



Effect of UV irradiation on linear optical parameters of PVA-MoO₃ Film

Mohamed Abu. Hamza^{1*}, Saad E. Sharada²

¹University of Tripoli, Faculty of Science, Tripoli/Libya

²University of Tripoli, Faculty of Education (Qaser Bin Ghashir), Tripoli/Libya

Corresponding author: Mohamed Abu. Hamza Moham.Hamza@uot.edu.ly

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ABSTRACT

A sample of polyvinyl alcohol doped with 5% by weight of molybdenum oxide forming (PVA-MoO₃) composite film was prepared using the solution casting technique. The film was exposed to UV irradiation (366nm wavelength) for different periods of time ranging from 5 to 60 min (5, 10, 20, 30, 40, 50 and 60 min) at room temperature. A computerized double beam UV-VIS spectrophotometer was used to characterize the sample film. The linear optical parameters such as (n) and (k) real and imaginary parts of refractive index, optical conductivity and dielectric constant were calculated. Also, the oscillator energy and dispersion energy (E₀, E_d) were evaluated. The experimental results showed that the extinction coefficient (K), reflectance (R), refractive index (n), dispersion energy (E_d), real (ε₁) and imaginary (ε₂) parts of dielectric constants and optical conductivity (σ_{op}) are increased, where, the transmittance (T) and oscillator energy (E₀) decreases with the increase of the exposure radiation time. Also, the results showed that (PVA-MoO₃) composite film can be used as UV sensor.

Keywords: PVA; MoO₃; UV irradiation; refractive index; dispersion energy.

1. Introduction

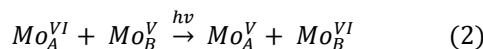
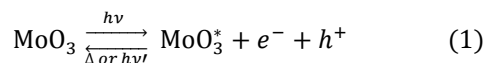
In recent years, increasing reports of ultraviolet aging owing to the collapse of the ozone layer has made people greatly aware of the danger to polymers from prolonged exposure to UV rays. The ultraviolet degradation of polymers is hugely important because resistance to aging, especially with UV light, is a key factor for outdoor applications. UV radiation, which accounts for approximately 7% of Earth's sunlight, has been shown to cause polymers to age, such as yellowing, fragility and even degradation. Organic ultraviolet light stabilizers and inorganic nanoparticles have been introduced in polymer matrices to improve polymers' UV stability. Compared to organic UV filters, inorganic nanoparticles are widely recognized as more stable and secure anti-UV agents [1]. Polymer

matrix nanocomposites, which exhibit distinct physicochemical characteristics by incorporating inorganic fillers into polymer networks, have picked up much attention due to their various industrial applications in drug delivery, water handling, food industry, aeronautical and aerospace structures [2]. Semiconductor films of inorganic materials, such as molybdenum oxide, have been an important part of research because of their future applications [3]. The optical and electrical properties of this material are very important features, which improve the application by varying the chemical structure of the material. Whereas, the low mechanical properties of the films produced from these materials restrict their application. Therefore, incorporation of these types of materials into polymer could improve the mechanical properties without affecting the optical and electrical properties to

high extent [4]. Polymer composite materials are compounds made from polymers or from polymers

along with other kinds of materials with good mechanical properties, low acoustic impedance, intermediate dielectric constant and high breakdown strength; they are used in a great variety of applications. Polymer composites are demanded due to their potential application in batteries, electrochemical sensor, capacitor and transducer [5]. Properties of metal oxide materials are directly or indirectly connected to the presence of defects and oxygen vacancies in particular [6, 7]. These defects determine the optical, electronic and transport properties of the material, are usually dominate the chemistry of its surface. Oxygen vacancies are naturally present in every oxide in the form of Shottky or Frenkel defects, and their concentration can be increased or reduced in several ways [7]. Point defects contribute significantly to the determination of the physical and chemical properties of inorganic materials. Their contribution in this respect extends not only for bulk properties but also for the surface of oxides, where several kinds of existing point defects display a rich and complex chemistry. Depending on the electronic structure of the material, the nature of oxygen vacancies changes dramatically. Examples include nonmetal vacancy on nonmetal site, metal vacancy on metal site, neutral vacancies, positively/negatively charged nonmetal vacancies, and free positive holes [8]. Oxygen vacancies are known as color centers. The color centers in oxide thin films, such as MoO₃, have been observed by irradiation with UV light from a high-pressure lamp in the fundamental absorption region at a wavelength of 330 nm. The formation of color centers has been associated with an increase in electrical conductivity, in which free electrons are produced as a result of band-to-band transitions and trapping of these electrons in oxygen ion vacancies. It was found that there is more than one type of defect responsible for the formation of color centers in MoO₃ thin films [9].

