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Abstract

Polymers blend PVA/PEO filled with different weight percent ratios of methyl orange was used to prepare films via casting method. Structural properties of the final thin films were carried out using XRD technique, FTIR and optical microscope. While the absorption spectra of these films were measured using UV-VIS double beam spectrometer in the wavelength range of (190-1100) nm. The optical coefficients such absorption coefficient and extinction coefficient were calculated from the optical absorption.

Direct and indirect allowed electronic energy transitions were studied under the influence of MO weight percent variation (0, 10, 20, 30, 40 and 50) wt %.

Keywords: Optical absorption, Methyl orange, Thin films, Energy gap, Extinction coefficient

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تحضير ودراسة خصائص اغشية رقيقة من الخليط البوليمري (PVA/PEO) المدعم بصبغة المثيل البرتقالي

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الخلاصة

تم تدعيم الخليط البوليمري (PVA/PEO) بصبغة المثيل البرتقالي بنسب وزنية مختلفة وحضرت منها اغشية رقيقة باستخدام طريقة الصب. الخواص التركيبية لهذه الاغشية تم فحصها بواسطة تقنية XRD و FTIR و المجهر البصري. في حين ان طيف الامتصاص لهذه الاغشية تم فحصه باستخدام جهاز UV-VIS ذو طول موجي (190-1100) نانومتر. ان معامل الامتصاص ومعامل الاخمد تم حسابهم من الخصائص البصرية للاغشية الرقيقة المحضرة. درست انتقالات الالكترونات المباشرة وغير المباشرة بتأثير تغير تراكيز المثيل البرتقالي (0، 10، 20، 30، 40، 50)%.

الكلمات المفتاحية: الخواص البصرية، المثيل البرتقالي، الاغشية الرقيقة، فجوة الطاقة، معامل الاخمد.

Introduction

Polymers play a very important role in man life. Our body is made of lot of polymers such as proteins and enzymes, in addition to natural polymers like wood, rubber, leather and silk. Many of useful properties of polymers came from their long chain molecular structure. For these unique properties there are huge various engineering applications of polymers, as refrigerator lining, highway safety devices, chemical pipes and valves, anti-adhesive coating, battery part, film wrapping materials, etc. [1]. Optical characterizations of polymer have allured much interest in view of their applications and optical apparatus such as super capacitors, fuel cells, gas sensors, solid state batteries, etc. [2] also can be modified by dopants additive [3]. Some routes, as copolymerization, plasticization, mixing, reducing of crystallinity, adding special salts and varying the salt concentration have been used to enhance of the conductivity of the polymers [4].

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Poly (ethylene oxide) (PEO) is the most familiar polymer, which solvates the high concentration of ionic salts [5]. The structure of PEO is $H-(O-CH_2-CH_2)_n-OH$ [6]. Poly (vinyl alcohol) (PVA) is one of the most significant polymeric materials as it has many applications in industry [7]. It is a potential material having a very high dielectric strength, high charge storage capacity and dopant-dependent [8]. Organic dye is an unsaturated hydrocarbon compound, consisting of large molecules which have complicated complex, wide absorption and fluorescence spectra in the regions of the visible and ultraviolet of the electromagnetic spectrum [9]. Methyl orange (MO) is a compound of a series of common water soluble azo dyes vastly used in chemistry, weavings and paper manufacturing [10].

In current work PEO polymer was melded with PVA polymer with the same mixing weight ratio filled with MO azo dye to prepare final samples via casting method and studying their structural and optical properties.

