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Research Article

Optical Properties and FWHM of Methylene Blue Doped Poly Vinyl Alcohol Films

Mahasin F. Hadi AL-Kadhemy*&Ammar N. Abed AL-Jabry

AL-Mustansiriyah Univ. –College of science- physics Dept.- Baghdad- IRAQ

* Corresponding author. Tel.: +964 07702732705
E-mail address:drmahasinf@yahoo.com

A b s t r a c t

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In this research the optical properties for pure PVA and PVA-Methylene blue (MB) films in different doping ratio that prepared by using casting method was been studied. The absorption and transmission spectra were measured by UV-Visible spectrophotometer. The optical energy gap was indirect transition for pure PVA film about 5.15eV for allowed and 5.17eV for forbidden. These energies were decreased with increasing doping ratio of MB contents to become 4.88eV and 4.85eV for allowed and forbidden, respectively. Whereas energy gap for Methylene blue in chloroform solution was 1.78 eV and 1.88 eV for allowed and forbidden indirect transition, respectively. The value of energy gap became 1.75 eV and 1.78 eV for allowed and forbidden indirect transition after doping with PVA polymer films for all doping ratio of dye solution. Full width half maximum absorption spectrum was calculated for all samples. Also, all optical constants (absorption coefficient, refractive index, extinction coefficient, and complex dielectric constants) were investigated and compared with other researches.

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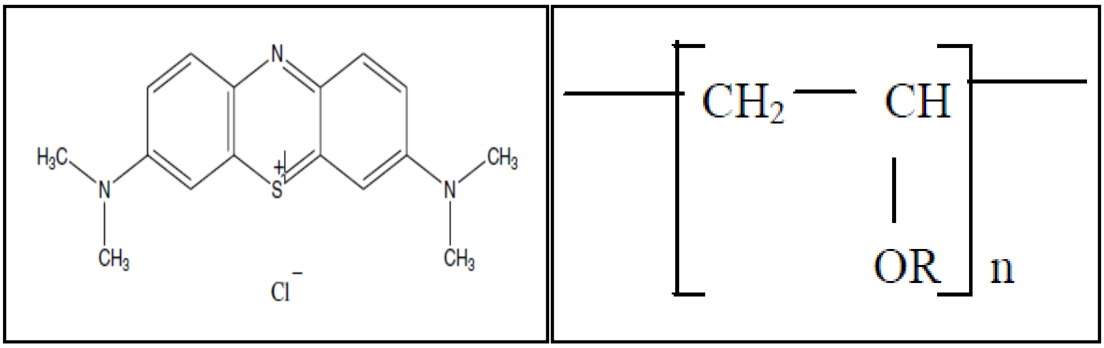
1. Introduction

Methylene Blue is a heterocyclic aromatic chemical compound that has physical form green powder soluble in water, ethanol, ethylene glycol, methyl cello solve. It has many applications in biology, industry, chemistry and medical as inks, bone marrow, eye lens, skin diseases [1]. Figure 1-a shows the chemical structure of methylene blue. Poly vinyl alcohol is a polymer with carbon chain back bone with hydroxyl groups attached to methane carbons, these OH-groups can be a source of hydrogen bonding and hence assist in the formation of polymer that showed in fig.(1-b)[2]. Poly vinyl alcohol (PVA) has several interesting physical properties, which are very useful in material science and technical applications [3].



(a) (b)

Fig.1: The chemical structure of (a) methylene blue, (b) polyvinyl-alcohol[1]

Many studies have addressed PVA and MB; Such as Omed and Dlear [4], studied optical absorption of PVA films doped with Nickel chloride and they concluded that the optical energy gap is due to the direct and indirect allowed optical transitions and the energy gap decreases with increasing $NiCl_2$ content. Mustafa et al [5] studied the optical properties of Poly (vinyl alcohol) doped Cupper Chloride and showed that the energy gap is due to allowed direct transition decrease with increase the concentration of cupper chloride. In our research the effect of doping ratio of MB solution on optical and FWHM properties of methylene blue doped PVA films has been studied.

2. Theoretical part

The relationship between incident light with intensity I_o and penetrating light intensity is given in eq.(1)[6]:

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

Where α is the absorption coefficient (cm^{-1}), and x is the thickness of sample (cm), the eq.(1) can be rewritten in the form of eq.(2)[6]:

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

Where the term log (I/I_o) is represent the absorbance (A), then the eq.(2) become[7]

