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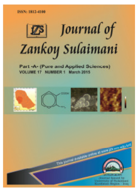

Linear Optical properties of Pheomelanine pigment extraction from red wool

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Abstract

The aims of this research are the extract of Pheomelanine pigment from red wool and prepared of it as a thin film by repeat-spray method. We study the optical properties of the Pheomelanine thin film such as the absorbance (A), Transmittance (T), absorption coefficient (α), refractive index (n) and extinction coefficient (k). We calculate the energy gap (E_g), Urbach tail (E_u), oscillator energy (E_o), dispersion energy (E_d), static refractive index (n_o), static dielectric constant (ε_o) and spectra moments (M_{-1} and M_{-3}).

Introduction

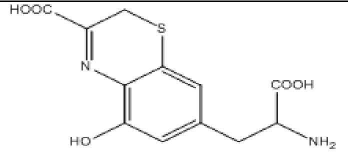
Pheomelanine is a yellow color. It is one of two types of melanin pigments [(1)]. They are a class of biological – macromolecules[(2)]. It is co- polymer structure [(3)]. Pheomelanine contains sulfur (10%) while another type of melanin (eumelanine) without sulfur. Melanins formed from the amino acid tyrosine by series of oxidations and other reactions [(4)]. Melanins (Pheomelanine and eumelanine) are colored skin, hair, wool and eyes and found in brain stem. They are playing an important photo- protective role against harmful UV radiation by scavenging free radicals and they are more efficient than chlorophyll in plants (thousands of times), transform photonic energy in to chemical energy, they are working even in the night, collect energy from lower- energy radiation sources, kicks electrons in to excited state. Melanines are very stable in water[(5)]. In this paper, we study the optical properties of Pheomelanine extraction from red wool and prepared as a thin film by repeat-spry method.

Experimental Regents

A. Extraction of pigment

The red wool washed with concentration ammonia and then boiled with 5 percent potassium hydrate solution (500 ml alkali to 100 gm. wool) for 7 days when solution was apparently complete. hydrochloric acid (10%) were added to strong acid reaction, the liquid decanted from the precipitate, the precipitate filtered, washed, and boiled for 8 hours with 5 percent hydrochloric acid. This left a fine brown powder which filtered off, dried on a water bath, dissolved in dilute ammonia , filtered precipitated with hydrochloric acid, washed, dried, powdered, dissolved in concentrated sulfuric acid, precipitated washed , dried, washed with alcohol , carbon disulphide and ether, and again dried. The resulting product was a dark red powder with ash content 6.722 gm. Table (1) shows the chemical structure (6).

Table 1: Physical properties of Pheomelanine.

Compound	**Chemical structure**	**Physical state**	**M.P (°C)**	**Color**	**M. W**	**Density g/cm^3**
Pheomelanine		**powder**	**>300***	**red**	**296**	**1.6**

*** = decomposition**

B. Preparation of thin film

(0.01 mol. 0.01gm) of pheomelanine pigment dissolved in 25 ml of Dimethyl- slphoxide (DMSO). The solvent heated up to 50 C and have been stirred for 60 min, and it leaved while the heat reaches to room temperature, then the solution filtered. The pheomelanine thin film have been deposited on the clean glass substrate of dimensions of (2.7, 2.5) cm, by repeat-spry method. The nitrogen gas have been used for produce the pheomelanine thin film, the thickness of the thin film have been calculated by using of equation below (7).

$$\mathbf{t = (m_2 - m_1)/\, \rho\, a \qquad (1)}$$

Where t: thickness, m_1: the mass of glass substrate, m_2: the mass of glass substrate and pheomelanine thin film, ρ: the density of Pheomelanine and a: the area of thin film. The thin film thickness was 5.6 $*10^{-5}$ cm.

Results and discussion:

A. Infrared spectrum

The dye powder was identified by IR spectroscopy in the range (4000–400) cm^{-1} as shown in Fig.(1)