Experimental part

The complexes films made from (PVA/PEO) with MO were synthesized with ratios of (50:50:0), (45:45:10), (40:40:20), (35:35:30), (30:30:40) and (25:25:50) as weight percent and labeled as (MOa, MOb, MOc, MOd, MOe and MOf) using casting method using distilled water as a solvent. The solutions of blended polymers were stirred for (5-7) hours in water bath to obtain a homogeneous mixture and then casted onto glass substrate at 130 °C for 5 hrs. The structure of the samples was tested using a Shimadzu 6000 X-ray diffractometer using $Cu K\alpha$ radiation ($\lambda=1.5406\text{\AA}$). Optical microscope (OM) (GENEX OPTIK 20) under a cross polarizer microscope with 40x was used to deduce the morphology of the final thin films. Infra-red spectra, from (4000 to 400) cm^{-1} , were recorded for samples using FTIR spectrometer, supplied by Shimadzu, on KBr pellets of the samples. The thickness of the obtained films was measured using the optical interferometer method (Mickleson interferometer) employing He-Ne laser 0.632 μm . The optical absorption spectra of thin films were investigated using UV-VIS double beam spectrometer in the wave length range of (190 to 1100) nm. The absorption coefficient (α) was computed using the equation [11]:

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$$\alpha = \frac{2.303A}{d} \quad (1)$$

Where (d) is the thickness of the thin film.

The direct allowed electronic transitions obtain using the equation [12]:

$$\alpha h\nu = b(h\nu - E_g)^m \quad (2)$$

Where: E_g : energy gap for direct transition

b: constant

ν : frequency of incident light

m: exponential constant, $m = 1/2$ for the allowed direct transition.

The absorption coefficient for transition with phonon absorption could be calculated using the following formula [13]:

$$\alpha h\nu = b(h\nu - E_g \pm E_p)^m \quad (3)$$

Where E_g : indirect transitions energy band gap

E_p : phonon energy.

($m = 2$) for the allowed indirect transition

The extinction coefficient (K) can be computed in terms of the absorption coefficient using the equation [14]:

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

Results and Discussions

XRD patterns of the PVA/PEO blended with MO dye thin films are shown in figure (1).

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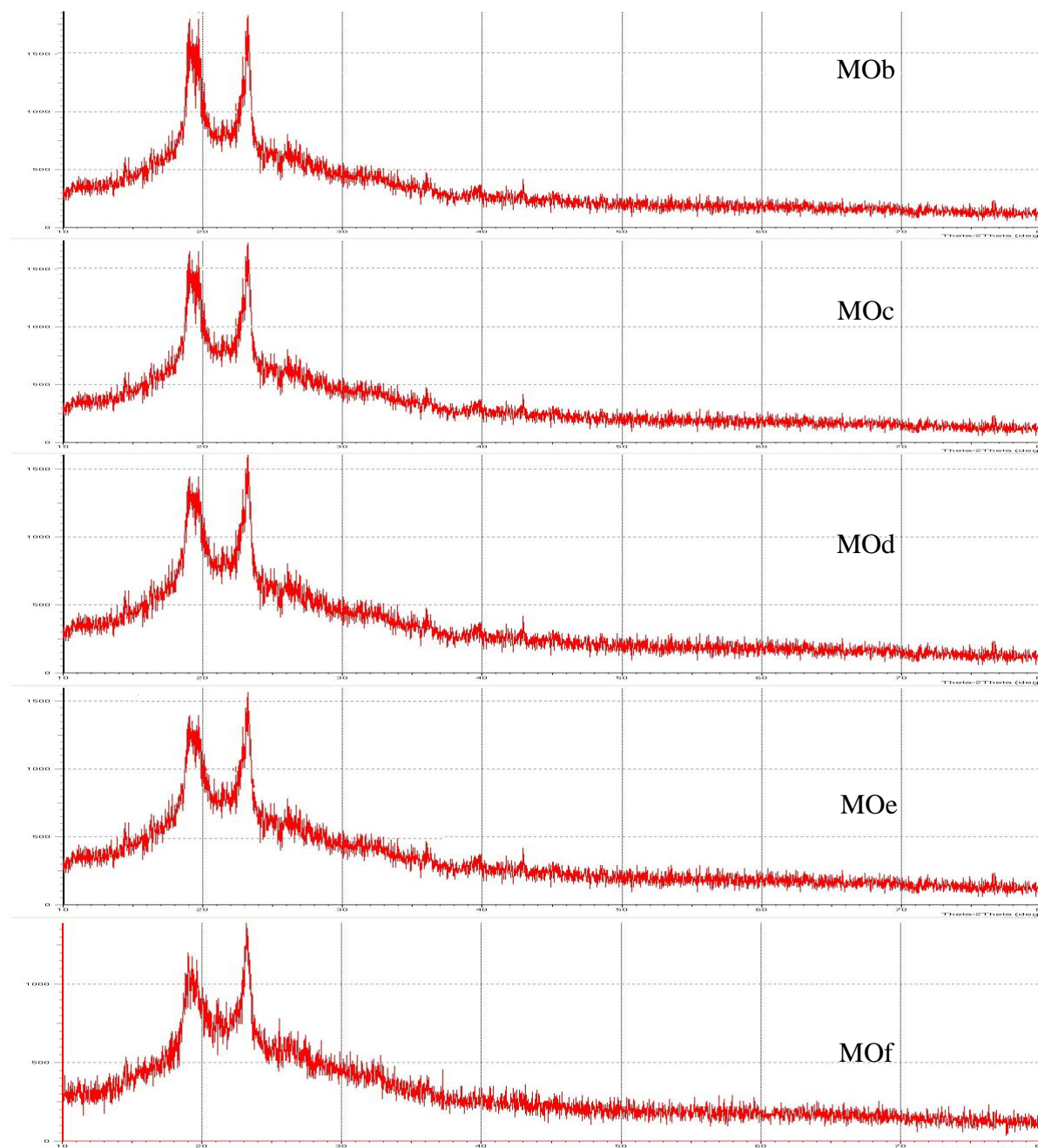