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

If $\alpha \geq 10^4$ cm^{-1}, then the electronic transitions are direct, the value of energy gap from this region can be given the relation [8]:

$$\alpha h\nu \ = p(h\nu - E_g)^m \tag{4}$$

Where $h\nu$ the energy of photon and p is the proportional constant, E_g is the allowed or forbidden energy gap of direct transition and m is a constant, depend on type of transition. The relation between reflectivity and refractive index is given by eq.(5)[9]:

$$R = \frac{(1-n)^2+K^2}{(1+n\ )^2+K^2} \tag{5}$$

Where R is the reflectivity, n is the refractive index and K is the extinction coefficient. The reflectance can be calculated by the following equation:

$$R + A + T = 1 \tag{6}$$

The extinction coefficient can be calculated by using eq.(7)[10]:

$$K = \frac{\alpha\lambda}{4\pi} \tag{7}$$

Where λ is the wavelength of the incident ray. The refractive index can be obtained from eq.(8)[9]:

$$n = \sqrt{\frac{4R}{(R-1\ )^2} - K^2} - \frac{(R+1)}{(R-1)} \tag{8}$$

The relation between the complex dielectric constant and the complex refractive index (n) showed in eq.(9)[9]:

$$\varepsilon = n^2 \tag{9}$$

It can be concluded that [9]:

$$(n - iK)^2 = \varepsilon_r - i\varepsilon_i \tag{10}$$

The real and imaginary complex dielectric constant can be expressed by eqs.(11) and (12) respectively:

$$\varepsilon_r = n^2 - K^2 \tag{11}$$

$$\varepsilon_i = 2nK \tag{12}$$

Also, full width half maximum (FWHM) of absorption spectrum is a parameter commonly used to describe the width of a peak on a curve or function. It is given by the distance between points on the curve at which the function reaches half its maximum value [11].

3. Experimental work

Methylene blue (MB) is a chemical compound with molecular formula ($C_{16}H_{18}N_3SCl.2H_2O$) and molecular weight M_W =355.89gm/mol made in a Fisher Scientific International Company (United Kingdom). We choose polyvinyl alcohol polymer (PVA) as host material for dye because Polyvinyl alcohol has excellent film forming with the molecular weight M_w =160000gm/mol, melting point 230 °C [12]. Casting method used to prepare dye doped polymer films [13]. The required amounts of PVA are dissolved in (10 ml) of distilled water is (0.5 g). Water is suitable solvent for both dye and polymer. The dye solution with concentration 1×10^{-5}mol/liter, was choose as a suitable dye solution prepared according to method as mentioned in ref.[14]. PVA powder and the distilled water put in the beaker and the solution was stirred continuously at room temperature for 3 hours. Then, different ratio of dye solution (10, 15, 20, 30, and 50) ml were added to polymer solution and mixed very well. The mixture poured in glass petri-dish with (10 cm) diameter and left to dry for 3 days to get homogeneous films. The value of thickness for these films ranged (55-80)µm. The absorption and transmission spectra were measured by UV-Visible spectrophotometer type (T70/T80 Series UV/Vis Spectrometer) in the wavelength range (200-900) nm.

4. Results and discussion

The absorption spectrum of methylene blue in distilled water solution with concentration 1×10^{-5} mol/liter was showed in Figure 2, the maximum peak of absorption for methylene blue at 665 nm with intensity 0.657, and shoulder at 620 nm. This shoulder may be attributed to the existence of hypothetical methylene blue dimer [15].

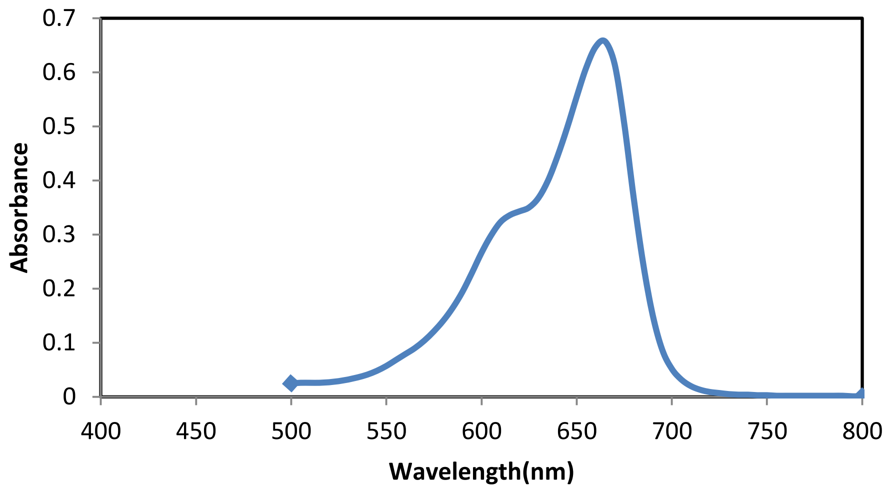


Fig.2: Absorption spectrum of Methylene blue dye in distilled water solution

The absorption spectrum for PVA polymer films shown in Figure 3with maximum peak at 280 nm with intensity 0. 68. These results matched with results obtained by Maher[16].

