,25]</td>
<td></td>
</tr>
<tr>
<td>1240</td>
<td>CH₂ symmetric twisting</td>
<td>[2,3,20,24,25]</td>
<td></td>
<td>1495</td>
<td>Vibration of C=N (pyridine ring)</td>
<td>[12,24,25]</td>
<td></td>
</tr>
<tr>
<td>956</td>
<td>C–O stretching motion with some contribution from CH₂ rocking</td>
<td>CH₂ rocking</td>
<td>[2,3,24,25]</td>
<td>1435</td>
<td>CH₂ wagging</td>
<td>[2,3,20,24,25]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>840</td>
<td></td>
<td></td>
<td>1375</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1290, 1230</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1172, 845</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>737</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>650</td>
</tr>
</tbody>
</table>

Table 2 – Assignments of the FT-IR characterization bands for pure PEO/PVP blend (70/30 wt.%).

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Pure PEO/PVP blend</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3435</td>
<td>–OH stretching</td>
<td>[21,24,25]</td>
<td></td>
</tr>
<tr>
<td>2880</td>
<td>Asymmetric C–H stretching of CH₂</td>
<td>[2,3,24,25,27]</td>
<td></td>
</tr>
<tr>
<td>1655</td>
<td>Symmetric &amp; asymmetric of C=O</td>
<td>[2,3,12,20,21,24,25]</td>
<td></td>
</tr>
<tr>
<td>1465</td>
<td>CH₂ scissoring</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
<tr>
<td>1345</td>
<td>CH₂ asymmetric bending (crystalline)</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
<tr>
<td>1285</td>
<td>CH₂ wagging or twisting</td>
<td>[2,3,12,20,24,25]</td>
<td></td>
</tr>
<tr>
<td>1240</td>
<td>CH₂ symmetric twisting</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
<tr>
<td>1145</td>
<td>C–C stretching</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
<tr>
<td>1110</td>
<td>Symmetric &amp; asymmetric C–O–C stretching (amorphous)</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
<tr>
<td>1068</td>
<td>–OH bending</td>
<td>[24,25,28]</td>
<td></td>
</tr>
<tr>
<td>960</td>
<td>C–O stretching with some CH₂ asym. rocking</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
<tr>
<td>845</td>
<td>CH₂ rocking in PEO and with some C–O stretching in PEO</td>
<td>[2,3,24,25]</td>
<td></td>
</tr>
</tbody>
</table>

increases [2,3,21], which was confirmed by XRD analysis. From FT-IR spectra, Au NPs fundamentally stabilized by chemical interaction with PVP through the oxygen atom of its poly (pyrrolidone) unit. This interaction is confirmed by appearing a new peak as a shoulder at 1665 cm⁻¹ which coincidence with appearing a new sharp peak in XRD analysis.

From Fig. 2b, the intensity of the stretching vibration of hydroxyl group (OH) band and its broadness increases for filled samples, so that the ability of filled samples to absorb water increase with increasing Au content. The band referring to CH₂ asymmetric stretching vibration appears at about 2880 cm⁻¹ become more broader after addition of Au NPs and its intensity decreases largely, especially at 0.72 wt.% of Au NPs [13,22].

The intensity of bands at 1465 and 1285 cm⁻¹ is increased with increasing Au content. In addition to the above variations, the small band at 1345 cm⁻¹ is assigned to amorphous region of PEO and shows a higher intensity at high content of Au NPs. This implies the change for crystalline regions of PEO into amorphous regions because of Au NPs addition. The intensity of the two bands at 960 and 845 cm⁻¹, referring to
Scheme 1 – Formation of Hydrogen bond within PEO/PVP blend occurs between carbonyl group of PVP and the methylene group of PEO.

Scheme 2 – Formation of coordination for Au NPs with ether oxygen atom of PEO.

Scheme 3 – Mechanism of interaction between Au NPs and PVP monomer [M⁺ = Au].

Some interactions/complexation with the polymer blend components. Subsequently, these interactions play vital role in governing conduction behavior in the complex polymer blend [24].