Figure 1: XRD Patterns for (MOb), (MOc), (MOd), (MOe) and (MOf).

From figure (1) the indexing of two polymers peaks are reported at 19.5° and 23.5° . The distinguished feature diffraction peaks of crystalline PEO are evident between $2\theta = 15^\circ - 40^\circ$ [15,16]. The two prominent peaks for PEO at $2\theta = 19.2^\circ$ and 23.2° are present in all patterns,

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indicating the presence of pure polymer. Nonetheless, the patterns show that the intensities of the prominent peaks decrease and become wider with the increasing weight percent of MO. The broadening of sharp peaks of PEO could be due to the disruption of the PEO crystalline structure by MO and indicates that the complexation has taken place in the amorphous phase [17]. It is also observed that the (PEO/PVA) blended with MO is freed from crystalline peaks and demonstrates only broad patterns (Figure 2), which shows that this composition consists primarily of an amorphous phase [18]. Figure (2) shows the optical microscope photographs for the different prepared samples (MOa, MOb, MOc, MOd, MOe, MOf).

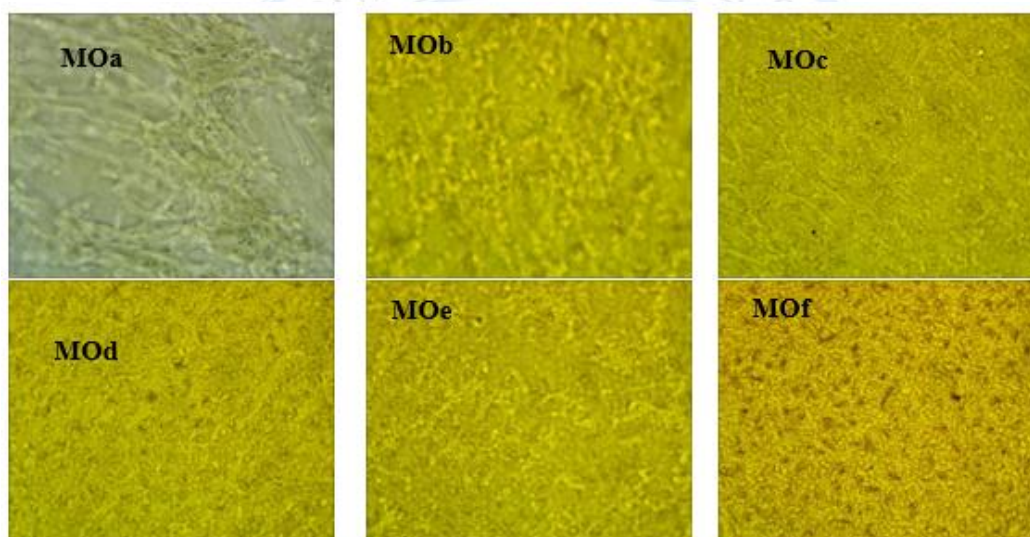


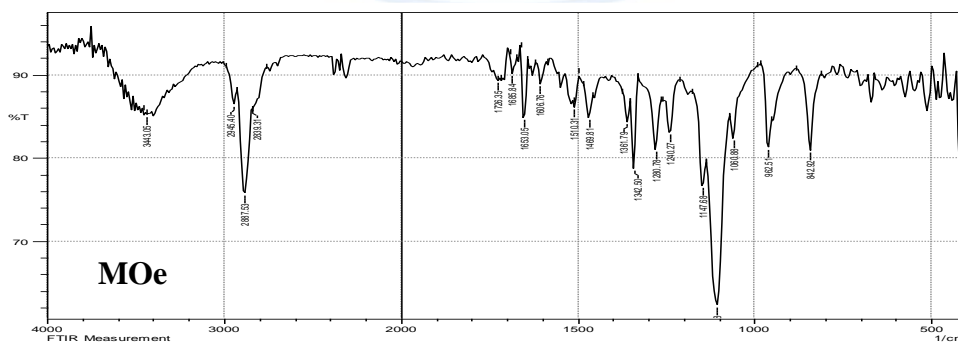
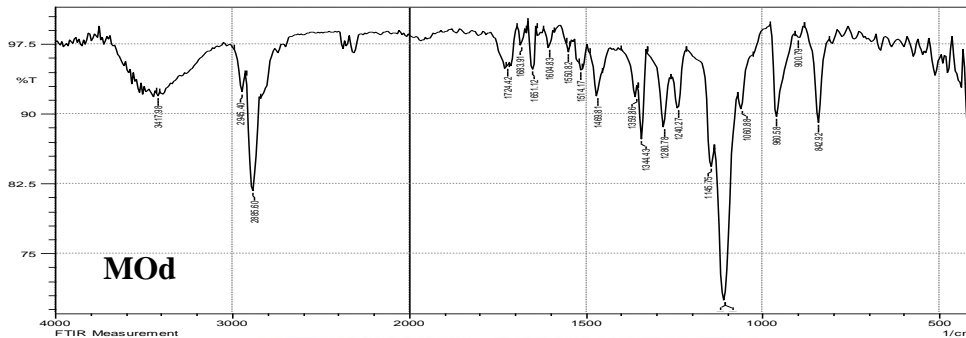
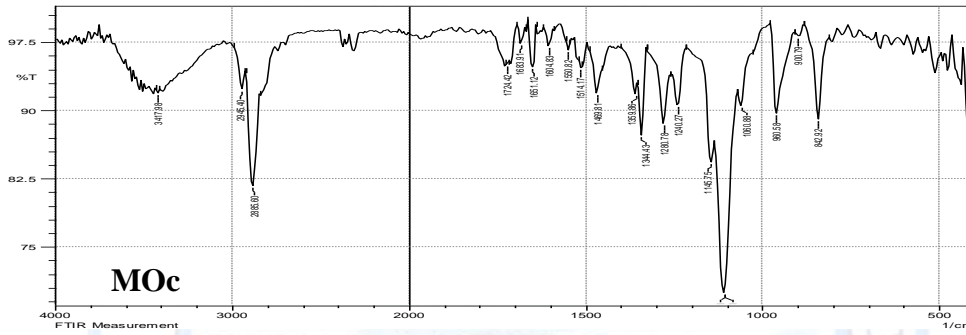
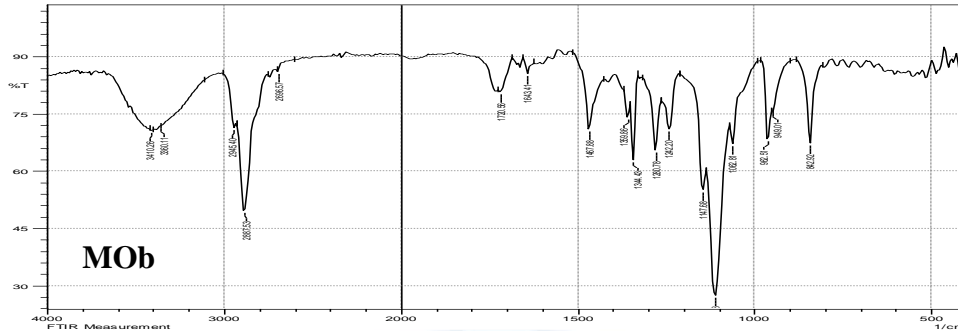
Figure 2: Optical micrographs for (MOb), (MOc), (MOd), (MOe) and (MOf).