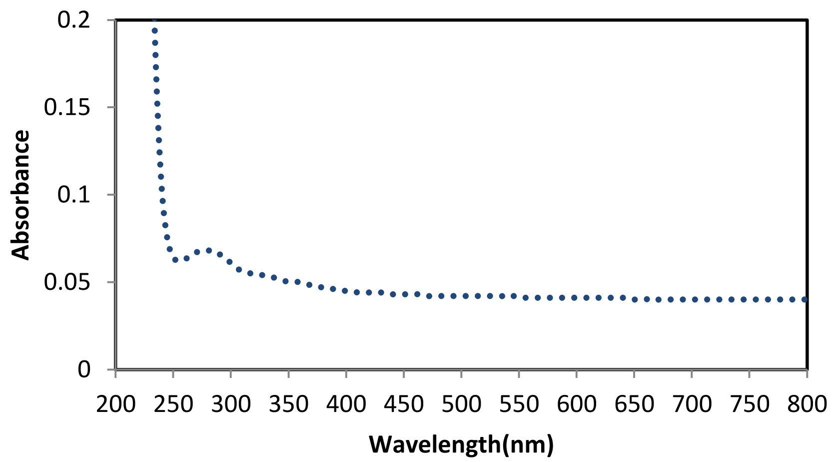


Fig.3: Absorption spectrum of PVA films

The addition of MB dye to PVA polymer gave red shift toward long wavelengths about 20 nm for wavelength of absorption spectrum of dye and polymer with increasing doping ratio of MB dye. The maximum wavelength of absorption spectrum for MB dye was appeared at 645 nm for doping ratio 10ml and reaches 665 nm for doping ratio 50ml. As well as, the wavelength of absorption spectrum for PVA polymer was appearing at 280 nm for doping ratio 10ml and reach 300 nm for doping ratio 50ml, as shown in fig.(4). The intensity of absorption spectrum of two peaks for all samples increased with increasing doping ratio of MB solution, this was due to increase the excited molecules; J. B. Birks[17] and I. Berlman[18].

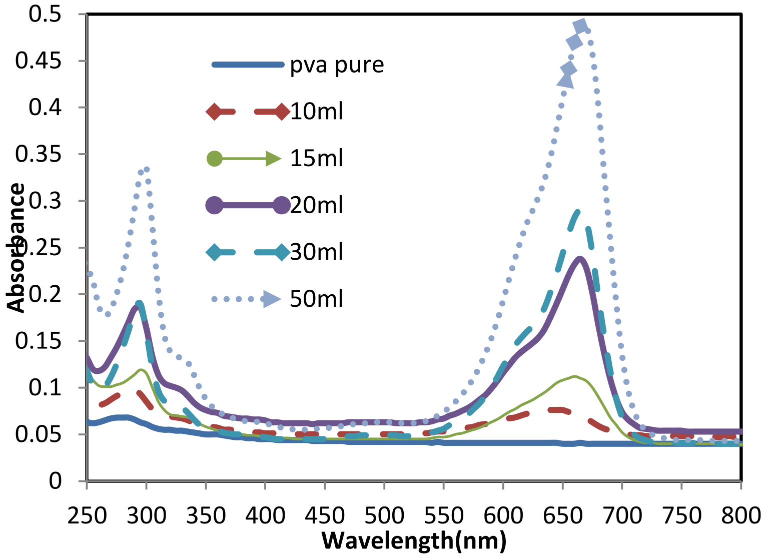


Fig. 4: Absorption spectrum of Methylene blue doped PVA films in different doping ratio of dye solution

The relation between concentration and wavelength illustrated in Figure 5 that showed increasing in wavelength (red shift) with increasing ratio of dye.

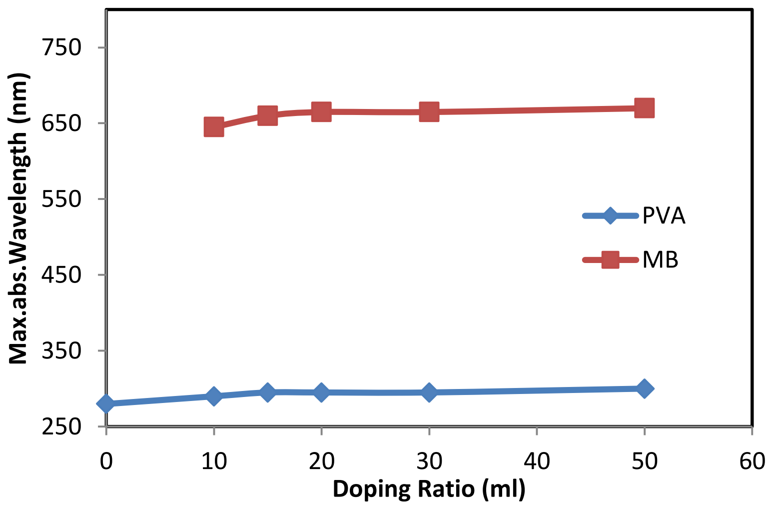


Fig. 5: The relation between Maximum absorption wavelength and doping ratio for PVA and MB .

