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Optical and Structural Properties of Methylene Blue Doped Poly Vinyl Alcohol Films after Gamma Irradiation

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Abstract

In this research the optical properties (absorption, transmission, reflection spectra, optical absorption coefficient, optical energy gap, extinction coefficient, reflective index and real and imaginary dielectric constants) and structural properties that contain FTIR spectra and FESEM have measured for un-irradiated and Gamma irradiated pure PVA and MB/PVA films. The Gamma irradiation emitted from ^{60}Co source with irradiation dose 17.8 KG for all samples. The results showed that the electronic transition is indirect for all samples and the optical energy gap of PVA decreased after irradiation for pure PVA and MB/PVA films, whereas for MB increased after irradiation for MB/PVA film. The FTIR spectrum showed that all bonds for PVA polymer remained the same and doping with dye and Gamma irradiation did not affect on it. FESEM photographs illustrated that the surface of all films became more roughness after irradiation.

الخصائص البصرية والتركيبية لأغشية بولي فنيل الكحول المطعمة بالمثلين الازرق بعد تشعيع كاما

أ.م. د. محاسن فاضل هادي الكاظمي وعمار نجم عبد الجابري

الجامعه المستنصرية-كلية العلوم-قسم الفيزياء

الخلاصة

في هذا البحث الخصائص البصرية (أطياف الامتصاص، النفاذية، الانعكاسية، معامل الامتصاص البصري، فجوة الطاقة البصرية، معامل الخمود، معامل الانكسار وثوابت العزل الكهربائي الحقيقية والخيالية) والخصائص التركيبية التي تتضمن اطياف FTIR و FESEM تم قياسها لأغشية PVA النقي و MB/PVA غير المشعة والمشعة بأشعة كاما المنبعثة من مصدر Co^{60} بجرعة تشعيع 17.8KG لكل النماذج والنتائج اظهرت ان الانتقال هو من النوع غير المباشر لكل الاغشيه وان فجوة الطاقة البصرية للPVA تتناقص بعد التشعيع لأغشية PVA النقي وMB/PVA، بينما للMB تزداد بعد التشعيع لأغشية MB/PVA. طيف FTIR بين ان كل الاواصر لبوليمير PVA تبقى نفسها والتطعيم بالصبغة وتشعيع كاما لايؤثر عليها. الصور الفوتوغرافية لFESEM اوضحت بأن سطوح كل الاغشية تصبح خشنة بعد التشعيع بأشعة كاما.

Key word: Gamma Irradiation, Optical Properties, Methylene Blue, Poly Vinyl Alcohol, FTIR, FESEM.

1. Introduction

The effect of high- energy radiation on organic polymers is to produce ionization and excitation. Subsequent rupture of chemical bonds yields fragments of the large polymer molecules, which may retain unpaired electrons from the broken bonds. The free radicals thus produced may react to change the chemical structure of the polymer and alter the physical properties of the material [1].

One of the most important characteristics of a polymer is its molecular weight. Radiation can affect on molecular weight in two ways. It can increase it by linking molecules together (cross-linking) or it can decrease it, by inducing main-chain degradation .A third process is possible in principle: scission might occur in the main chain of the polymer, and at least one of the fragments might link to the main chain of a polymer[2]. Polyvinyl alcohol (PVA) is a well-known polymer for many technological applications since it forms a film with high transparency, very good flexibility and wide commercial avaibility. Photo sensitizable dyes incorporated in the PVA solid matrix[3], like Methylene blue that is sensitized poly vinyl alcohol[4]. Many researchers studies the effect of irradiation on polymers and dyes; such as Chan Kok Sheng *et al*[5],

studied UV-Visible photo degradation of Methylene blue doped in Poly(Vinyl Alcohol)(PVA) solid matrix, the results showed that the absorption observed at 660nm decreases with increasing of the exposure time. The blue color of the MB doped PVA sample turned completely colorless after irradiation for 360 seconds. E.M. Antar [6], studied effect of γ-ray on optical characteristics of dyed PVA films, the results showed that the energy gap decreases when increasing absorption dose. In our research the effect of Gamma irradiation on optical properties, FESEM, and FTIR spectra for Methylene blue doped Polyvinyl Alcohol films.

2. Theoretical part

In the absorption measurements, the light intensity I after traversal of a thickness x of material as compared with the incident intensity I_o will be studied by defining the absorption coefficient α [7]:

$$I = I_o e^{-\alpha x} \quad (1)$$

Eq.(1) can be rewritten in the form of eq.(2)[8]:

$$\alpha x = 2.303\ log(I/I_o) \quad (2)$$

The absorbance (A) is represent by the term (log I/I_o), eq.(2) become [8]:

$$\alpha = 2.303\ (A/x) \quad (3)$$

The optical energy gap E_g of thin films is calculated by using the following eq.(4)[9]:

$$\alpha h\upsilon = j(h\upsilon - E_g)^m \quad (4)$$

Where j is a constant, h is Planck's constant, υ is the frequency of the incident photon and n the exponent which depends on the type of transition that occurred. The reflectance (R) can be calculated by the following equation:

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

The relation between reflectivity and refractive index (n) is given by eq.(6)[10]:

$$R = \frac{(1-n)^2+K^2}{(1+n)^2+K^2} \quad (6)$$

The extinction coefficient (k) can be calculated by using eq.(7)[11]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (7)$$

Where, λ is the wavelength of the incident ray. The refractive index can be calculated by using eq.(8)[12]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (8)$$

The real (ε_r)and imaginary (ε_i) complex dielectric constant can be expressed by eqs.(9) and (10), respectively [7]:

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

$$\varepsilon_i = 2nk \quad (10)$$

3. Experimental work

Poly (Vinyl Alcohol) used in this research as host material for dye because PVA has excellent film forming with the molecular weight M_w = 160000 g/mol, melting point 230 ^{0}C [13]. The dye is Methylene blue (MB) with chemical formula ($C_{16}H_{18}N_3SCl.2H_2O$) and molecular weight M_w = 355.89 g/mol made in a Fisher Scientific International Company (United Kingdom). Pure PVA and MB/PVA films were prepared by casting technique [9]. PVA solution was prepared by dissolving (0.5 g) PVA in (10ml) distilled water. The PVA solution was stirred until polymer become completely soluble then, the solution was cast onto a petri dish with diameter (10cm). Homogenous pure PVA film was obtained after drying at room temperature about (35^{0}C) for three days. To prepare MB/PVA films first prepare MB solution with concentration ($1*10^{-5}$ mol/liter), and (30ml) of this dye solution added to PVA solution and stirred very well at magnetic stirrer until the MP/PVA solution become homogenous solution. Then the mixture solution cast onto glass petri dish and leave at room temperature (35 ^{o}C) for three days to obtain homogenous film. The thickness of pure PVA and MB/PVA films that found (61.6 and 66)μm, respectively.

4. Irradiation samples

The samples were irradiated with irradiation dose of 17.8 kGy, using ^{60}Co Gamma Cell-900, of strength rate 3.7 Ci and dose rate 53 Gy/h, which emits mono-energetic 1.17 &1.33 MeV, and a half-life of 5.3 years. The source used has been built into a lead container with facilities for

inserting chemicals without exposing the operator to the radiation, installed at the physics Department, University of Baghdad. The absorption and transmission spectra were measured by UV-Visible spectrophotometer type (T70/T80 Series UV/Vis Spectrometer) in the wavelength range (250-800) nm.

Fourier Transform-Infrared (FTIR) Spectroscopy gives information on the structural composition of the material and the type of bonds in this material. FTIR was carried out using (SHIMADZU-8400S), the measurements are performed over the range between (500-4000) cm^{-1} for the prepared samples.

Field-emission Scanning Electron Microscope (FESEM) is used to visualize very small topographic details on the surface or entire or fractioned object, the object is scanned by electrons according to a zig-zag pattern, the FESEM study has been carried out by Hitachi (S-4160)

5. Results and discussion

The optical properties, FTIR and FESEM for un-irradiated and irradiated pure PVA and MB/PVA films were studied.

5.1 Optical Properties

Fig.(1) illustrate the UV/VIS absorption spectra of un irradiated and irradiated pure PVA and MB/PVA films. The absorption spectrum for samples showed blue shift for peak of MB dye toward long wavelength about 55nm after irradiation. There is a weak band at $\lambda = 280$ nm for pure PVA film with intensity (0.068), this peak is increasing after irradiation, because of larger molecules has exited to high levels. For un irradiated MB/PVA film there is two peaks 295nm with intensity (0.195) for PVA and 665nm with intensity (0.29) for MB. After irradiation the absorbance of MB/PVA film is increasing for peak of PVA and shifted to 280 nm, this mean there is a blue shift toward a short wavelength about 15nm. The peak of methylene blue decreasing after irradiation and shifted to 610nm, this mean there is a blue shift toward a short wavelength about 55nm.

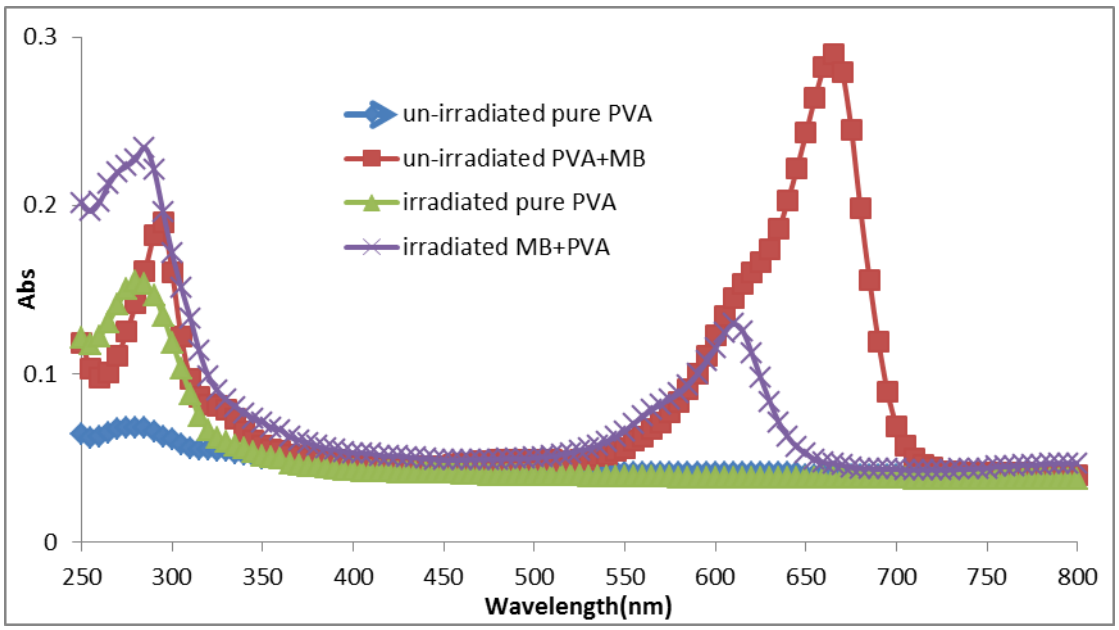


Fig.(1) The absorption spectrum of un-irradiated and irradiated pure PVA and MB/PVA films

The transmission (T), defined as the ratio between the intensity of transmitted radiation and the intensity of incident radiation that showed in fig.(2). The transmission for pure PVA film is decreasing after radiation. For MB/PVA film, the transmission is decreasing for PVA and increasing for MB after irradiation.