It was clear that the pure PEO/PVA film (Figure 3MOa) shows well the semicrystalline nature in which large size PEO/PVA molecules are tightly interconnected with each other. Adding MO into the PEO/PVA matrix (Figure 3MOb, MOc, MOd, MOe and MOf), the MO size becomes small, while the amorphous region (darker portion) is increased. This shows good agreement with our FTIR and XRD measurements.

The composites of PEO/PVA filled with MO films were confirmed using FTIR spectra of different samples and shown in figure (3).

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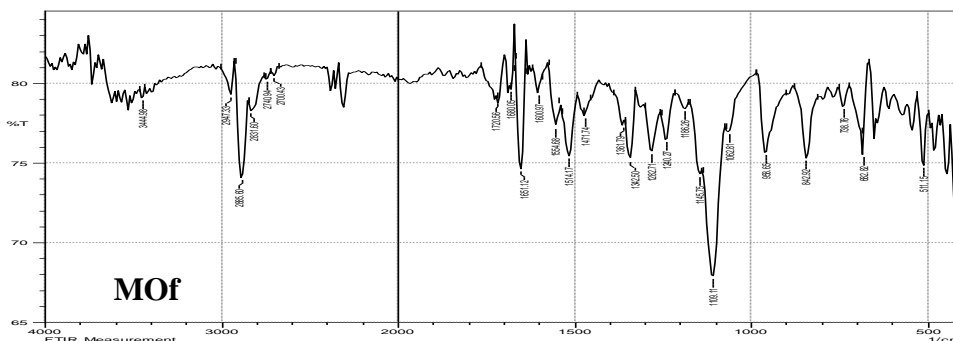


Figure 3: The FTIR spectra for (MOb), (MOc), (MOd), (MOe) and (MOf).