The word "photochromism" derived from two Greek words meaning light and color, which refers to such a phenomenon that the material can change color in a reversible way by electromagnetic radiation (UV, visible, and IR illumination) [10]. The change in color implies a change in the absorption spectrum in the visible range of light (400–700 nm). The Photochromic mechanism of transition-metal oxides specifically that for MoO₃ when the oxide film is irradiated with UV-light ($h\nu \geq E_g$) charge separation (production of electron-hole pairs) will take place (see Equation (1)). As a result of this the optical absorption changes markedly, and molybdenum oxide turns from colorless to blue. The change in the color of the film is due to the intervalence-charge transfer from the newly formed Mo⁵⁺ (valence band-like) to adjacent Mo⁶⁺ (conduction band) according to the Equation (2) [11].



The reverse process can take place by the exposure to the light with different frequencies, by heating in the dark places, by electrochemical polarization, or by chemical oxidation [10].

Consequently, the main aim of the present work was to study the effect of UV-irradiation on optical properties of PVA doped with 5% by weight of MoO₃. Optical properties and parameters like reflection, transmission, refractive index, optical dielectric, and optical conductivity were investigated.

2. Experimental methods

2.1. Materials

Polyvinyl alcohol (PVA) was obtained from Riedel-de Haen, (Germany) as a yellowish color nontoxic polymer with a 4-6 CP viscosity and 4% moisture content at 20 °C. Molybdenum trioxide (MoO₃) was obtained from Riedel-de Haen, (Germany), as a light gray powder, with a molecular weight of 143.94 g/Mol, 99.5% purity and was used without further purification. Distilled water was used as the solvent throughout the experimental work.

2.2. Preparation of composite films

The solution casting technique was implemented in the preparation of the polymer composite film (5.0% MoO₃). One gram of PVA powder was introduced into a beaker containing 25 ml of distilled water, placed on a hot plate fitted with a magnetic stirrer and heated at 70 °C to dissolve PVA, Exact weight of MoO₃ proportional to the percentage of PVA was added while stirring is continued. The dissolved mixture was then poured into a flat bottom glass container of 9 cm diameter, placed on a flat surface and left to evaporate the solvent at room temperature. The obtained dry film was extracted from the flat container and stored in polyethylene bags in dark place prior to use in the study. The thickness of the film was measured using micrometer having a precision of 0.01 mm at different parts and the average thickness was 0.11 mm calculated to evaluate the uniformity of thickness.

2.3. Ultra Violet irradiation of the film

The obtained film of the PVA-MoO₃ composition was subjected to UV-irradiation using a UV lamp (Desaga Cab UVIS, Sarstedt AG&Co.). The irradiation zone has dimensions of (395 mm×390 mm) and height of 280 mm. The lamps emit UV ray of 366 nm wavelength and illumination strength about 4.8 mW/cm² at a distance 10 cm. The dimensions of the sample were 3 cm length by 1.5 cm width was subjected

to UV irradiation for different periods of time ranged from 5 to 60 minutes (5, 10, 20, 30, 40, 50 and 60 min).

The UV-irradiation to PVA film was carried out at room temperature. The sample was placed on the middle of the plate 10 cm far from the UV lamp and subjected to UV radiation.

2.4. Optical characterization

The most significant parameters for optical applications are the refractive index (n) and the extinction coefficient (k). These optical parameters were determined from the reflectance and absorption coefficient (α) according to the following equations [12,13,14,15]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (4)$$

$$R + T + A = 1 \quad (5)$$

Where R is the reflectance calculated from the transmission (T), absorption (A) data and λ is the wavelength of the incident light.