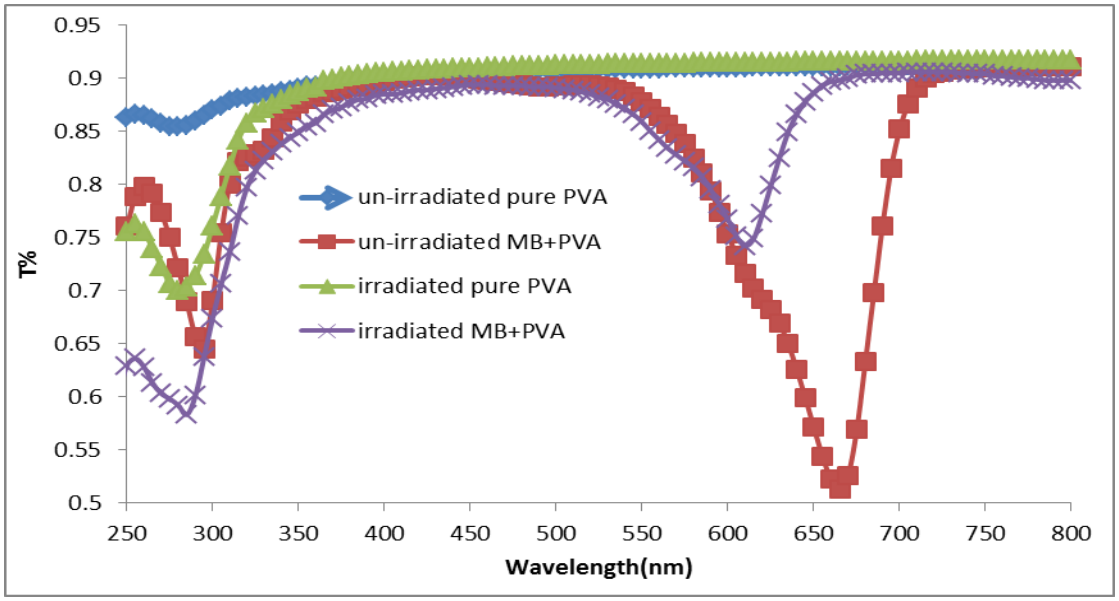


Fig.(2) The transmission spectrum for un-irradiated and irradiated pure PVA and MB/PVA films

The reflectance can be obtained by using Eq.(5), this parameter illustrated in fig.(3) for un-irradiated and irradiated samples.

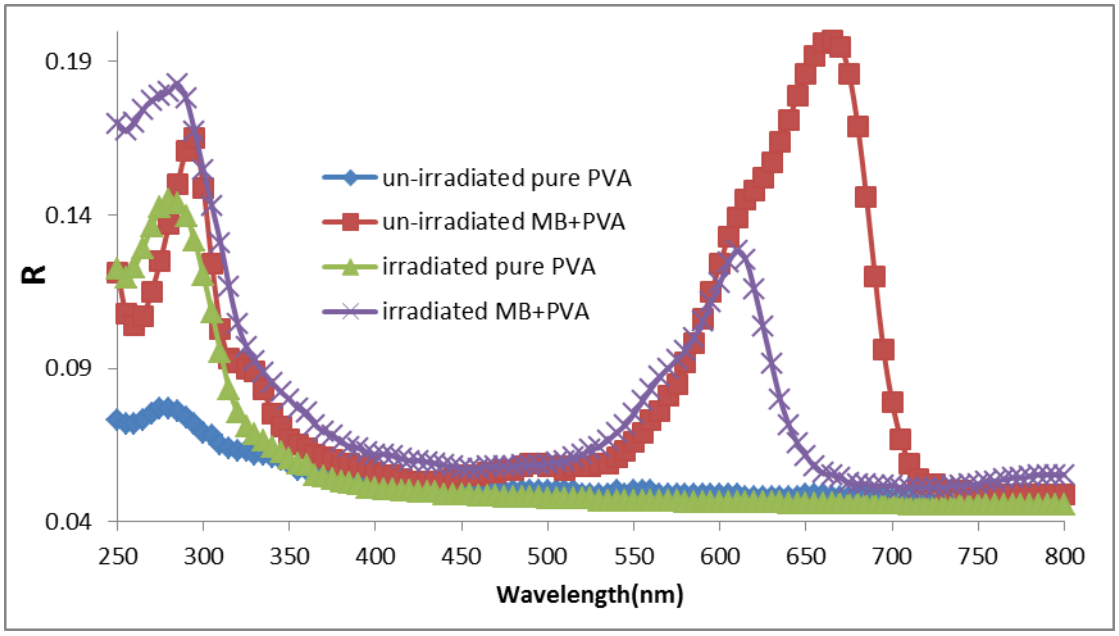


Fig.(3) The reflectance for un-irradiated and irradiated pure PVA and MB/PVA films

The absorption coefficient is defined as the ability of material to absorption light with a limited wavelength per unit length and it is a characteristic property for every absorber molecule or ion [14]. From eq.(3) the absorption coefficient can be calculate. The value of the absorption coefficient give us information about the nature of electronic transition. When the high absorption coefficient values ($\alpha > 10^4 cm^{-1}$) at higher energies, the direct electronic transitions expected and the energy momentum preserve of the electron and photon. While the value of absorption coefficients low ($\alpha < 10^4 cm^{-1}$) at low energies, indirect electronic transitions expected. Fig.(4) showed the absorption coefficient for un-irradiated and irradiated pure PVA and MB/PVA films.