In the IR spectra of MO, the -C=C- stretching was observed at $(1600\text{-}1655)\text{cm}^{-1}$, the -S=O stretching was observed at $(1100\text{-}1130)\text{cm}^{-1}$. In the IR spectra of PEO/PVA for PEO, C-H stretching mode can be noticed at $(2885\text{-}2946)\text{cm}^{-1}$, CH_2 shearing stress mode at $(1466\text{-}1516)\text{cm}^{-1}$, CH_2 waggish mode at $(1340\text{-}1360)\text{cm}^{-1}$, CH_2 twisting mode at $(1275\text{-}1285)\text{cm}^{-1}$, CH_2 rocking and C-O-C vibration mode at $(955\text{-}965)\text{cm}^{-1}$, CH_2 rocking at $(845\text{-}854)\text{cm}^{-1}$. The semi-crystalline phase of PEO is promoted by the existence of triplet peak of C-O-C stretching [19, 20]. C-O-C stretching vibrations are observed at $(1147, 1060)\text{cm}^{-1}$ [21]. The O-H stretching vibration peak at 3360cm^{-1} was decreased when compared to PVA (Figure 3). The hydrogen bonding becomes weaker in cross-linked PVA because of the shortage in the number of OH groups and acetal formation. The relative increase of the C=O band at about at $(1724\text{-}1727)\text{cm}^{-1}$ refers that the aldehyde groups did not completely react with O-H groups of PVA chain [22,23]. In the IR spectra of complex (PVA/PEO) blend with MO, the aromatic -C-H stretch was observed at $(3400\text{-}3445)\text{cm}^{-1}$, the -C=C- stretching was observed at $(1600\text{-}1650)\text{cm}^{-1}$, the -C-H stretching was observed at 2945cm^{-1} .

Absorbance spectra for the prepared samples are shown in figure (4) for the prepared thin films.

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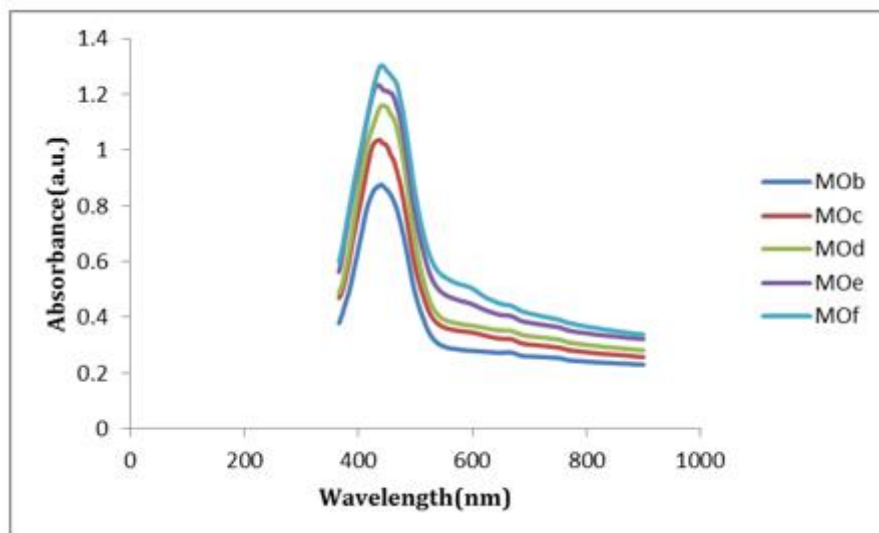


Figure 4: Absorbance versus Wavelength for (MOb), (MOc), (MOd), (MOe) and (MOf).

It is clear from the absorbance spectra that the absorption intensity was increased with increasing the concentration of MO ratio. Also, one can notice that the maximum absorption occurs around 424nm which represents the absorption peak of the MO dye. The reason of the increasing in absorption intensity with increasing of dye concentration is due to the increase in the number of molecules in volume unit which leads to change in energy level of dye as result of increasing in perturbation field on the molecules [24].

Absorption coefficients are shown in figure (5) for PEO/PVA doped with different weight ratios of MO.