Figure 6 illustrate the change in FWHM with increasing doping ratio of MB solution added to PVA for absorption band of PVA and MB dye.

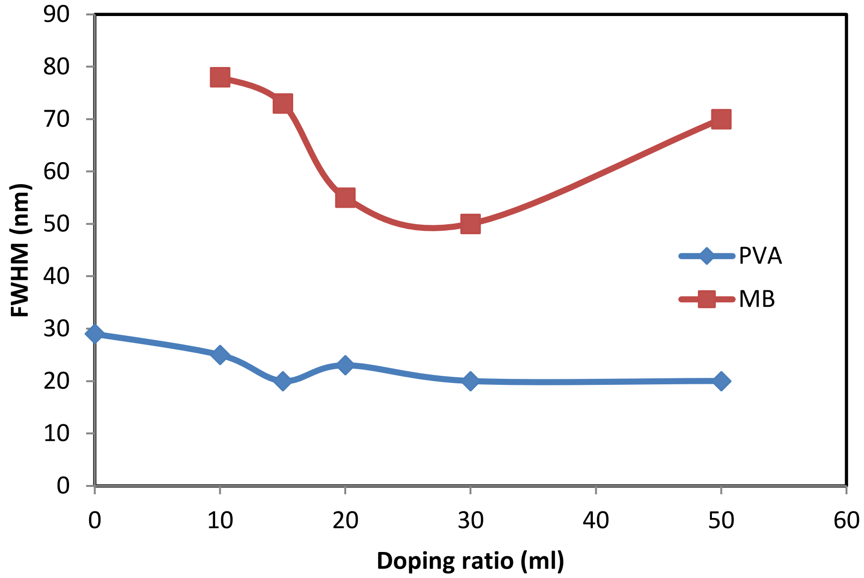


Fig. 6: The relation between FWHM and doping ratio of MB solution

The transmission spectrum of pure PVA and MB-PVA films with different doping ratio of MB dye shown in fig.(7), the transmission was decreased with increasing doping ratio of MB dye.

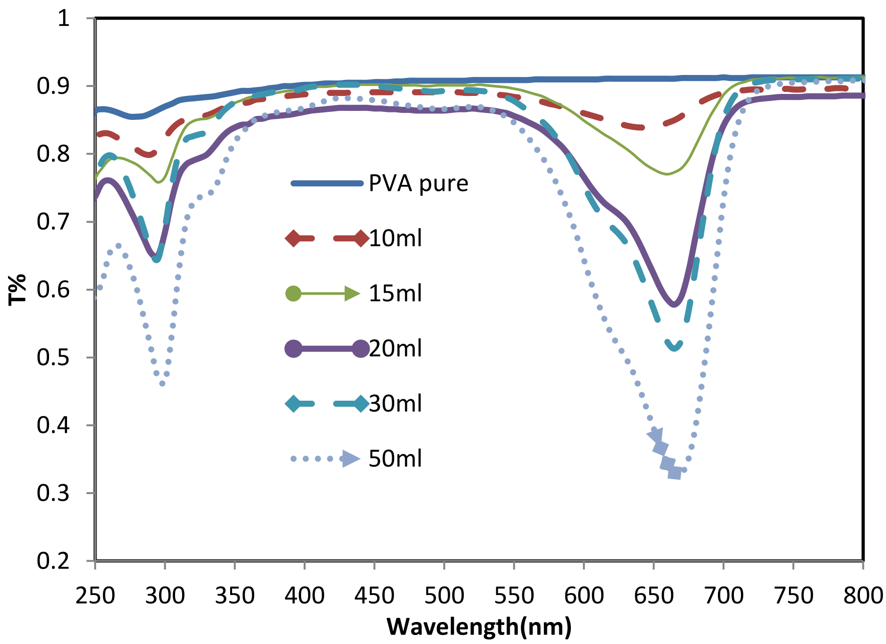


Fig. 7: Transmission spectrum of MB-PVA films in different doping ratio

From absorption and transmission spectra; reflection spectrum can be calculated according to eq.(6). Reflection spectrum of pure PVA polymer and MB-PVA films for different doping ratio shown in

Figure 8. Reflection increased for peak of PVA and MB with increasing doping ratio of MB dye solution.

