Melanin Doping Potential Effect on the Optical Properties Polyvinyl Alcohol

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Abstract: PVA (polyvinyl alcohol) was the common biopolymer that used in medical applications due to its unique properties. Melanin is widely distributed in the most all living organisms and displays the photo-protection, metal ion chelation, antibiotic, antibiotic activity, thermoregulation, free radical scavenging and some involvement in the nervous system. The aim of work provided a new biomaterial that had unique properties in optical applications. The absorbance increased with increasing concentration of melanin. The optical density data show that the absorbance band of PVA shifts from 280nm after doping by melanin to 272 for all concentration. The energy gap of pure PVA was 5.2 eV and reduced to 3.42 eV as melanin concentration increases up to 4%. The fluorescence emission spectra of pure PVA and PVA-Mel in different concentration at excitation wavelength $\lambda_{ex} = 280\text{nm}$ show emission peaks $\lambda_{em}$ at 307, 333, and 405 nm. Emission spectra for all samples of PVA-Mel were shifted toward long wavelength (red shift). FTIR was measured in the range of 4000 – 400 cm$^{-1}$ for all studied samples. The data indicate that melanin has two peaks; broad with 3256.07cm$^{-1}$ and the second is sharp with 1635.01cm$^{-1}$. Pure PVA and PVA-Melanin shows that there are two peaks for PVA; the first is broad with 3307.05cm$^{-1}$ and the second is sharp with 1638.87cm$^{-1}$. Doping Melanin with different concentration indicates a peak shift.

Keywords: PVA, Melanin, Optical density, FTIR, fluorescence.

1. INTRODUCTION

PVA is a polar polymer that has a hydroxyl group, hydrophilic, non-toxicity, biocompatibility, low cost, easy to form, and required physicomechanical properties beside the high chemical resistance. PVA is an vital polymer material due to its solubility in water, desirable physicochemical properties, biocompatibility, semi-crystalline polymer, host in polymer electrolyte systems, noncarcinogenic nature, high fiber-forming ability, relative cost-effective value, non-toxic, eco-friendly and chief synthetic polymers (Parameswaran et al., 2017, Mohammad et al., 2015).

The increase of intensity of the emission peak may be due to the strong interaction between the dopant and the polymer where the falling in the emission intensity of PVA-TiCl$_2$ may be because of aggregation of dopant molecules. (Abdelaziz, and Ghannam 2010)

Melanin is about pigment which responsible for the coloration of animals and plants. It's found in the most all living organisms, skin, brain, eyes retina, inner ear. It displays a photo-protection, metal ion chelation, antibiotic, antibiotic activity, thermoregulation, free radical scavenging and some involvement in the nervous system. (Yang Wang et al., 2015).

Melanin can be considered a promising material for sensor and photovoltaic devices, due to broadband spectral and charge transport properties. (Ligonzo et al., 2009). In vitro oxidized melanin (greenish yellow) may be due to the different physicochemical environments or different concentration of the fluorophore. Melanin undergoes autofluorescence in skin, hair, and blood due to oxidation of the melanin in tissues. (Kayatz et al., 2001).

The strong hydrogen bonding between the $\text{–OH}$ (or $\text{–NH}$) of melanin and $\text{–OH}$ of PVA confirmed by FTIR, which played a key factor to prevent the aggregation of nanoparticles in PVA matrix and contributed to the high performance of PVA. (Wang et al., 2015).
Increasing of extinction coefficient at high wavelengths is related to the higher concentration of the dopant salt, and thus more scattering of photons have occurred with the added imperfections. (Muhammad et al., 2015)

However, there are some parameters extracted from optical properties such as energy gap, absorption coefficient, and extinction coefficient.

This work is aims to provide new biomaterial (PVA- Mel) with some new properties and put valuable information about the melanin doping potential effect on both optical properties, fluorescence, and FTIR of PVA- melanin system in the different concentration.

2. MATERIALS AND METHODS

In the present work, polyvinyl alcohol (PVA) doped with Melanin at different weight percent ratios were prepared.

2.1. Preparation of Polyvinyl Alcohol (PVA) Solutions

Polyvinyl Alcohol is a water-soluble polymer. The polymer is supplied in powder form, and it is soluble in hot and cold water. A PVA solution would typically be prepared as follows:

30g PVA powder is slowly added to 1L cold water to avoid the formation of lumps, as it becomes sticky and the tendency to form lumps increases as temperature rises.

Once the powder is thoroughly dispersed the mix is heated to the temperature at which the polymer becomes solubilized (70 °C), and the solution was stirred thoroughly with a magnetic stirrer for 4 h to get a homogenous mixture of concentration 30mg/ml.