3.3. Ultraviolet and visible analysis UV/Vis.

UV/Visible absorption spectra of prepared colloidal Au NPs and PEO/PVP/Au nanocomposites in the wavelength range 200–1000 nm are shown in Fig. 3. In the present system, the spectra of the filled PEO/PVP films exhibit a red shift for the sharp absorption edge toward longer wavelength with increase the Au NPs content in PEO/PVP blend. This red shift for the absorption edge of nanocomposite samples indicates the complexation between Au NPs and the polymeric matrix. Furthermore, it indicates the change in the optical energy gap, which is caused due to the change in crystallinity within the polymer matrix of blend [13,19,22,24], which was confirmed by XRD analysis. A hump or shoulder at 215 nm may be due to n → π⁺ (R-band) electronic transitions [13,19].

From Fig. 3, the UV/Vis. spectrum for biosynthesized Au NPs showed SPR peak at maximum absorption wavelength \( \lambda_{\text{max}} = 531 \text{ nm} \) in the visible region, which is a main property for the formation of Au NPs [27–29]. It can be seen, after adding Au NPs in PEO/PVP blend, the SPR peak starts emerging with a red shift and the intensity continuously increases with increasing concentration of the nano-filler. The increase in \( \lambda_{\text{max}} \) (i.e. red shift) means that the size of Au NPs increases with increasing its concentration within the PEO/PVP matrix. This experimental observation matches with theoretical predictions, which indicate that the position of SPR peak for
n nanoparticles enclosed within the polymeric matrix moves to longer wavelengths [30].

3.4. Optical constants

3.4.1. Determination of optical energy gap \( E_g \)

It is obvious that the spectra of UV/Vis. analysis (Fig. 3) characterized by a main absorption edge for all curves are moved toward longer wavelength upon increasing the Au NPs concentration. This means that the width of forbidden band decreases with increasing the Au NPs content. The absorption coefficient \( \alpha \) can be obtained using the Beer–Lambert’s relation [13,22]:

\[
\alpha(v) = 2.303 \left( \frac{A}{L} \right)
\]  

(1)

where, \( A \) is the absorbance and \( L \) is the film thickness, defined by \( \log(I_0/I) \) where \( I_0 \) and \( I \) are the intensity of the incident and transmitted beams. Concerning the optical transitions arising from photons of energy \( hv > E_g \), the present optical data can be determined according to the following expression for the near edge optical absorption [31]:

\[
\alpha(v)hv = B(hv - E_g)^r
\]  

(2)

where, \( hv \) is the energy of incident photons, \( E_g \) is the optical energy gap, and \( r \) is the power, that describes the transition process in the K-space. Specially, the value of \( r \) has 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. For direct and direct transitions, Davis and Mott plots of \( (\alpha hv)^{1/2} \) and \( (\alpha hv)^{2} \) versus \( (hv) \) near the absorption edge for the present experimental data produce a linear fit over a wider range of \( hv \) as shown in Fig. 4 for pure blend and one filled sample (PEO/PVP/0.72 wt.% Au NPs) as an example. Extrapolating the straight parts of these curves to the \( hv \) axis gives the corresponding \( E_g \) owing to the following equation:

\[
(\alpha hv)^{1/2} = B^{1/2}(hv - E_g)
\]  

(3)

\[
(\alpha hv)^{2} = B^{2}(hv - E_g)
\]  

(4)

The calculated \( E_g \) values of the films are summarized in Table 3. From this table, 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. It is remarkable that these observations were in agreement with XRD analysis. This implies that the optical energy gaps are significantly affected by the crystal structure. Assuming that \( E_g \) to be influenced by the induced states due to Au NPs filling of PEO/PVP blend, one may attribute the optical gap behavior to the change of the filling level (FL) mode. The increment of Au NPs into polymer blend causes a resultant effect on the optical band gap. Au NPs is responsible for defects formation within the filled samples. These defects create localized states in the optical band gap. The localized states density is proportional to the defects concentration [32]. The nanofiller may make the changes in the localized states to overlap. These overlaps give a proof for decreasing the gap of optical band when the content of Au NPs is increased in the polymeric matrix [33,34]. Also, this decrease can be understood by the increase in the disorder degree in the nano-composite samples.

More generally, it has been well documented in literature that PEO/PVP displays the indirect band transition between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) band edges [35]. From Table 3, the optical energy gap \( E_g \) value decreases from 4.86 eV for pure PEO/PVP to 2.46 eV for sample 0.72 wt.%. Such a decrease may be attributed to the chemical bonding formation between blend chains and Au NPs, which is responsible for the localized
Fig. 4 – (a, b) $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ versus photon energy for (a) pure PEO/PVP blend and (b) PEO/PVP/0.72 wt.% Au NPs.