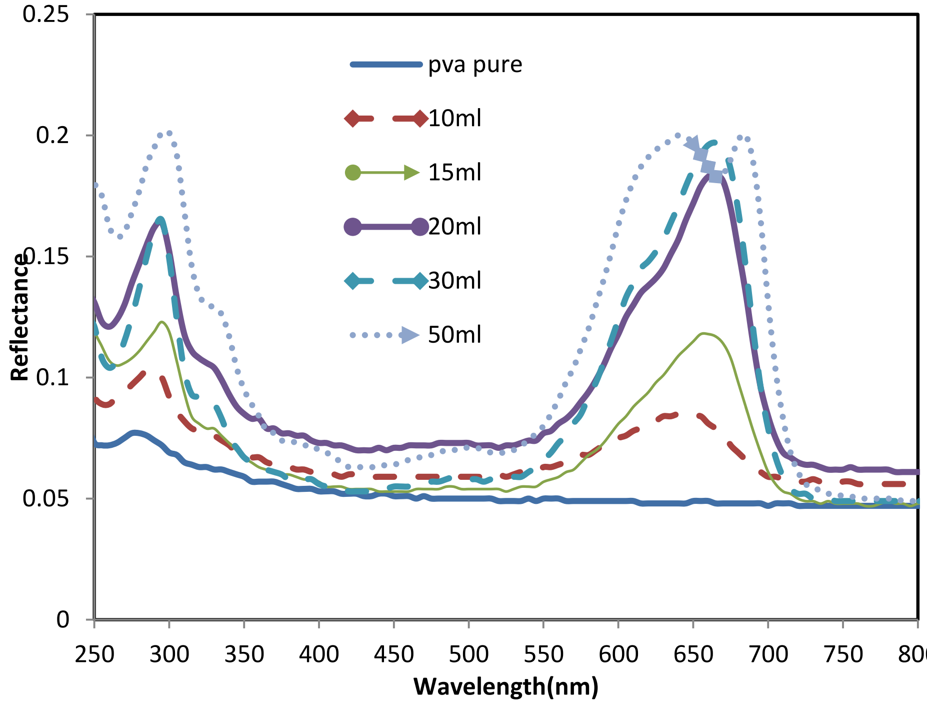


Fig. 8: Reflection spectrum of MB-PVA films in different doping ratio

The absorption coefficient (α) demonstrated the nature of electronic transmission, and shows the ability of material to attenuate the light of a given wavelength per unit length [19]. The value of (α) was calculated from eq.(3) for all samples, as illustrated in Figure 9. When the high absorption coefficient values ($\alpha > 10^4 cm^{-1}$) at higher energies, direct electronic transitions had been expected and the energy momentum preserve of the electron and photon. Whereas the values of absorption coefficients low ($\alpha < 10^4 cm^{-1}$) at low energies, indirect electronic transitions had been deduced. From (α) results shown in Figure 9, indirect electronic transition was concluded.

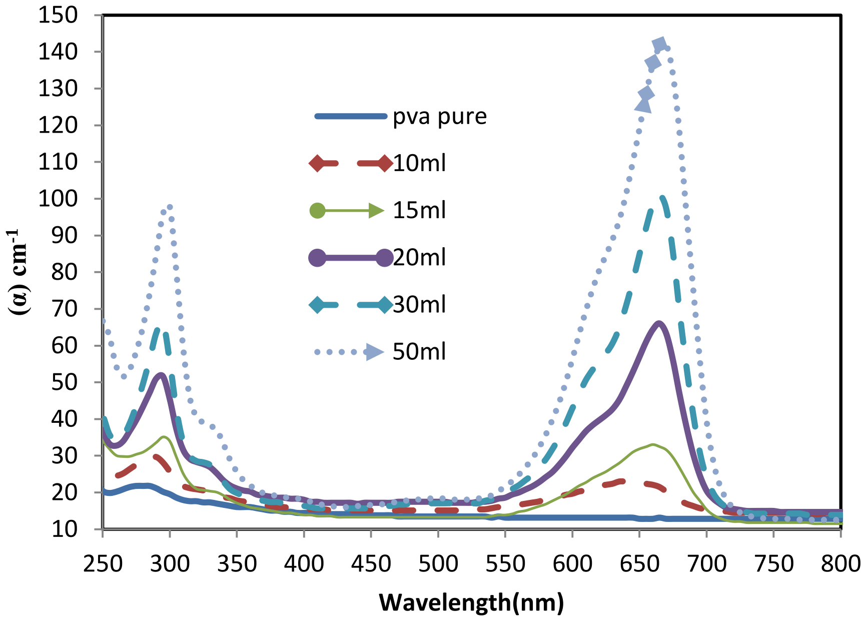
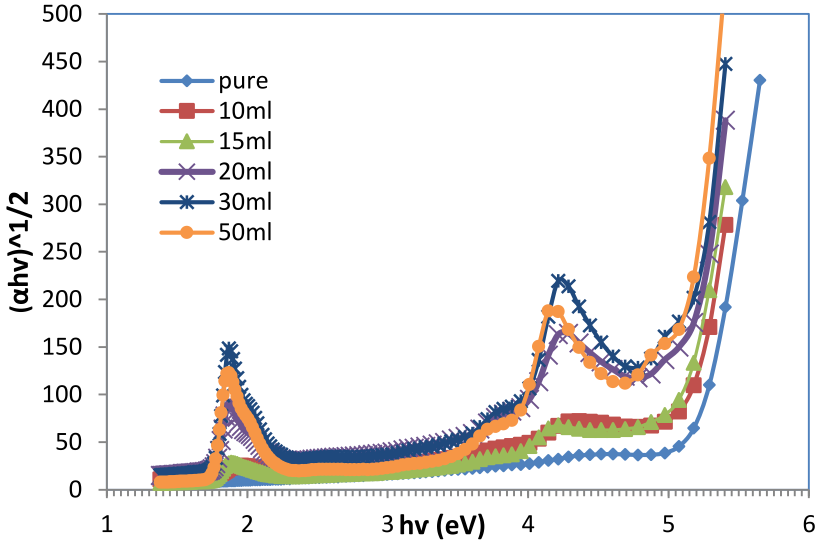