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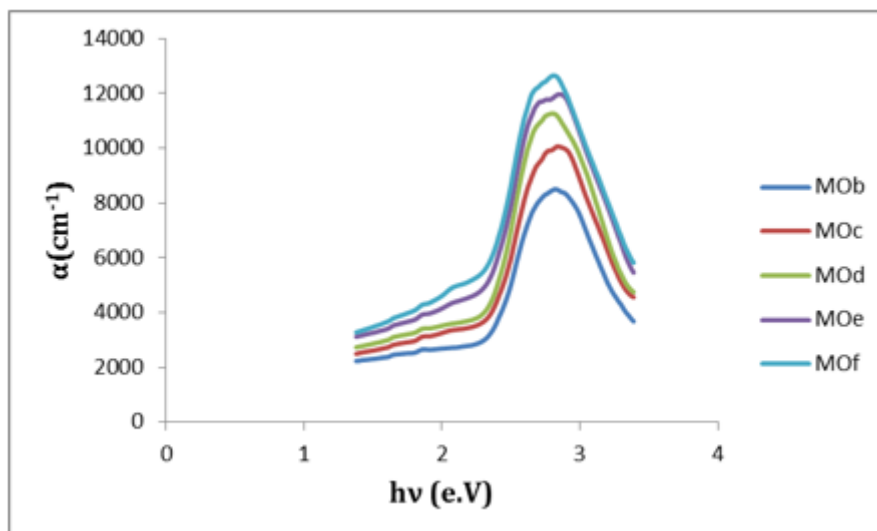


Figure 5: Absorption coefficient versus the photon energy for (MOb), (MOc), (MOd), (MOe) and (MOf)

Absorption coefficient values at exponential range are less than 10^4cm^{-1} which indicates that the charge carriers transport from the energy levels extended within covalent band to the local energy levels within conduction band, these values refer to the probability of direct electronic transitions. From figure (6), allowed electronic transition energy gaps could obtain and the values of these energy gaps are shown in table (1). While the values of absorption coefficients more than 10^4cm^{-1} refer to the probability of indirect electronic transitions. Direct energy gaps could be calculated in same way, from figure (7), one can obtain the indirect energy gaps and the results are listed in table (1) for all sample.

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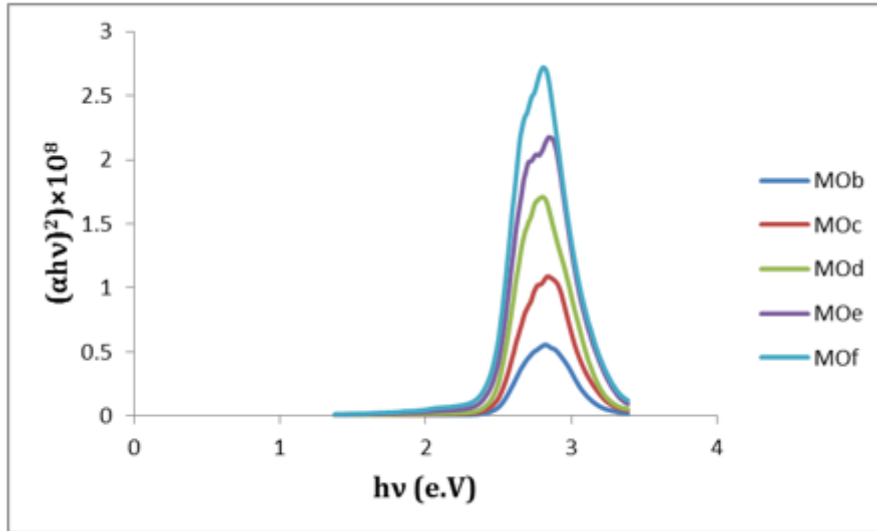


Figure 6: $(\alpha h\nu)^2$ versus (photon energy) for (MOb), (MOc), (MOd), (MOe) and (MOf).