Table 3 – Optical energy gap $E^{\text{DM}}_g$, absorption edge $(\lambda_g)$, SPR peak position, Urbach Energy $E_u$ and refractive index $n$ absorbance at SPR position for pure PVP, pure PEO, pure blend PEO/PVP sample and its filled samples with nano gold at different concentrations.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E^{\text{DM}}_g$ (eV)</th>
<th>Absorption edge $(\lambda_g)$ (nm)</th>
<th>SPR position</th>
<th>Absorbance at SPR position</th>
<th>$E_u$ (eV)</th>
<th>$n$</th>
<th>$E_a$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Blend PEO/PVP</td>
<td>4.86</td>
<td>5.15</td>
<td>–</td>
<td>–</td>
<td>0.21</td>
<td>325.06</td>
<td>2.02</td>
</tr>
<tr>
<td>0.06 wt.% Au NPs</td>
<td>4.67</td>
<td>5.00</td>
<td>263.20</td>
<td>525.44</td>
<td>0.23</td>
<td>380.78</td>
<td>2.05</td>
</tr>
<tr>
<td>0.12 wt.% Au NPs</td>
<td>4.71</td>
<td>5.04</td>
<td>261.42</td>
<td>515.45</td>
<td>0.22</td>
<td>352.67</td>
<td>2.04</td>
</tr>
<tr>
<td>0.24 wt.% Au NPs</td>
<td>4.54</td>
<td>4.84</td>
<td>270.90</td>
<td>522.38</td>
<td>0.25</td>
<td>390.79</td>
<td>2.07</td>
</tr>
<tr>
<td>0.48 wt.% Au NPs</td>
<td>3.38</td>
<td>4.06</td>
<td>333.72</td>
<td>542.82</td>
<td>0.73</td>
<td>411.09</td>
<td>2.30</td>
</tr>
<tr>
<td>0.72 wt.% Au NPs</td>
<td>2.46</td>
<td>3.60</td>
<td>418.82</td>
<td>537.42</td>
<td>0.97</td>
<td>437.64</td>
<td>2.56</td>
</tr>
<tr>
<td>Prepared Au NPs</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>531</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

states generation between the HOMO and LUMO energy bands. This observation makes the lower energy transitions feasible. The decrease in energy gap value in PEO/PVP/Au nanocomposites makes them efficient materials for optoelectronic devices and electrochemical applications such as polymer electrolyte. This is due to the fact that such devices require the band gap tunability [36].

3.4.2. Urbach energy $E_u$

Below the energy gap edge, the exponential absorption sub-edge refers to the Urbach’s energy and calculated from the following relation [36,37]:

$$
\alpha(u) = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)
$$

(5)
where, $\alpha_0$ is a constant and $E_g$ is the Urbach energy tail that is a measure of the width of the localized states tail in the forbidden band gap. The exponential dependence for $\alpha(\nu)$ on the photon energy ($h\nu$) for the prepared films implies that it obeys the Urbach’s formula. For indicating this dependence, $\log(\alpha(\nu))$ is plotted versus ($h\nu$) for the investigated samples, the figure not presented here. The $E_g$ values are calculated by taking the reciprocal of the slopes of the linear portion of these curves and are listed in Table 3. From this table, the values of $E_g$ increase from 0.21 eV for pure blend sample to 0.97 eV for sample 0.72 wt.%. The increase in Urbach’s energy leads to a decrease in optical energy gap. Such result confirms the increase in the traps number as a result of embedded Au NPs, which leads to the lower energy transitions feasible and thus, decreasing the optical energy gap values.

In other words, the change of $E_g$ magnitude in these samples, which can be understood by taking account of the mobility concept as suggested by Davis and Mott [31], implies that filling process significantly affects the $E_g$. The filling process introduces additional states of defect in the polymeric matrix of blend. The localized states density is found to be proportional to the defects concentration [37] and so concentrations of Au NPs. An increase in Au NPs content may cause the localized states of different color centers to extend and overlap in the mobility gap [38]. The values of $E_g$ are indicators as to the levels of different defect taking place in optical band gap of the samples where the Au dopant changes the localized states width in the optical band gap of the samples [39]. Thus, the value of optical energy gap is opposite to the Urbach energy.