2.2. Preparation of Nigella Sativa L. Melanin

The extraction and characterization of melanin from Nigella Sativa L. have been carried as described previously by El-Obeid et al. (2006a).

2.3. Absorption Spectrum Measurement

The absorption spectra of sample solution for PVA, melanin, and PVA-Mel were measured by using UV/Visible spectrometer (Biochrom-Libra S60PC) in the range (200-800nm) at room temperature. To calculate the energy gap for all samples, the energy (hν) of the incident wavelengths (eV) were plotted as a function of (α hν)² as shown in figure 2. The inset curve shows the same plotted for pure melanin (1mg/ml) in the studied wavelength range. The energy gap was calculated using figure 2 and summarized in table 1; it was found that the energy gap of melanin (1mg/ml) equal 3 eV, the energy gap of pure PVA (30mg/ml) equal 5.20 eV. It was noticed that the total energy gap of polymer (PVA-Mel) is decreasing with increasing the melanin dopant concentration to 3.42 eV for 4% of melanin when an absorbance coefficient α = 2.303A/d (Obeid et al., 2013, Muhammad et al., 2015). Ais the absorbance (a.u), and d is the thickness of the cuvette which equals 1cm.

2.4. Fluorescence Emission Spectra Measurement

The fluorescence emission spectra of pure PVA, pure melanin, and PVA-Mel with different concentration were measured by using spectrofluorometer machine: (Shimadzu RF-6000) with several excitation wavelengths λex at room temperature.

2.5. FTIR Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) for structure detection (functional groups) of PVA-Mel solution sample by using Thermo Scientific Nicolet 6700 in the range (4000-400 cm⁻¹) which causes stretching or bending vibration of molecules as the peak. Wave number of peak indicated group function.

3. RESULT AND DISCUSSION

3.1. Optical Properties (Absorbance)

The optical density of pure PVA, pure melanin, polymer (PVA-Mel) was measured in the range of 200-800nm. Figure (1) shows the absorbance of polymer (PVA-Mel) at different Mel doping concentration wt%. The inset curve indicates continues range of melanin absorbance in the studied wavelength range. The absorbance of PVA 30mg/ml shows an absorbance band at 280nm with a
shoulder at 326nm. It is clear from the figure the absorbance of PVA 30mg/ml with absorbance band at 280nm, the wide-ranging absorbance of melanin decreased with increasing of wavelength (nm), and the absorbance of polymer (PVA-Mel) with absorbance band of pure PVA was shifted to 272nm while the shoulder band was gone. Figure (2) shows the incident photon energy (eV) Vs. \((\alpha h\nu)^2\) on the PVA at different concentration of melanin, and pure melanin. Figure (3) show the extinction coefficient \(k\) of pure PVA, pure melanin, PVA-Mel with concentration 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 3, and 4%wt. respectively as a function of incident photon energy. Extinction coefficient \(k\) was proportional to incident photon energy, figure show decreasing of \(k\) value with increasing the doping of PVA via melanin. So, the last concentration 3, and 4% the curve \(k\)-incident photon energy shifted to the lower value of incident photon energy (E).

**Figure 1.** The absorbance of polymer (PVA-Mel) at different Mel doping concentration wt. %. \(\lambda_{\text{EX}} = 280\text{nm}\). The inset curve indicates continues range of melanin absorbance in the wavelength range 200 -800 nm.

**Figure 2.** The incident photon energy (eV) Vs. \((\alpha h\nu)^2\) on the PVA at different concentration of melanin, and pure melanin.

**Table 1.** The energy gap of pure Melanin, PVA, PVA-Mel at different concentration.

<table>
<thead>
<tr>
<th>Concentration wt.%</th>
<th>Energy gap(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure melanin</td>
<td>3.00</td>
</tr>
<tr>
<td>Pure PVA (30mg/ml)</td>
<td>5.20</td>
</tr>
<tr>
<td>0.2</td>
<td>5.18</td>
</tr>
<tr>
<td>0.4</td>
<td>5.11</td>
</tr>
<tr>
<td>0.6</td>
<td>5.0</td>
</tr>
<tr>
<td>0.8</td>
<td>4.99</td>
</tr>
<tr>
<td>1</td>
<td>3.8</td>
</tr>
<tr>
<td>1.2</td>
<td>3.8</td>
</tr>
<tr>
<td>1.5</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>3.42</td>
</tr>
</tbody>
</table>
Absorbance band of pure PVA =280nm it's close to Chahal et al. result's (2015) at 276nm, and Mohammad et al. result's (2015) at 288nm. The absorbance of melanin was tended to linear- shape; there's no absorbance band in absorbance of melanin due to the presence of the carboxylic acid group in the construction of melanin as a source of plant. This result agrees with Mboniyiriyuzve et al. (2015a). The absorbance of PVA after doping Melanin combined between absorbance of melanin and PVA, but the shoulder was gone. With an absorbent and at 272nm. The absorbance of Mel-PVA was increased with increasing the concentration of melanin, due to rising of molecules entire PVA that it causes to increasing carboxylic acid group in the structure of PVA (Mbonyiriyuzve et al., 2015a). Thus, a higher concentration of melanin obtained higher absorbance which supports some optical properties of PVA polymer such as enhancement contact lens function to protecting eyes against radiation. It was also used for transplantlenses if human eyes were infected by cataract.