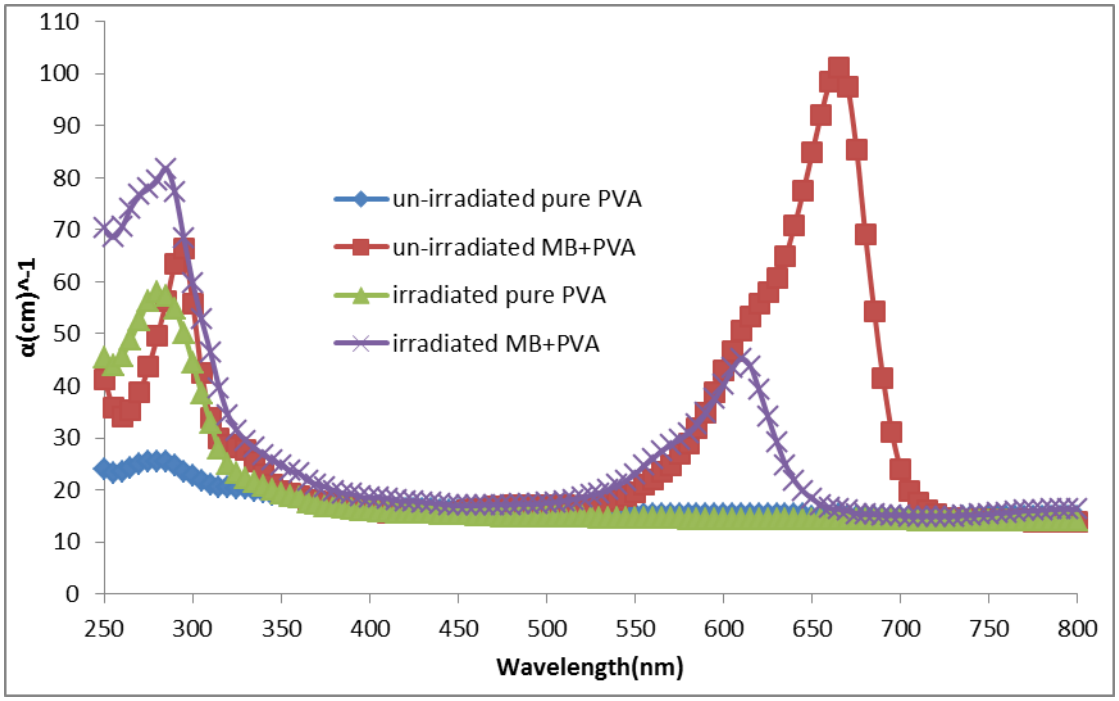
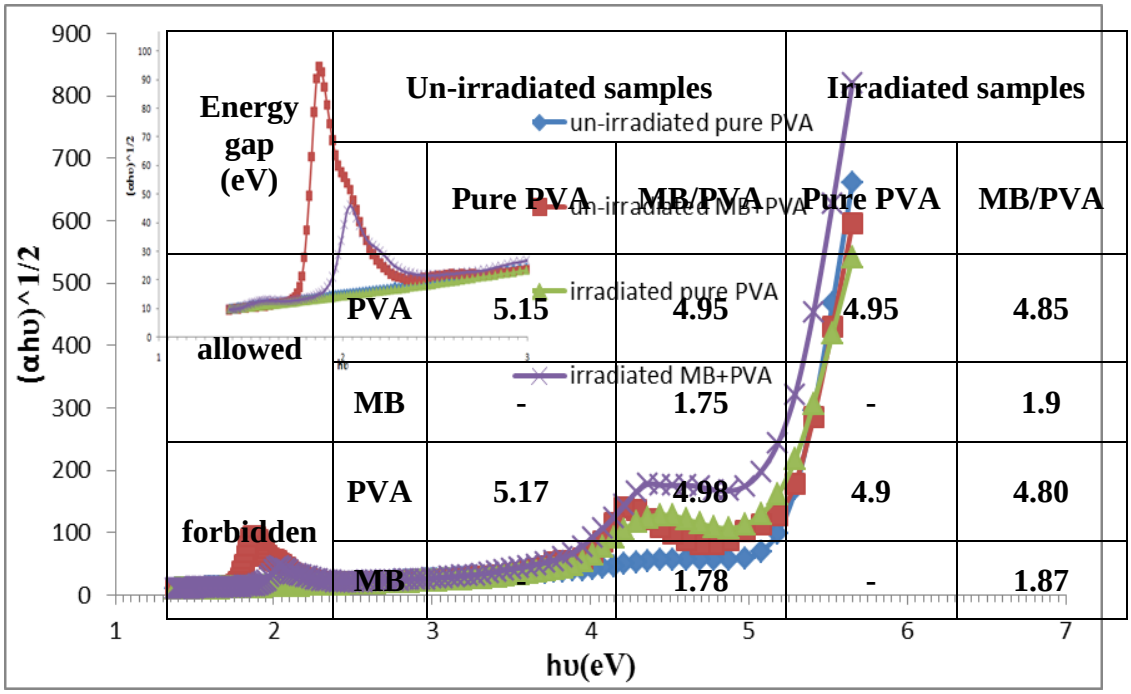


Fig.(4) the absorption coefficient for un-irradiated and irradiated pure PVA and MB/PVA films