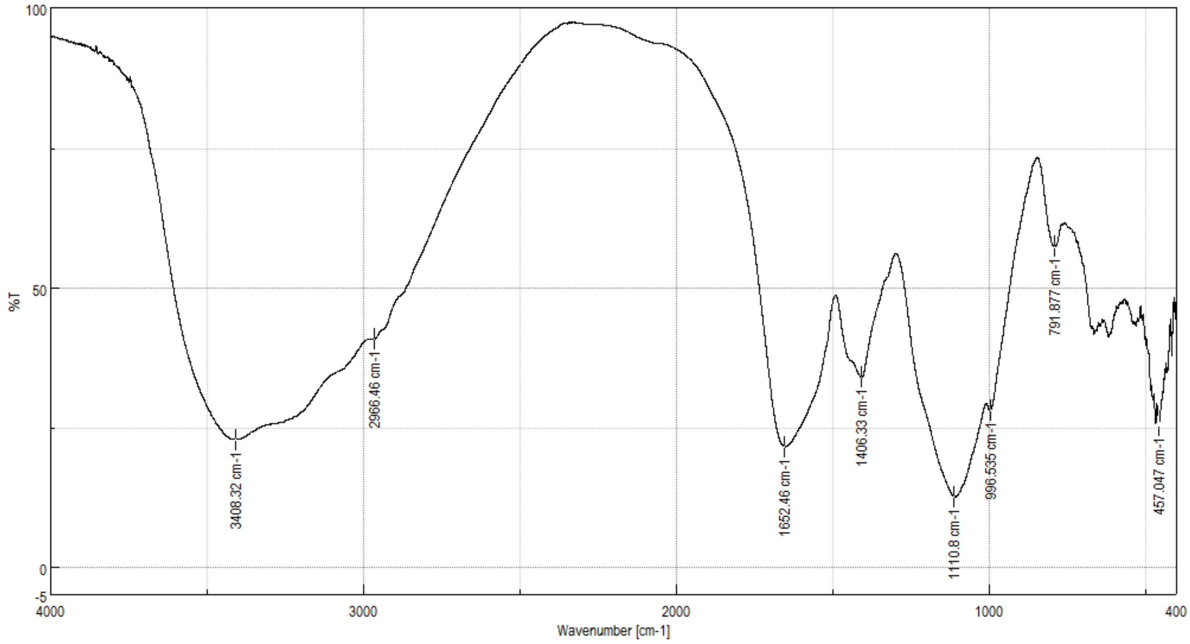


Fig.1 : IR-spectrum of Pheomelanine

The stretching vibration of the OH group which appeared in the region of (3408-3300) cm^{-1} cancels the absorption peak of (-NH_2) group supposed to appear at same region. The band shows broad appearance due to its relatively low frequency. It can be concluded that the (-OH) group may form a hydrogen bonding with nitrogen atom. As well a strong absorption band at 1652 cm^{-1} which was attributed to the stretching vibration of C=N. The (-C=C-) stretching vibration of the aromatic ring cited at (1562) cm^{-1}. Stretching vibration of the (-C-H) aliphatic appears at (2966) cm^{-1}. The all mentioned bands are given in Table 1.

Table 2: Major IR absorption bands (cm^{-1}) of Pheomelanin.

Functional group	OH and NH	C=N	C=C	C-H aliphatic
ν(cm^{-1})	3408-3300	1652	1406	2966

B. *Optical properties*

• Absorption (A) and Transition (T)

In this study, the UV-visible spectroscopies have been used to investigate the pheomelanine thin film in the range (300-900) nm. The Absorbance (A) and Transmittance (T) of the thin film measurements by double beam UV-visible spectrophotometer (CE-7200) at room temperature. Fig.(2) shows the absorption and transmission of the Pheomelanine thin film between (300-900) nm of wavelength

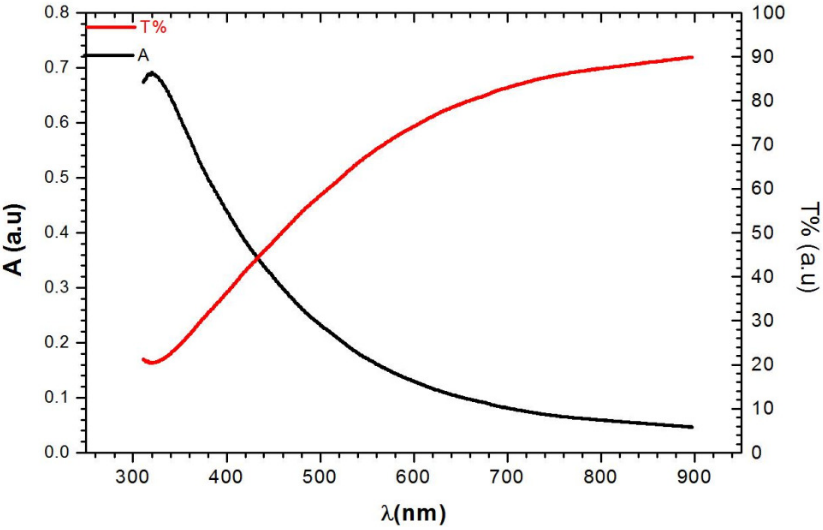


Fig (2): Absorption and transition of Pheomelanine thin film.