Fig.9: Absorption coefficient spectrum of MB-PVA films in different doping ratio

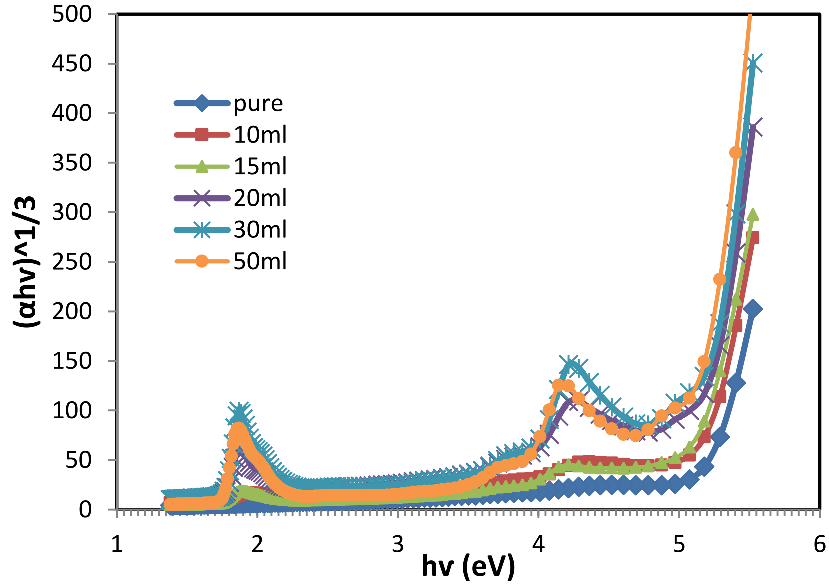
The optical energy gap was the value of optical energy gap that necessary to develop the electronic band structure of film material. It can be obtained by plotting $(\alpha h\nu)^{1/m}$ versus $(h\nu)$ in the high absorption range followed by extrapolating the linear region of the plots to$(\alpha h\nu) = 0$ [20]. Fig.(10-a, b) showed the relationship between absorption edge $(\alpha h\nu)^{1/2}$ and energy of photon for the dye, PVA film and MB-PVA films which represented the indirect allowed and forbidden transition, respectively. We found that the energy gap for pure PVA film can be measured and equal to 5.15eV, and Methylene blue solution has energy gap equal to 1.78 eV for allowed transition. Whereas for forbidden transition became 5.17 eV and 1.88 eV for pure PVA and Methylene blue in chloroform solution, respectively. When Methylene blue added to PVA polymer with different doping ratio, the value of energy gap for PVA decreased with increasing doping ratio to become 4.88eV and 4.85 eV for allowed and forbidden transition, respectively. While the energy gap for Methylene blue after doping with PVA polymer decreased to be 1.75 eV and 1.78 eV for allowed and forbidden indirect transition, respectively. That mean energy gap became constant independent for change ratio of doping of dye solution. These different changes in energy gap occurred between allowed and forbidden transitions for PVA and methylene blue illustrated in Table1.

Table 1: Energy gap of PVA films with different doping ratio of MB dye for indirect transition different doping ratio

Energy gap (eV)		Doping ratio (ml)					
		0	10	15	20	30	50
allowed	PVA	5.15	5.07	5.03	4.98	4.95	4.88
	MB	1.78	1.75	1.75	1.75	1.75	1.75
forbidden	PVA	5.17	5.1	5.05	5.03	4.98	4.85
	MB	1.88	1.78	1.78	1.78	1.78	1.78



(a)



(b)

Fig.10: Energy gap for PVA films with different doping ratio of MB dye solution for (a) allowed indirect transition, (b) forbidden indirect transition

The refractive index (n) was an important optical parameter. Figure (11) illustrated the behaviour of refractive index for pure PVA film and MB-PVA films in different doping ratio of MB solution. It might be showed that the refractive index increased with increasing doping ratio because of increasing reflectivity.