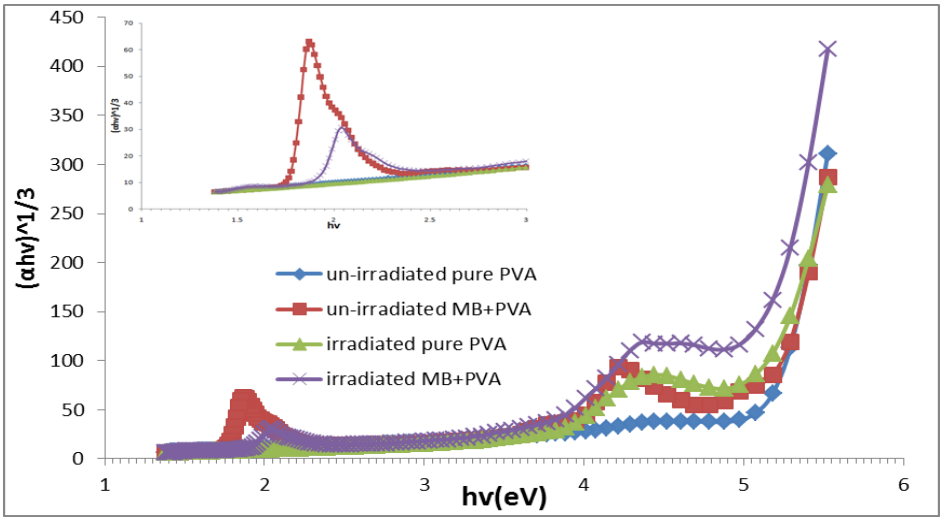
According to fig.(4), the value of absorption coefficient less than 10^4 cm^{-1} so that indirect electronic transitions have been deduced. Fig.(5-a, b) illustrate the relationship between absorption edge $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ and the energy of photon for pure PVA and MB/PVA films before and after irradiation which represent the indirect allowed and forbidden transition, respectively. The energy gap for un-irradiated and irradiated for all samples showed in table (1). The energy gap for PVA in pure PVA and PVA/MB films decreased after irradiation for both of allowed and forbidden indirect transition, these result may be attributed to the creation of electronic disorder which appeared after irradiation [6].Whereas the energy gap for MB dye in MB/PVA film increased after irradiation for allowed and forbidden indirect transition, and this result may be attributed to blue shift in absorbance.



Energy gap (eV)		Un-irradiated samples		Irradiated samples	
		Pure PVA	MB/PVA	Pure PVA	MB/PVA
allowed	PVA	5.15	4.95	4.95	4.85
	MB	-	1.75	-	1.9
forbidden	PVA	5.17	4.98	4.9	4.80
	MB	-	1.78	-	1.87

Table.(1) Energy gap of un-irradiated and irradiated pure PVA and MB/PVA films for indirect electronic transition.

(a)



(b)

Fig.(5) Energy gap for un-irradiated and irradiated pure PVA and MB/ PVA films: (a)allowed indirect transition, (b)forbidden indirect transition

According to eq.(7), the extinction coefficient depend on absorbance so that the behavior of extinction coefficient is similar to absorption spectrum for all samples. Fig.(6) illustrate the extinction coefficient for un-irradiated and irradiated pure PVA and MB/PVA films.

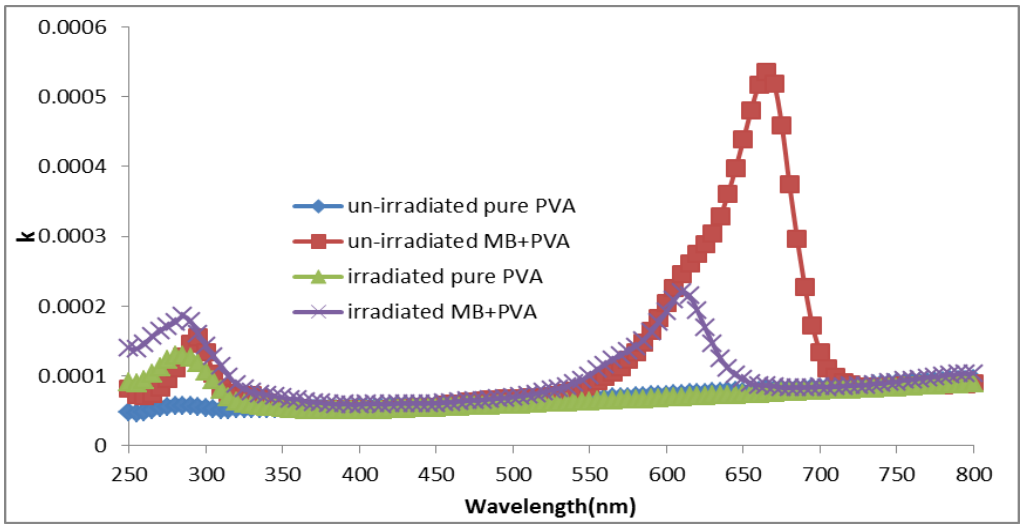


Fig.(6) The extinction coefficient for un-irradiated and irradiated pure PVA and MB/PVA films

The refractive index can be calculated according to Eq.(8) that depend on reflectance, so that the refractive index for all samples is similar to behavior of reflectance. Fig.(7) show the refractive index for un-irradiated and irradiated pure PVA and MB/PVA films.