From the distribution of the spectrum, the maximum of absorption (minimum transition) appear in the UV region at 320 nm. While the absorption decreases and transmission increases gradually with increase of wave length, and they become approximately fixed between (800-900) nm.

• The absorption coefficient (α), extinction coefficient (k) and refractive index (n)

The absorption coefficient (α) was taken by using Beer-Lamberts law:

$$\alpha = 2.303A/d \qquad (2)$$

Where A the absorbance and d the thickness of the pheomelanine thin film, Fig (3) explained the behavior of the absorption coefficient (α) with incident photon energy (hν), the absorption coefficient (α) at low energies of incident photons is small, means low electron transitions and its big at high photon energies leads to high electron transitions. The values of absorption coefficients refer to direct transitions for the electrons between valance bands and conductions bands ($\alpha > 10^4$ cm^{-1}) (8).

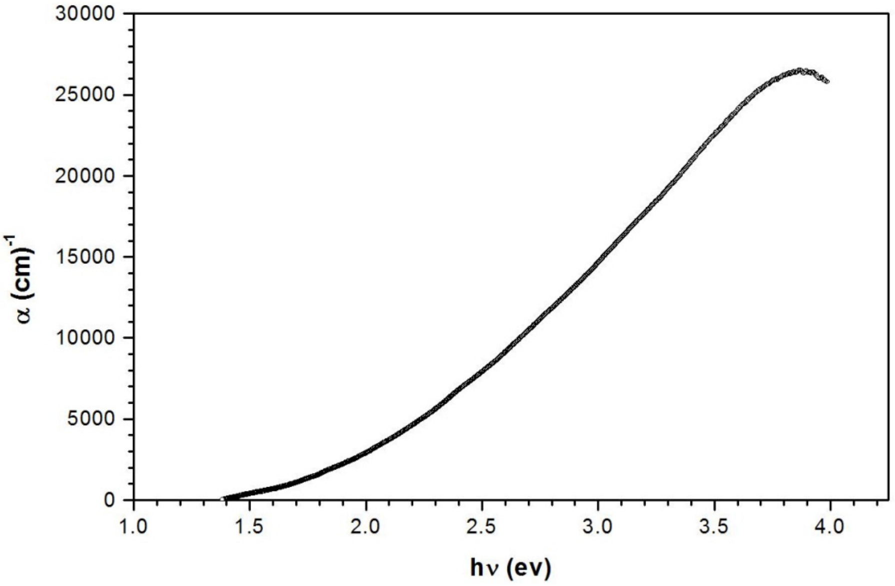


Fig (3): Absorption coefficient (α) for pheomelanine thin film.

The extinction coefficient (k) and the refractive index (n) are calculated by using equations (3) and (4).

$$\mathbf{k = \alpha\lambda / 4\pi} \qquad \mathbf{(3)}$$

$$\mathbf{n}= \left(\frac{\mathbf{1+R}}{\mathbf{1-R}}\right) + \sqrt{\left(\frac{\mathbf{4R}}{\mathbf{(1-R)^2}} - \mathbf{K^2}\right)} \qquad \mathbf{(4)}$$

Where R is the reflection and λ the wavelength(9). Fig. (4) shows the extinction coefficient (k) and the refractive index (n) against the incident photon energies. The increase in k and n can be attributed to the increase of photons were diffusion throw the material, the extinction coefficient increase sharply and at 4.6 eV decreasing while the refractive index stays increasing