3.4.3. Refractive index ($n$)
Refractive index $n$ for the nano-composite is calculated in terms of $E_g$ through the relation proposed by Dimitrov and Sakka [40]:

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

The $n$ dependence on filling level is listed in Table 3. It is obvious that the value of $n$ increases with increasing $E_g$. This increase can be explained by orientation of the dipole molecules of Au NPs (high polarizability), which in turn results in a permittivity increase in the filled samples. In other words, an addition of Au NPs in the polymeric matrix may be the main reason for the localized electronic states formation in band gap. These localized electronic states control the structural and optical properties of host material vis-à-vis their role as recombination and trapping centers, so improving the low energy transitions, resulting in the observed change in $n$ [30].

With the substitution of Au NPs into PEO/PVP matrix, bridging C–O–C bonds are broken and non-bridging C–O–Au bonds are formed and the same behavior is also occurred by for C=O of PVP. The non-bridging oxygen (NBO) bonds have much lower bond energies and much greater ionic character [25]. Thus, the NBO bonds have higher polarizability strength of bonds, molecular weight and density. Increasing the concentration of Au NPs will alter all of these parameters in a manner that increases the corresponding $n$. The change of the optical constants such as $E_g$ and $n$ on changing the filling level introduces a useful way in the development of functional materials with a wide range of applications in the optoelectronic field.

3.5. Scanning electron microscope SEM

Fig. 5 shows the SEM micrograph for the surface of pure and filled samples at magnification 1500 times. SEM micrographs suggest that the morphological structure depends on the filling level of Au NPs. From Fig. 5a, the image of pure blend PEO/PVP (70/30 wt.%) shows a rough morphology structure which has several crystalline domains i.e. spherulites, because of the semicrystalline nature of blend that was confirmed by XRD.

After the addition of Au NPs to the pure blend, the size of spherulites is largely decreased and there is an improvement of surface morphology from rough, where the surface texture becomes somewhat smoothened as shown in Fig. 5b and c. A
continuous incorporation of Au NPs in the matrix of PEO/PVP blend leads to smoother surface, where the spherulites forms are completely diminished and disrupted and Au NPs addition becomes an obstacle for the spherulites growth rate. The smooth surface morphology of nanocomposite films is clearly indication for reduction in the degree of crystalline of pure PEO/PVP blend after Au NPs addition. This is due to the interaction between polymer and Au NPs through ether oxygen group for PEO and carbonyl group of PVP as confirmed by FT-IR analysis. In other words, this originates from random dissociation and distribution of Au NPs which may present topological disorder in the electrolyte, which produces more amorphous phase, associated with disruption of crystalline phase in the system and makes the polymeric matrix more flexible.

Also, size of pores increases and its distribution becomes sparser with increasing the content of Au as shown in Fig. 5d–f. For high concentration of Au NPs, Au NPs aggregates at the surface in the form of granules that appears as bright spot as shown in Fig. 5f. The existence of pores between Au NPs and polymer blend interfaces with increasing Au NPs content is due to the shrinkage of spherulites and is considered as a type of complexation/miscibility between PEO/PVP and Au NPs. Also, these pores are corresponding to the interconnected networks of polymers.

### 3.6 Transmission electron microscope TEM

Fig. 6 shows TEM images of prepared Au NPs by C. murale leaf extract and sample (0.72 wt.%) together with the corresponding size distribution histogram of Au NPs. From the figure, it can be observed that the Au NPs are almost spherical in shape with average particle size 2–22 nm as in its histogram that was confirmed by the breadth of its SPR peak in UV/Vis. spectrum. For sample containing amount (0.72 wt.%) of Au NPs, it is observed that Au NPs are uniformly dispersed inside PEO/PVP matrix and have a homogeneous distribution within nanocomposite films. TEM micrograph reveals that size of Au NPs is increased with increasing Au NPs content in the PEO/PVP matrix where the ability of coalescence phenomenon is increased. The particle size range is between 2 and 35 nm. This result was confirmed by UV/Vis. absorption spectra where the SPR position is red shifted to longer wavelengths. This result matches with theoretical predictions, which denote that the SPR peak position for nanoparticles implanted in the polymeric matrix moves toward longer wavelengths [30].
Fig. 7 – TGA thermograms of pure PEO, pure PVP, PEO/PVP blend and blend filled with different concentrations of Au NPs.