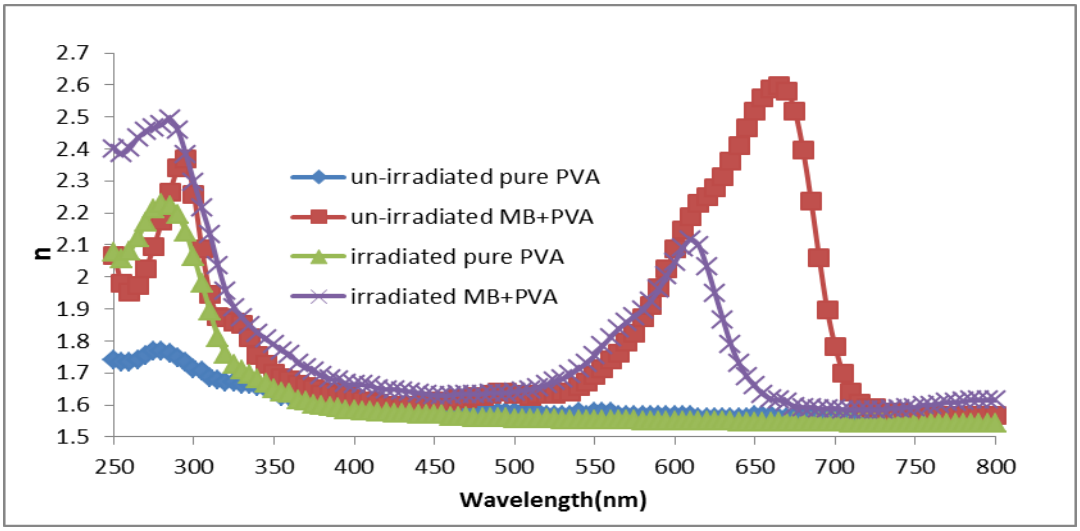


Fig.(7) The refractive index for un-irradiated and irradiated pure PVA and MB/PVA films

The dielectric constants are the important parameters for the quantitative determination of the electronic band structure of solids. The Eq.(9) and (10) represent the real and imaginary parts dielectric constants, respectively. The real part decreases the peak of mthylene blue and increases the peak of PVA after irradiation, that mean the real dielectric constant depend on the square of the refractive index and the square of the extinction coefficient, fig.(8) illustrate the real part of dielectric constant for all samples.

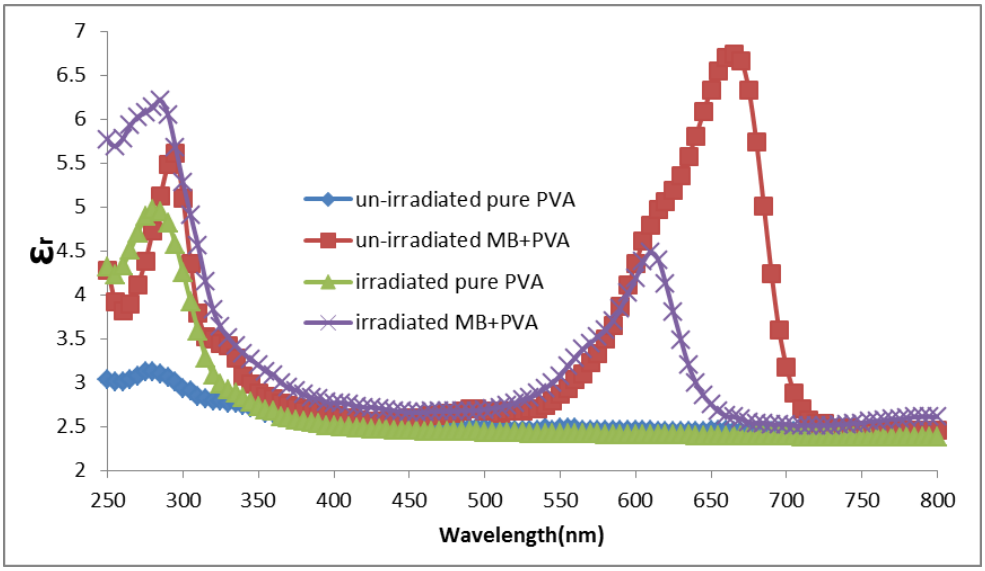


Fig.(8) The real part of dielectric constant for un-irradiated and irradiated pure PVA and MB/PVA films

The imaginary part of dielectric constant for un-irradiated and irradiated pure PVA and MB/PVA films illustrated in fig.(9); the behavior of curves similar with refractive and extinction constants.

Fig.(9) The imaginary part of dielectric constant for un-irradiated and irradiated pure PVA and MB/PVA films