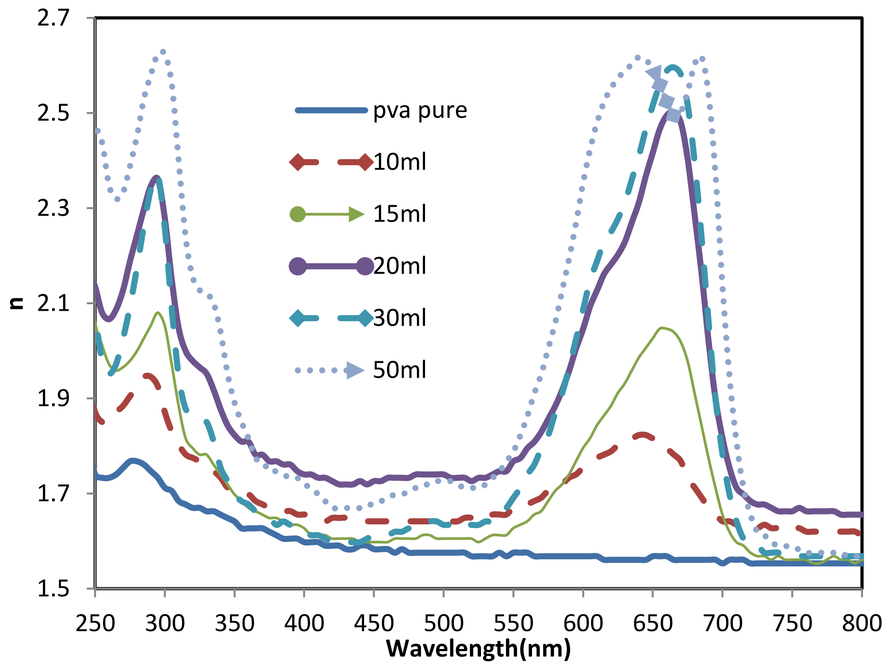


Fig.11: Refractive index of MB-PVA films in different doping ratio

The extinction coefficient depended on absorbance according to eq.(7), so that the behavior of all samples was similar to absorption spectrum, that mean the extinction coefficient increased with increasing doping ratio of MB dye, as shown in Figure 12.

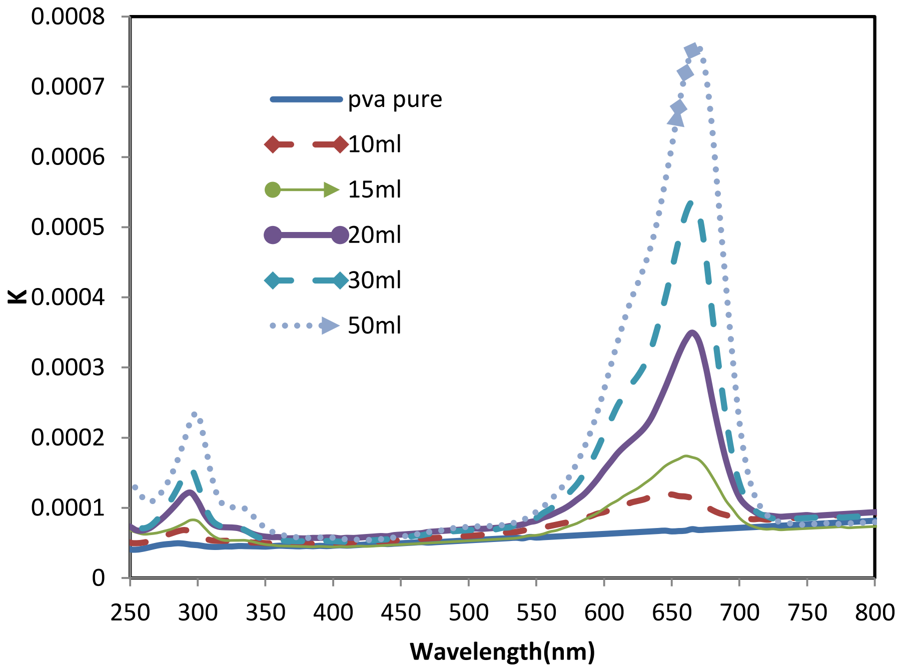


Fig. 12: Extinction coefficient for MB-PVA films for different ratio

From information of optical reflectivity, transmission and refraction provided the way to determine the dielectric constants of solid, which related to the band structure. Eqs.(11) and (12) represented the real and imaginary parts of dielectric constants, respectively. The real part of dielectric constants for pure PVA film and MB-PVA films in different doping ratio illustrated in Figure (13). The real dielectric constant increased with increasing doping ratio that mean the real dielectric constant depend on the square of refractive index and the square of extinction coefficient. The behaviour of these figures is similar to refractive index.