3.7. Thermogravimetric analysis (TGA)

The TGA thermograms of residual weight as a function of temperature for pure blend and its nanocomposite samples are shown in Fig. 7. The TGA curves for blend and its nanocomposites show a complete homogeneity because the degradation process occurs in a single step [41–44]. For nanocomposite of low content of Au NPs (0.06 and 0.12 wt.% AuNPs), the position of weight loss curve moves toward higher temperatures because of the extra-interaction between the PEO/PVP and NPs. Thus, it can be assumed that the present polymer blend exhibited excellent thermal stability. This matches with the previous literatures where Au NPs enhance the thermal degradation of the polymer because of their catalysis ability and also their ability in increasing the crosslink density in the polymeric matrix [45].

For nanocomposite of high Au NPs content, it is observed that the TGA curve moves toward lower temperatures with increase in Au NPs content, which implies that the blend with higher concentration of Au NPs decomposes at lower temperatures. This is because of the high flexibility acquired by the polymer samples with high concentration of NPs. Polymers with highly flexible chains needless energy and hence degrades at lower temperatures and show low thermal resistance. Therefore, the existence of high content of Au NPs causes a decrease in the thermal stability of the nanocomposite matrix.

3.7.1. Determination of the activation energy $E_a$

The $E_a$ for the thermal decomposition of the prepared nanocomposites was determined through integral equation of Coats and Redfern [46]

$$\log \left[ \frac{1 - (1 - \omega)^{1-n}}{T^2} \right] = \log \frac{R}{E_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{1}{2.303 RT} E_a$$  

(7)

where $T$ is the absolute temperature, $E_a$ is the activation energy in J/mol, $R$ is the universal gas constant (8.3136 J/mol K), $n$ is the order of reaction and $\omega$ is the fractional weight loss at that particular temperature calculated as:

$$\alpha = \frac{w_i - w_f}{w_i - w_f}$$  

(8)

where $w_i$ is the initial weight, $w_f$ is the weight at given temperature and $w_f$ is the final weight of the sample.

For $n \neq 1$, Eq. (7) reduces to:

$$\log \left[ \frac{-\log(1 - \omega)}{T^2} \right] = \log \frac{R}{E_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{1}{2.303 RT} E_a$$  

(9)

By plotting $-\log[-\log(1 - \omega)/T^2]$ versus 1000/$T$ for each sample, we have straight line as shown in Fig. 8. The activation energy values $E_a$ were determined from the slope of the plot as:

$$E_a = 2.303R \times \text{slope}$$  

(10)

The calculated values of $E_a$ for the nanocomposite samples are listed in Table 3, where it is obvious that the $E_a$ values are increased from 325.06 for pure blend to 437.64 kcal/mol for blend/0.72 wt.% Au NPs sample. This implies that the Au NPs largely affects the polymeric matrix of blend.

4. Conclusion

PEO/PVP blend complexed with Au NPs was successfully prepared by casting technique. XRD scans revealed the decrease of degree of crystallinity of the polymer blend/Au NPs complexes. FT-IR studies confirmed the complexation between the polymer blend and Au NPs through the interaction between Au NPs and the polar groups of polymer blend. UV/Vis. absorption spectra for PEO/PVP/Au nanocomposites showed the appearance of SPR peak in the visible region which is a characteristic for Au NPs and its intensity increased with increasing Au NPs content associated with shifting to longer wavelengths. The values of optical parameters for nanocomposite films were enhanced due to Au NPs addition within the polymeric matrix. The surface morphology changes from rough to smooth revealed an increase for amorphous region within
the polymeric matrix due to the existence of Au NPs. TEM micrograph revealed that size of Au NPs is increased with increasing Au NPs content in the PEO/PVP matrix, which was confirmed by the red shift of SPR peak position in UV/Vis. analysis. TGA curves moved toward lower temperatures with continuous increase in Au NPs content. This implied that the thermal stability for nanocomposites was decreased. The values of the activation energy were increased from 325.06 to 437.64 kcal/mol which implies that the Au NPs intensively affects the polymer. Such an enhancement in the structural and optical properties may lead to optimize the various optical parameters of PEO/PVP/Au nanocomposite samples as per specific requirements in the filters, switches, optical coatings, etc. Due to enhancement in the optical and thermal properties for nanocomposites with low content of Au NPs, it can be utilized in optical and optoelectronic applications.

Conflicts of interest

The authors declare no conflicts of interest.

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