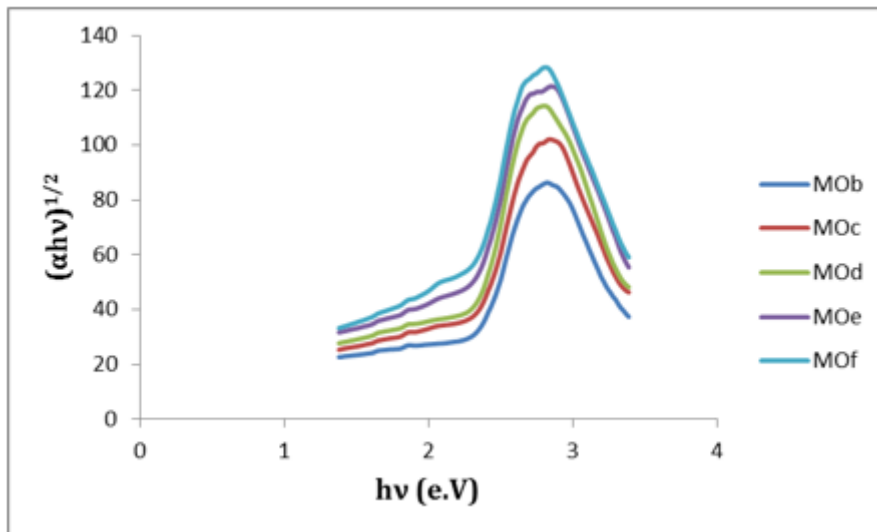


Figure 7: $(\alpha h\nu)^{1/2}$ versus (photon energy) for (MOb), (MOc), (MOd), (MOe) and (MOf)

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Table 1: Allowed electronic transition energy for (MO_b), (MO_c), (MO_d), (MO_e) and (MO_f)

Samples	Direct	Indirect
Mob	2.49	2.11
MOc	2.46	2.7
Mod	2.44	2.3
Moe	2.41	1.92
MOf	2.34	1.90

Extinction coefficients for PEO/PVA blend with MO thin films are calculated using eq. (4).

The variation of these coefficients with incident photon energy is shown in figure (8).

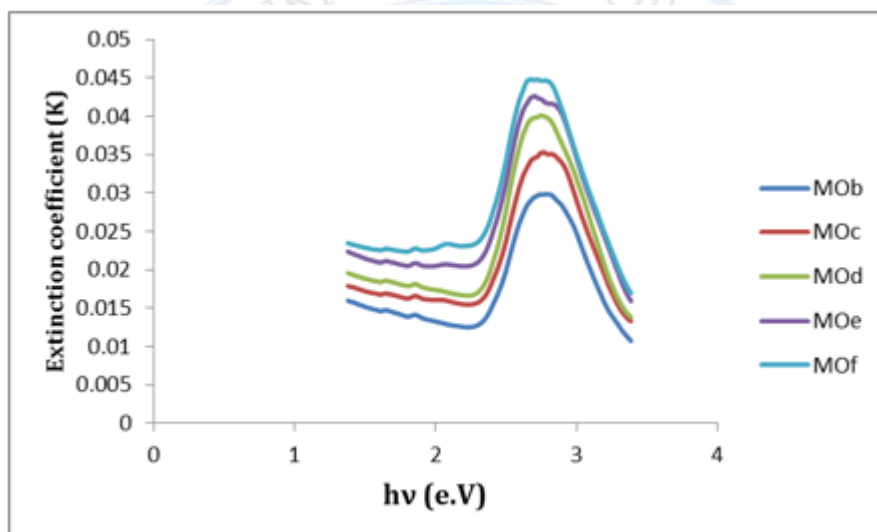


Figure 8: Extinction coefficient versus photon energy for (MO_b), (MO_c), (MO_d), (MO_e) and (MO_f)

It is clear from figure (8) that the extinction coefficient is increased gradually with increasing the photon energy at low energies. Also, one can notice that the extinction coefficient has similar behavior with the absorption spectra for PEO/PVA filled with MO thin films. The similarity in this behavior results from the dependency of the extinction coefficient on the absorption coefficient according to equation (4).

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Conclusion

Polymer blend (PVA/PEO) thin films filled with various concentrations of MO were synthesized using casting method. Structural analysis using different techniques were called out for these films. Effects of varying MO weight percent were studied on the allowed direct electronic transitions and indirect. Increasing MO percent ratio from 10% to 50% leads to decreasing in the direct electronic energy gap from 2.49eV to 2.3eV and in the same range of this weight percent valuation, the indirect energy gap for allowed electronic transition is decreasing from 2.11eV to 1.9eV. The blending effects on the optical properties of (PVA/PEO) were also studied.

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