The energy gap of pure melanin equal 3eV while it's 2.6eV for Obeid et al. (2013) and the energy gap of pure PVA was 5.2eV, result agreement with Abdelaziz and Ghannam 2010. This value reduced to 3.42 eV as melanin concentration increases up to 4%. The energy gap of PVA after doping by melanin was decreased may be due to the disorder of molecules within the structure of PVA.

Extinction coefficient k is related to the fraction of electromagnetic energy lost due to scattering and absorption per unit thickness in a specific medium. Extinction coefficient K was increasing with increasing of energy at pure PVA, but it's decreased with increasing of the incident energy for pure melanin and PVA-Mel in the different concentration. The explanation for this behavior due to increasing of concentration led to increase in scattering of the photon which causes to lose a lot of incident energy.

3.2. Fluorescence

Fluorescence spectroscopy (FL) technique has been used over many years to investigate the physical properties of eumelanin. These spectra are often fluorescence signature or finger point. No compounds have the same fluorescence signature. Fluorescence compounds have two characteristic spectra: excitation and emission spectra. (Perna et. al 2009). Melanin fluorescence occurred when it exposed to oxidation with hydrogen peroxide or light, and it will be growing with exposure time. Melanin in vivo may be due to oxidation resulting from the constant irradiation by light during a lifetime. Melanin also suffers from spontaneous autoxidation without the addition of exogenous hydrogen peroxide (Kayatz et al., 2001).

Figure (4) shows the excitation and emission spectra of pure melanin 1mg/ml. Emission peak of pure melanin was 443 nm with $\lambda_{ex} = 350nm$. Figure (5) shows the emission spectra of pure PVA and PVA-Mel in different concentration at excitation wavelength $\lambda_{ex} = 280nm$ with emission peaks $\lambda_{em}$ at 307,333, and 405 nm.
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Figure 4. The excitation and emission spectra of pure melanin 1mg/ml.

Figure 5. Emission spectra of pure PVA and PVA-Mel for melanin concentration of 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 3, 4wt %, at excitation wavelength 272 nm.

Emission peak energy of pure melanin was 2.8eV, which is closed to that reported by Prena et al., (2009) of 2.85 eV. Emission energy was the difference of energy between excited state and ground state. Emission peak as shown in figure (4) was 442nm with excitation wavelength 350nm. Riesz (2007) found an emission peak of melanin at 450, 460, 465nm while excitation peaks at 300, 325, 350, 375nm respectively. The difference of emission spectra of melanin was depended on the source, excitation wavelengths, solvent, and concentration. (Jennifer Riesz 2007).

It clears from the figure (4) that PVA has an emission peak at 307, 332, 406 nm. After doping PVA with melanin emission peak 307 shifts to 302nm. Peak's PVA at 332nm was shifted to 323nm with concentration 0.2wt%, other concentration its peak emission shift to 337nm except for concentration 0.8, 2, 3, 4 changes to 340nm. Finally, the third emission peak of pure PVA was shifted to 420nm with concentration 1, 1.5wt% while in other concentration it was changed to 450nm. These shifts of emission spectra may be referred to adding different concentrations of melanin. Emission spectra for all samples that shown in figures (4) & (5) were shifted toward long wavelength (red shift) due to the HOMO/LUMO gap. The HOMO/LUMO gap is about the difference between the highest occupied molecular orbital and lowest occupied molecular orbital. Lower energies excited caused to the HOMO/LUMO (Perna et al., 2009).
3.3. FTIR Analysis