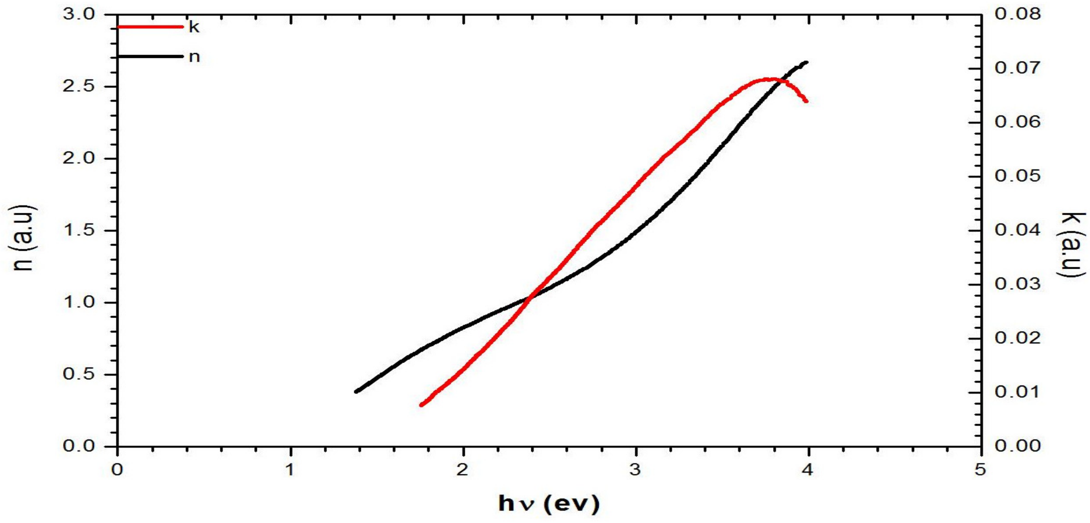


Fig (4): Extinction coefficient (k) and refractive index (n) for the thin film.

- **Energy gap (E_g) and Urbach tails (E_u)**

The direct energy gap have been calculated from eq. (5)

$$\alpha h\nu = C(h\nu - E_g)^n \qquad (5)$$

Where n is 1/2 for direct optical transition and 2 for indirect transition where allowed. C is constant known as band tail (10). Fig. (5) shows the allowed direct transition, plotting $(\alpha h\nu)^2$ against incident photon energy (hν), the energy gap was determined from the intercept on the axis of incident photon energy of the liner fit of the larger energy of photons. The direct energy gap was 3 eV, these value attributed to (π-π^*) transition comes from (-c=c-) bond (11).

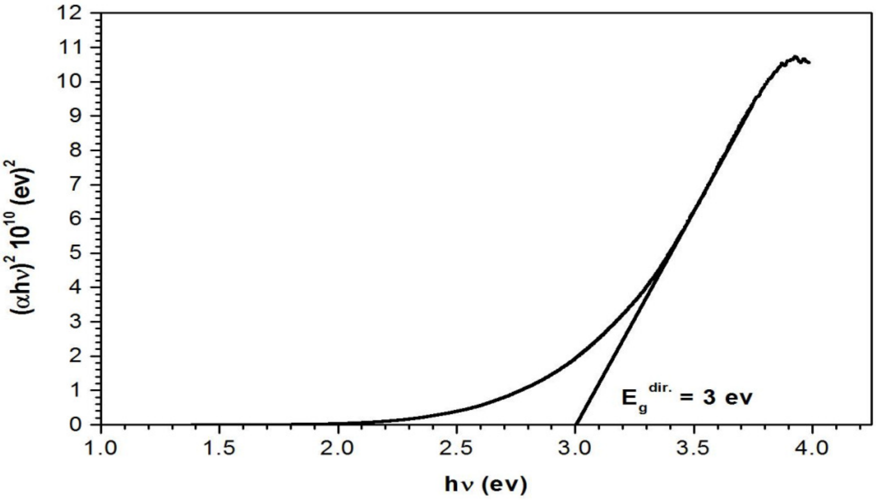


Fig (5): Energy gap ($E_g^{dir.}$) for pheomelanine thin film.

Urbach tails are scales for chemical disorder in materials, clear in materials have big molecules such as pigments and polymers (12). Urbach tails are given by using exponential equation (6)

$$\alpha = B \exp (h\nu / E_u) \qquad (6)$$

B is constant, taken ln for two sides of eq. (6) becomes

$$\ln (\alpha) = \ln B + h\nu/E_u \qquad (7)$$

From the curve of ln (α) and photon energy (hν) in Fig. (6), Urbach tail is calculated by taking invers of the slop of the liner portion of the curve (13). It is 0.62 eV.

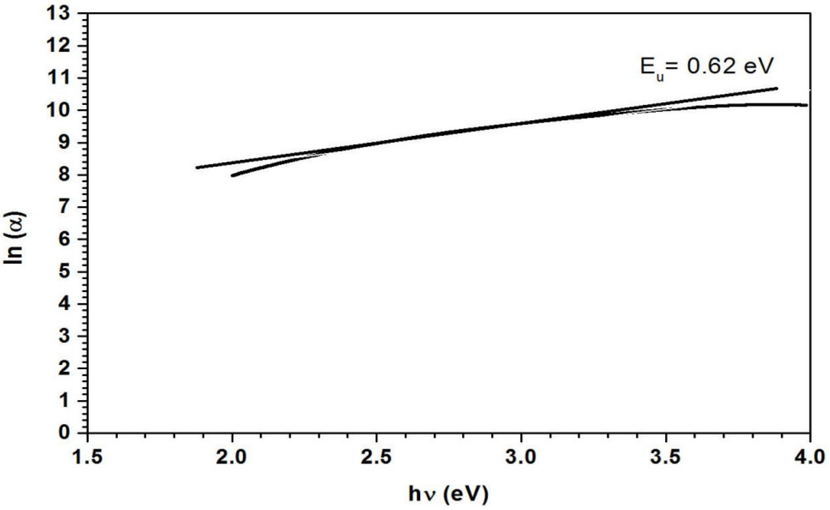


Fig. (6): Urbach tail for pheomelanine thin film.