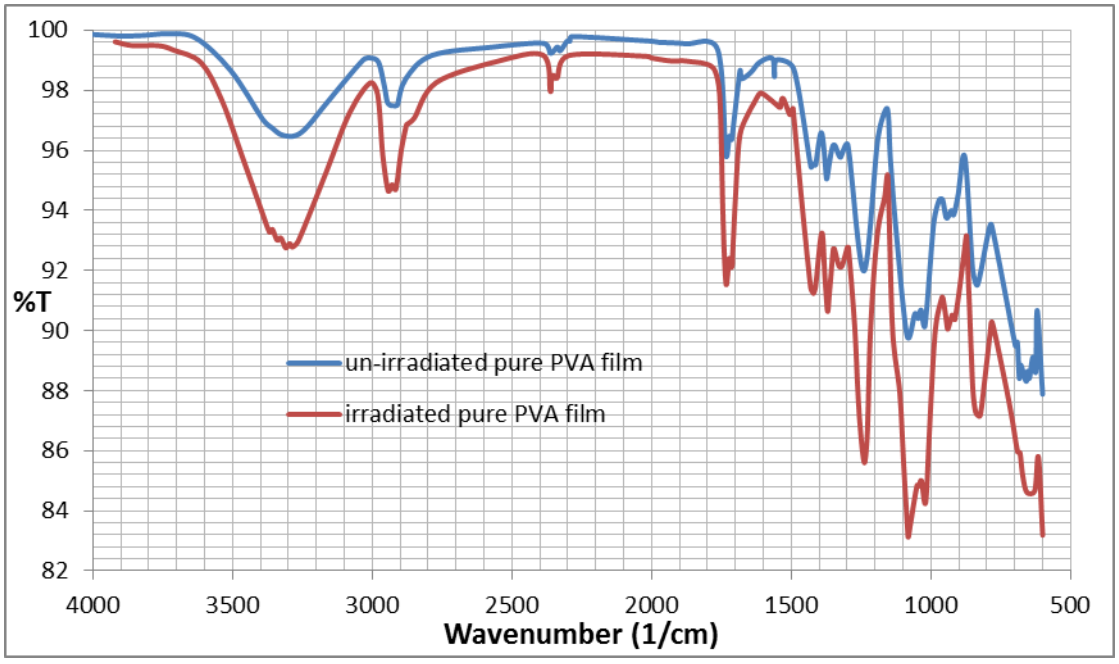
5.2 FTIR measurements

The most importance of (FTIR) spectroscopy is to identify the main characteristics peaks of pure PVA, MB/PVA films, and demonstrate the effect of irradiation on the samples. Fig.(10) shows the FTIR spectrum of un-irradiated and irradiated pure PVA and MB/PVA films. The FTIR of un-irradiated pure PVA showed the transmission bands corresponding to C–H out of plane that appeared at 659cm^{-1}, 718cm^{-1} and 835cm^{-1}. The peaks (940, 946 and 1242cm^{-1}) correspond to the C–O stretching. The

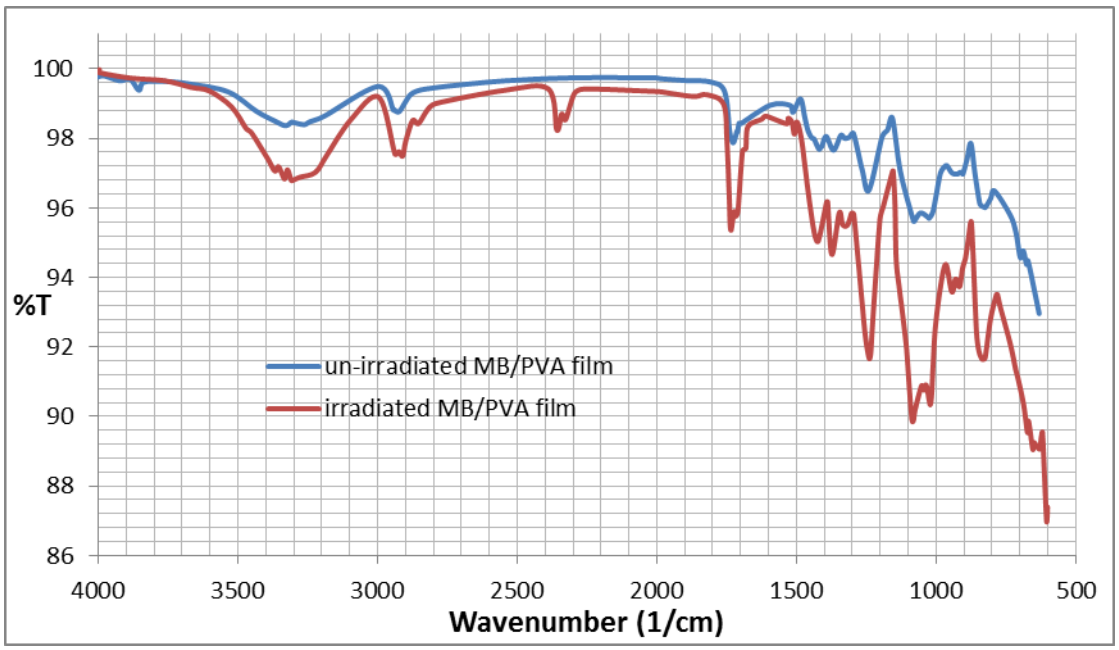
peaks (1024, 1047 and 1087cm^{-1}) refers to C–H bending vibrations in of plane. The transmission around1435cm^{-1} characterizes the asymmetric bending vibrations of (C–CH3) bond. The C=O stretching vibration of ester group appears around 1732cm^{-1}.The C–H stretch aliphatic that found around 2910cm^{-1}. The O–H showed a broad band at (3221-3387cm^{-1})

The FTIR of un-irradiated MB/PVA showed in 702cm^{-1} corresponding to C–H aromatic. The bond around 829cm^{-1} that represents C–H out of plane. The C–O stretching appeared in (923 and 1244cm^{-1}). The peaks (1028 and 1084cm^{-1}) refers to C–H bending vibrations in of plane. The C–N amines showed in 1371cm^{-1}. The transmission around 1423cm^{-1} characterize the asymmetric bending vibrations of (C–CH3) bond .The C=C aromatic showed around 1510cm^{-1}. The C=O stretching vibration of ester group appears around 1728cm^{-1}. The C–H aliphatic appeared at 2914cm^{-1}. The O–H showed a broad band at (3221-3387cm^{-1}).

After irradiation samples, the change in the peaks of FTIR spectra has not exist, just found decreases in the transmission of peaks, that mean all peaks that found in un-irradiated and irradiated samples are the same.