The dispersion is an important factor in optical communication and also in designing devices for spectral dispersion [16]. The Wemple and DiDomenico single oscillator models are used to analyze the dispersion of refractive index, which provides the useful parameters regarding the strength of inter-band transitions [17]. The dispersion of refractive index below the inter-band absorption edge according to the Wemple-DiDomenico single oscillator model, the dispersion of the refractive index below the inter-band absorption edge is calculated by [18]:

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad (6)$$

Where E_0 is the average value of the single oscillator energy of the electronic transitions, which is usually considered as an average energy gap, and E_d is the dispersion energy that measures the average strength of inter-band optical transitions. Moreover, E_d can be regarded as a parameter that has a close relation with the chemical bonding [19]. The derivation of the moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} follows from Eqs. (7) and (8) in Ref. [20], whereas the evaluation of the static refractive index at a zero photon energy stems from Eq. (9) in Ref. [19].

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \quad (7)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (8)$$

$$n_0^2 = 1 + \frac{E_d}{E_0} \quad (9)$$

The complex dielectric constant ε measures the ability of a material to interact with an electric field that makes it polarized. On the other hand, the real part of the dielectric constant displays the level of slowing down the speed of light through the material and it is related to the stored energy within the medium, and the imaginary part shows the absorbing energy from the electric field by the material due to dipole motion. The ratio of the imaginary part (ε_2) to the real part (ε_1) of dielectric constant is called the lose factor. Both parts can be estimated using the relation [21,22]:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad (10)$$

Where

$$\varepsilon_1 = n^2 - k^2 \quad (11)$$

$$\varepsilon_2 = 2nk \quad (12)$$

The optical conductivity (σ_{opt}) is termed as the optical response of the material to the diffusion of charge carriers due to excitation caused by the incident photon energy. Optical conductivity depends directly on the refractive index and absorption coefficient of the materials according to the following equation [15,23,24]:

$$\sigma_{op} = \frac{\alpha n c}{4\pi} \quad (13)$$

Where (c) is the speed of light in a vacuum

3. Results and discussion

Figure 1 represents the transmittance spectra of PVA-MoO₃ film before and after UV exposure for different periods of time. It is clear from the figure that the transmittance value decrease with the increasing of the exposure radiation time, which due to the change in the absorbance as a result of the change in the color of the film.

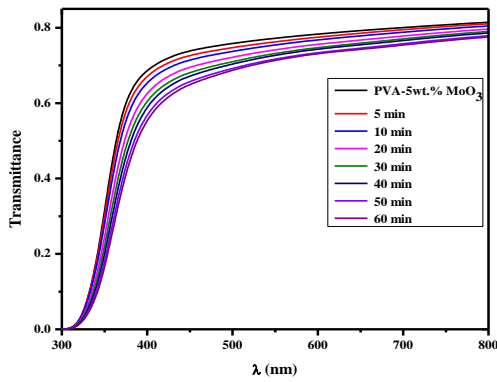


Fig.1. Transmittance spectra of PVA-5wt. % MoO₃ film before and after different UV radiation exposure time

The variation of the extinction coefficient (k) with the incident photon wavelength of the PVA-MoO₃ film after UV light irradiation is shown in Figure 2. The variation is simple in the low energy region while it increased in the high photon energy region, this behavior may be as a result to the variation of the absorption coefficient which leads to spectral deviation in the location of the charge polarization at the attenuation coefficient due to the loses in the energy of the electron transition between the energy bands [25].

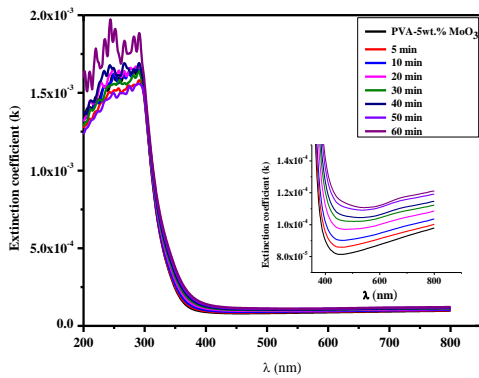


Fig.2. Variation of the extinction coefficient with the incident photon wavelength of PVA-5wt. % MoO₃ film after different UV radiation exposure time.