- **Dispersion parameters**

The dispersion parameters are very important in optical properties because of its role in communication devices. The oscillator energy ($E_\circ$) and the dispersion energy (E_d) are given in equation (8)

$$(n^2-1)^{-1} = E_\circ/E_d - 1/E_\circ E_d (h\nu)^2 \qquad (8)$$

A Plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$, $E_\circ$ and E_d are obtained from the slope and intersection from extrapolation of the line to zero photon

energy [(14)] as show in fig. (7), $E_\circ$ and E_d are 5 eV, 12.11 eV respectively.

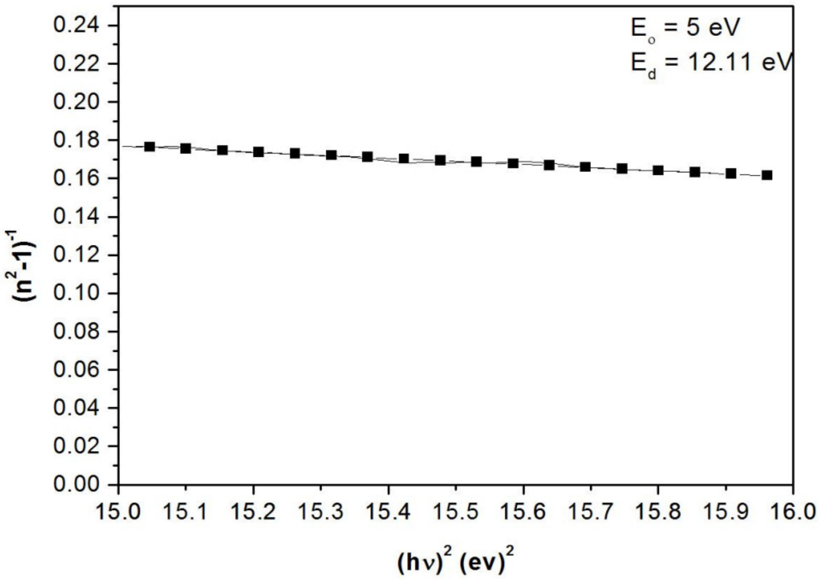


Fig. (7): The oscillator energy ($E_\circ$) and the dispersion energy (E_d) for Pheomelanine thin film.

The optical spectra moments M_{-1} and M_{-3} related with $E_\circ$ and E_d by the equation (9).

$$E_\circ^2 = M_{-1} / M_{-3} \qquad \text{and} \qquad E_d^2 = M_{-1}^3 / M_{-3} \qquad (9)$$

The value of M_{-1} and M_{-3} are 2.4 $(eV)^2$ and 0.1 $(eV)^2$ respectively.

The static refractive index ($n_\circ$) and the static dielectric constant ($\varepsilon_\circ$) are given from equation (10).

$$\varepsilon_\circ = n^2_\circ (h\nu=0) = E_d/E_\circ + 1 \qquad (10)$$

They are 1.84 and 3.4 respectively.

Table (3) explained of the optical constants of *pheomelanine thin film*

$n_\circ$	$\varepsilon_\circ$	$E_g^{dir.}$ (eV)	E_u (eV)	$E_\circ$ (eV)	E_d (eV)	M_{-1} $(eV)^2$	M_{-3} $(eV)^2$	$E_\circ E_d$ $(eV)^2$	$E_\circ / E_g^d$
1.84	3.4	3	0.62	5	12.11	2.4	0.1	60.55	1.66

Conclusions

The thin film of pheomelanine was extraction from read wool prepared by repeat - spray method, the optical constants has been calculated. The pheomelanine pigment has high values of optical constants ($n_\circ$ =1.84 and $\varepsilon_\circ$ =3.4). The optical transition was direct and energy gap of it was 3 eV, and 0.62 eV for Urbach tail, this means that the Pheomelanine pigment has semiconductor characteristics and high chemical disorderly.

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