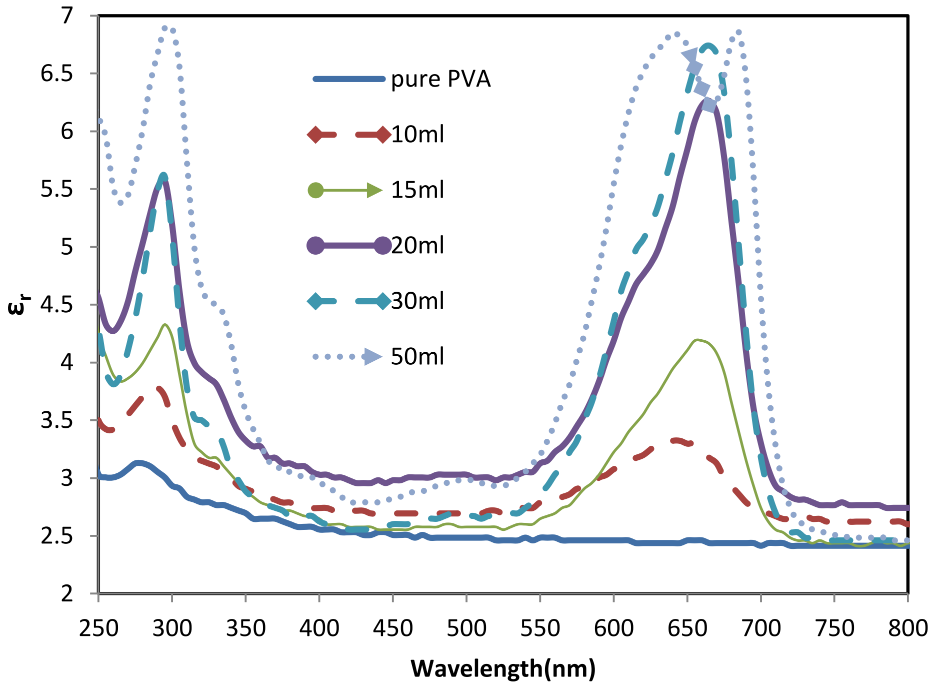


Fig. 13: Real part dielectric constant for pure PVA and MB-PVA films at different doping ratio

The imaginary part of dielectric constants for pure PVA film and MB-PVA films in different doping ratio were shown in Figure (14). Imaginary dielectric constants for pure PVA film and MB-PVA films increased with increasing doping ratio of MB solution**.**

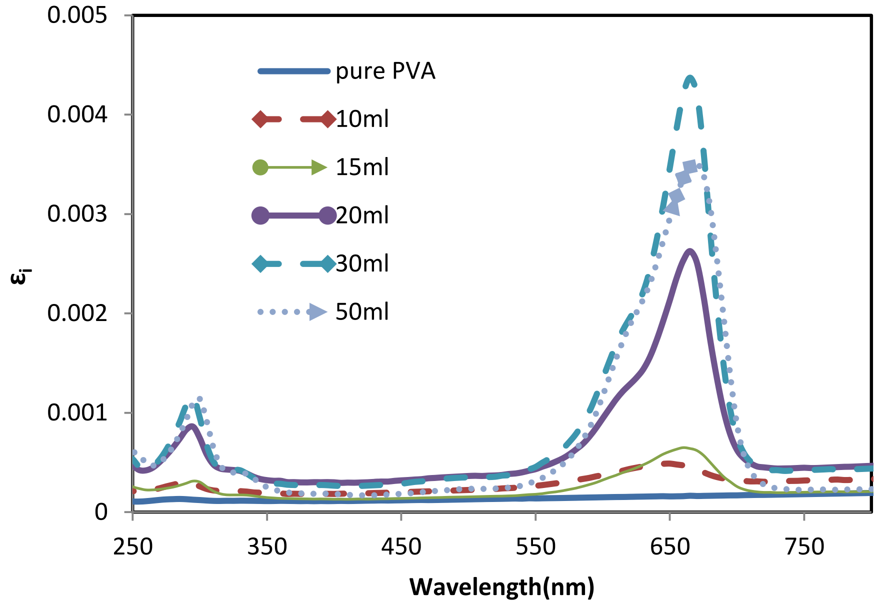


Fig.14: Imaginary part dielectric constant for pure PVA and MB-PVA films at different doping ratio

5. Conclusion

From this study, we can concluded that the addition of methylene blue dye effect on optical properties of PVA films. The energy gap for PVA polymer decreased with increasing doping ratio of MB dye while for Methylene blue still constant for allowed and forbidden indirect transition. FWHM for absorption spectra for PVA and Methylene blue change with doping ratio of dye solution.

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