The relationship between the reflectance and the wavelength before and after UV irradiation (Figure 3) shows that the reflectance sharply increases with wavelength and the time of irradiation, which due to the change in the absorbance as a result of the change in the color of the film to blue.

The effect of UV irradiation on refractive index (n) of the PVA-MoO₃ film is shown in Figure 4. The values

of refractive index decrease with increasing photon wavelength. This decrease indicates that the electromagnetic radiation passing through the material is faster in the low photon energy [25]. It is also observed that the value of the refractive index increases with the increase of the exposure radiation time.

The values of E_0 and E_d were calculated directly from the slope ($-1/(E_0 E_d)$) and the intercept (E_0/E_d) on the vertical axis of the linear fitted part of $1/(n^2-1)$ plotted versus $(h\nu)^2$ as shown in Fig.5. The calculated values of E_0 and E_d for the PVA-MoO₃ film after UV exposure for different times are listed in table 1. The values of E_0 decrease and E_d increase with the increase of time of irradiation. The increase in the dispersion energy (E_d) indicates the increase in bond strength, which leads to increase in the degree of disorder [19].

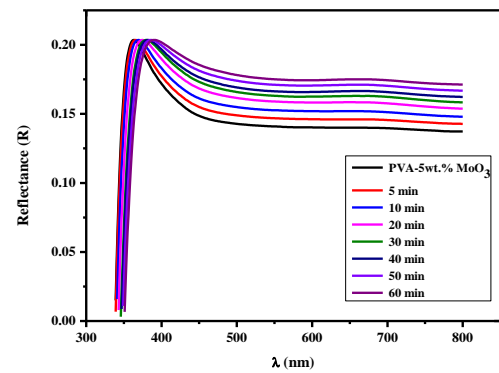


Fig.3. The reflectance of PVA-5wt. % MoO₃ films as a function of wavelength before and after UV irradiation.

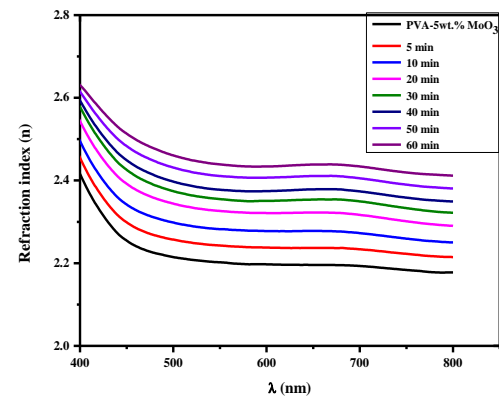


Fig.4. The refractive index of PVA-5wt. % MoO₃ film as a function of wavelength before and after UV irradiation.

The obtained M_{-1} , M_{-3} , the static refractive index (n_0) and the static dielectric constant ($\epsilon_{\infty} = n_0^2$) values are also increased with UV irradiation. The optical moments are related to macroscopic quantities similar to dielectric constants and the effective number of valence electrons in the investigated material [26].

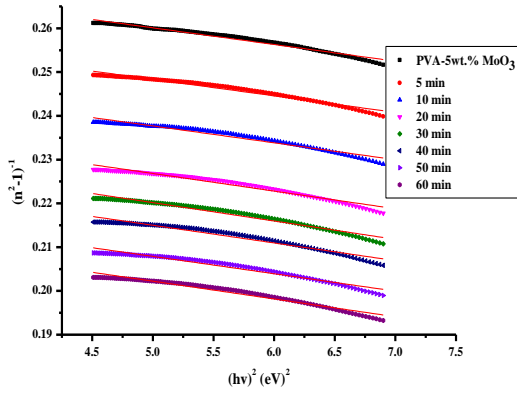


Fig.5. The relationship between $(n^2-1)^{-1}$ and $(hv)^2$ for PVA-5wt. % MoO₃ film before and after UV irradiation.