FTIR was measured in the range of 4000–400 cm\(^{-1}\) for pure PVA, pure melanin, and PVA-Mel. Figure (6) shows FTIR of pure melanin 10mg/ml of two peaks; broad with 3256.07 cm\(^{-1}\) and the second is sharp with 1635.01 cm\(^{-1}\). Figure (7) shows FTIR of pure PVA of 30mg/ml and PVA-Melanin which indicates that there are two peaks for PVA; the first is broad with 3307.05 cm\(^{-1}\) and the second is sharp with 1638.87 cm\(^{-1}\). Doping Melanin with different concentration indicates a peak shift. The broadband of OH group was observed at 3400 cm\(^{-1}\) for PVA solution both on the alcohol and solution, the reason for the higher intensity of the peak at 3400 cm\(^{-1}\) in PVA solution due to the formation of strong hydrogen bonds between the interaction of the oxygen and hydrogen atoms between the molecules (Arda et al., 2015). While for melanin, it is about 3600-3200 cm\(^{-1}\) for OH or NH stretching vibration modes of carboxylic acid, and phenolic (Mbonyiryivuze et al., 2015b). The original strong band between 1647-1531 cm\(^{-1}\) is attributed to the bending vibrations modes of aromatic ring C=C and C=N bond of the aromatic system in addition to C=O double bond (COOH) of carboxylic function. (Mbonyiryivuze, et al., 2015b, Tarangini, and Susmita, 2013). The vibration from 500-400 cm\(^{-1}\) indicated to C-Cl aromatic which was very weak. Bending vibration of C-C approximately appeared at 500 cm\(^{-1}\).

Figure 6. FTIR of pure melanin 1mg/ml.

For pure melanin 3256.07 cm\(^{-1}\) indicated to stretching broad of bonding -OH in a carboxylic acid, and phenolic. 1635.01 cm\(^{-1}\) indicated to Stretching vibration of symmetric of C=C aromatic ring or stretching of C=N with strong intensity and sharp peak. Finally, absorbance at 477 cm\(^{-1}\) was indicated to C-Cl with weak intensity.

Figure 7. FTIR of PVA and PVA-Mel with different concentration.
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In pure PVA a broad peak observed at 3307.06 cm$^{-1}$ indicated to OH stretching vibration of hydroxyl groups. Aytimur et al. (2015) observe this peak at 3400 cm$^{-1}$ while Yang Wang et al. (2015), Xihai, and. Shu (2015) were also observed this peak at 3287, 3427 cm$^{-1}$ respectively. Another peak observed at 1638.87 indicated to stretching vibration of C-C or C=O group. The group which bonding with the OH. (Khatua et al., 2015, Parameswaran et al. 2017). 455 cm$^{-1}$ was indicated to bending C-C with very weak intensity. Stretching bonding OH of pure PVA shift from 3307 cm$^{-1}$ to 3288.82, 3270.86, 3303.03, 3301.29, 3266.37, 3268.24, 3274.63, 3323.75, 3294.18 cm$^{-1}$ by doping of melanin with concentration 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 3, 4 wt. % respectively.

Peaks at 1638.87 cm$^{-1}$ of PVA shift to 1635.30, 1634.91, 1635.41, 1638.71, 1635.20, 1636.71, 1634.95, 1633.70, 1635.06, 1635.58 cm$^{-1}$ by doping of melanin with concentration 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 2, 3, 4 wt % respectively, which indicated here to C=Nand C=C or C-C groups. Hao and Wen 2015 observed this peak after doped with Glycerol at 1621 cm$^{-1}$.

455 cm$^{-1}$ in PVA shift to 472.460.66, 472.437, 438.43, 503.80, 487, 449.89 cm$^{-1}$ by doping of melanin with concentration 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 3, 4 wt % respectively, which indicated to bending of C-C or C-Cl. OH-bonding of PVA reducing with add melanin into the structure of PVA, increasing OH of melanin cause destroy order of PVA chains Figure (6) illustrate the FTIR of pure PVA& PVA after doped with a different concentration of melanin; they are similar shape curves because the two-polymer joined together by H-bonding without any chemical interaction. A Small position reflected the different concentration of melanin. This result is agreement with Yang Wang et al. 2015., Xihai, and. Shu (2015). The change in the spectra reflects the change in the concentration of carboxylic groups not bonded to metals ions. (Magarelli et al., 2010).

4. CONCLUSION

Increasing concentration of melanin within PVA polymer caused increasing the absorbance due to increasing the carbonic acid groups that provide a new biomaterial with unique properties. So, contact lenses that manufactured from this biomaterial exhibit more protective against radiation. The absorbance band of PVA shifted to 272nm after doping by melanin. The energy gap of PVA reduced after doped with melanin up to 3.4eV at the highest concentration of Melanin 4%. Also, OH-bonding effected on emission spectra of PVA that caused to some shifts on the emission peak of PVA polymer after doping by different concentration of melanin. The optical density of melanin tends to linear-shape due to the multiple of carboxylic acid. Fluorescence of melanin used to find its excitation spectra. The small size of HOMO/LUMO caused to emission spectra at large wavelength (red shift) and bleaching of intensity. A small shift in FTIR of PVA due to increasing the concentration of melanin that caused to increase OH in PVA and deformation of PVA polymer by melanin. HOMO–LUMO size depended on the excited energy size.

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"All views, conclusions, conclusions, and recommendations mentioned in this publication are for the author (s) and do not necessarily reflect the views of KACST."

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