(a)



(b)

Fig.(10) The FTIR spectra for un-irradiated and irradiated of pure PVA and PVAMB/films: (a)pure PVA films, (b)MB/PVA films

5.3 FESEM

Fig.(11) showed the pure PVA and MB/PVA films with doping ratio 30ml of the dye solution, it noted from the pictures that the surface of the pure PVA film is rough plane, while the MB/PVA film is clearly smooth because the molecules of dye filled the distances between the molecules of PVA.

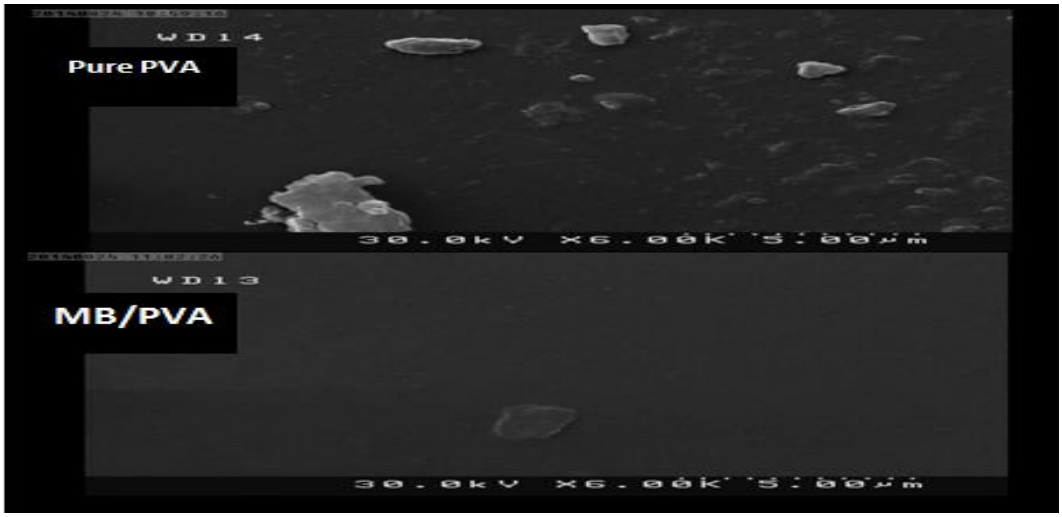


fig.(11) FESEM microstructure for un-irradiated samples

The effect of irradiation by γ-ray on the surface morphology for pure PVA and MB/PVA films illustrated in fig.(12). The images showed that the surface molecules were broken and this process increased the surface roughness, this effect is reduced in the presence the dye.

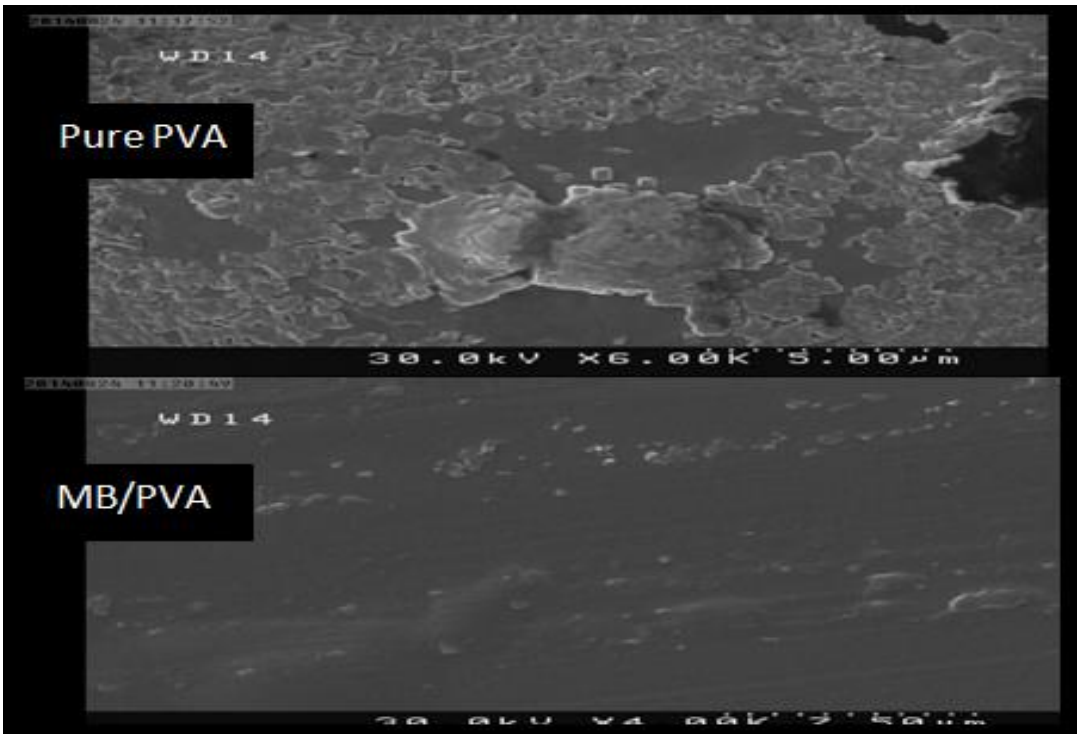


fig.(12) FESEM microstructure for irradiated samples

6. Conclusion

From this research the optical energy gap of PVA decreasing after irradiation for pure PVA and PVA/MB films, whereas the optical energy gap for MB increasing after irradiation for PVA/MB film. The results of FTIR showed no change in the structure of the polymeric dye after irradiation. FESEM photographs illustrated that the surface of all films became more roughness after irradiation.

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