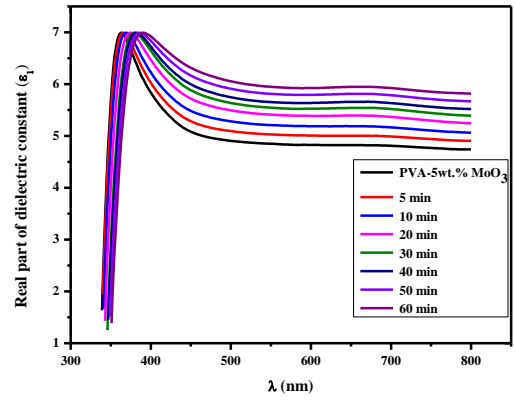


Fig.6. The real dielectric constant of PVA-5wt. % MoO₃ film as a function of wavelength before and after UV irradiation.

Table1. The dispersion parameters and static refractive index of PVA- MoO₃ film after different UV radiation exposure time.

Time	E ₀ (eV)	E _d (eV)	n ₀	ε _∞	M-1	M-3 (eV) ⁻²
0	8.55	30.6	2.14	4.58	3.58	0.0489
	98	619	06	22	29	
5	8.40	31.4	2.17	4.74	3.73	0.0529
	79	643	77	22	96	
10	8.16	31.7	2.21	4.89	3.89	0.0583
	95	940	17	18	09	
20	7.82	31.6	2.24	5.04	4.05	0.0661
	88	955	69	86	13	
30	7.58	31.4	2.26	5.14	4.14	0.0721
	61	606	87	93	93	
40	7.63	32.4	2.29	5.25	4.29	0.0737
	02	399	16	15	08	
50	7.57	33.2	2.32	5.39	4.39	0.0766
	36	584	19	14	14	
60	7.40	33.2	2.34	5.49	4.49	0.0819
	37	676	38	34	34	

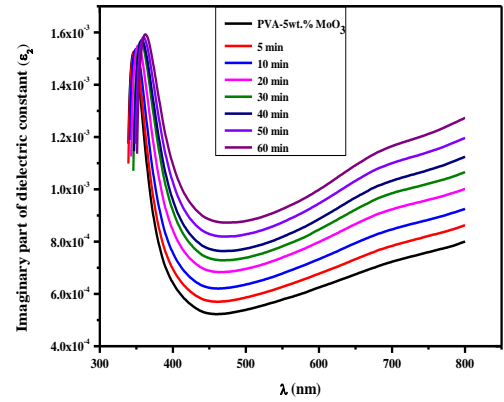


Fig.7. The imaginary constant of PVA-5wt. % MoO₃ film as a function of wavelength before and after UV irradiation.

The variation of real and imaginary parts of the dielectric constant for the PVA – MoO₃ film after different UV radiation exposure time with photon wavelength are shown in Figures 6 and 7. The real and imaginary parts of dielectric constant increase with the increase of the time of irradiation. The increase of real and imaginary parts of dielectric constant with UV radiation exposure time due to the increase of refractive index and extinction coefficient [21].

Figure 8 shows the variation of optical conductivity of the PVA – MoO₃ film after different UV radiation exposure time with photon energy. It is clear that the optical conductivity of the film increases with the increase in irradiation time, this behavior attributed to the increase in density and absorption coefficient [27].

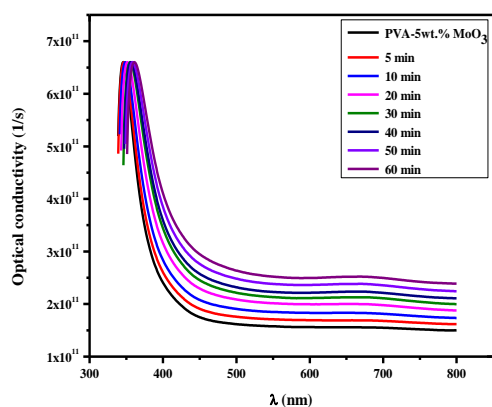


Fig.8. The optical conductivity of PVA-5wt. % MoO₃ film as a function of wavelength before and after UV irradiation.

4. Conclusion

Polyvinyl alcohol-Molybdenum oxide composite film is prepared by solution casting method. The effects of UV irradiation on optical parameter of PVA-5wt. % MoO₃ film were investigated. The transmittance (T) and the average values of single oscillator energy for electronic transitions (E_0) are decreasing while the other optical parameter increases with increase in irradiation time. These results indicate that the film we have prepared can be used in many applications, including anti-reflective coating, photonic devices and as a UV sensor.

5. References

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