

Optical Properties of PolyVinyl Alcohol with Phenol Red Dye Films

**Sara Ammar Ibrahim¹, Mahasin F. Hadi Al- Kadhemy²,
Jehan Abdul Satter Salman³**

^{1,2}Physics of Dept. / College of Science / Mustansiriyah University

**³Biology of Dept. / College of Science / Mustansiriyah University
Baghdad/Iraq**

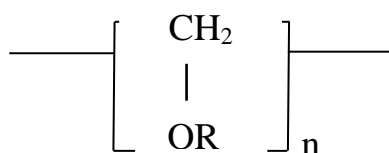
Abstract:

In this paper, pure PVA and phenol red/PVA films with several doping ratio of phenol red (5, 10, 15, 20 and 25) ml have been obtained by solution casting method. The optical properties were measured in range of wavelength (200-650) nm. The experimental results show that the absorbance of phenol red /PVA films was increased with increasing the doping ratio of phenol red. The values of energy gap were decreased with increasing the doping ratio of phenol red from (5.00 to 4.40) eV.

Keywords: PolyVinyl Alcohol (PVA), Polymer, Phenol Red Dye, Organic Dye, Optical Properties.

1- Introduction:

PolyVinyl Alcohol (PVA) is one of the earliest and best known polymers, it was seen to use in a variety of applications and is currently used extensively in semiconductors applications. The transmission for visible light is very high. Polymeric composites of (PVA) are known for their importance in technical applications [1]. PVA has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food [2]. PolyVinyl Alcohol for food use is an odorless and tasteless, translucent, white or cream colored granular powder. It is most important soluble in water [3]. The general chemical structure of PolyVinyl Alcohol (PVA) is shown in Figure (1) [4].



Where R= H or COCH₃

Fig. (1): Chemical structure of PVA polymer [4].

Unlike most organic compounds, dyes possess color because they: absorb light in the visible spectrum (400–700 nm), have at least one chromophore (color-bearing group), have a conjugated system, i.e. a structure with alternating double and single bonds, exhibit resonance of electrons, which is a stabilizing force in organic compounds [5]. Phenol red (also known as phenolsulfonphthalein or PSP) is a pH indicator frequently used in cell biology laboratories. Phenol red was used in the phenolsulfonphthalein test to estimate the overall blood flow through the kidney and is now obsolete. Also use as Indicator for cell cultures, Estrogen mimic, in swimming pool test kits [6]. The general chemical structure of Phenol Red is illustrated in Figure (2) [6].

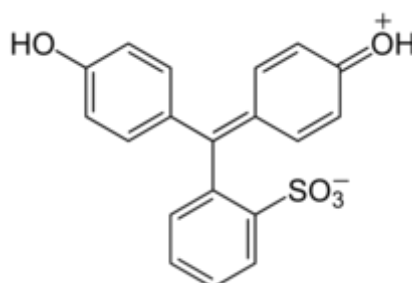


Fig. (2): Chemical structure of Phenol Red Dye [6].

Liu Z. et al (2005) [7], developed novel method to immobilize phenol red into poly (vinyl alcohol) (PVA) membrane for an optical pH sensor with two determination ranges and long-term stability. Phenol red was first reacted with the formaldehyde to produce hydroxymethyl groups, and then attached to PVA membrane via the hydroxymethyl groups. The dynamic response ranges of the sensor membrane became somewhat wider than those of free forms, from pH 0–3 and pH 6.5–9.5 to 5M [H⁺]-pH 3.0 and pH 6.5–10.5, respectively. Sreedhar S. et al (2016) [8] demonstrated that blending an organic dye (guest/filler), with a vinyl polymer (host template), is an inexpensive and simple approach for the fabrication of

multifunctional photonic materials which could display an enhancement in the desirable properties of the constituent materials and, at the same time provide novel synergistic properties for the guest-host system. A new guest-host nanocomposite system comprising Phenol Red dye and poly (vinyl alcohol) as guest and host template, respectively, which exhibits tunable optical characteristics and saturable absorption behavior, is introduced. The dependence of local electronic environment provided by the polymer template and the interactions of the polymer molecules with the encapsulated guest molecules on the observed optical/nonlinear absorption behavior is discussed. Ganesh V. et al (2018)[9] Study the growth of dyed Bis thiourea Zinc acetate single crystals of size $\sim 30 \text{ mm} \times 7 \text{ mm} \times 5 \text{ mm}$ is achieved by solution technique. X-ray diffraction and FTIR spectroscopy are used to verify crystal structure and functional groups. Intensity of diffraction peaks confirms good crystalline nature of dyed Bis thiourea Zinc acetate crystals than pure. Two absorption bands at ~ 387 and 558 nm were observed in diffused reflectance spectra of dyed crystals. The energy gap was calculated for both crystals and establishes to be $\sim 4.87 \text{ eV}$ for pure and $\sim 4.93 \text{ eV}$ for dye crystals. Photoluminescence spectra were recorded and a green emission band was observed in dyed Bis thiourea Zinc acetate crystal at $\sim 513 \text{ nm}$ was observed in dyed crystal. The aim of this work is studying the optical properties of PolyVinyl Alcohol/ Phenol red dye films.

2- Experimental Part:

Phenol red dye ($\text{C}_{19}\text{H}_{14}\text{O}_5\text{S}$) is pH indicator ($\text{pH} = 6.4 - 8.2$) yellow to red with molecular weight (354.38 g/mole) equality product of (Qualikems fine Chem Pvt. Ltd.) the amount was chose (0.3549 g). The phenol red dye solutions in distilled water with concentration (0.5×10^{-4}) mol/liter were prepared according to the following equation (1) [10]:

$$m = C V M_w \quad (1)$$

Where:

m: The amount of the dye needed to obtain the desired concentration in (g)

C: the concentration needed to prepare in mol /liter.

V: the volume of solvent in liter needed to add to the dye.

M_w : molecular weight of the dye used in g/mol.

PVA ($[-\text{CH}_2\text{CH}(\text{OH})-]_n$) is a granular powder with molecular weight ($M_w = 70,000 \text{ g/mole}$) obtained from (Sigma-Aldrich); Certain amount (0.5

g) of polymer was dissolved in constant volume of distilled water (10 ml). The casting method was chosen to prepare dye doped polymer film [10, 11]. Different doping ratio from phenol red solution in distilled water (0.5×10^{-4}) mol/liter was chosen: (5, 10, 15, 20 and 25) ml to add to polymer solution. The mixture shake very well then poured into glass Petri- dish with (8 cm) diameter, and left for (7 days) at room temperature which approximately (30° C) to have homogenous films, with thickness about (0.0097- 0.0146) mm, respectively.

The Transmittance and absorbance spectra for all samples were measured by using UV-Visible spectrophotometer type (T80- series UV-Visible spectrometer.

3- Theoretical Part

The absorption coefficient (α) is characterized as the ability of a material to absorb the light of a given wavelength [12]:

$$\alpha = 2.303 \frac{A}{t} \quad (2)$$

Where:

(A) is the absorbance of the material.

(t) is the thickness of the sample in (cm), To calculate optical energy gap from eq. (2) [13]:

$$(\alpha h\nu) = B (h\nu - E_g)^r \quad (3)$$

Where:

$h\nu$: photon energy, E_g : Optical energy gap, B: constant depends on the type of transition, $r = 2$ for allowed indirect transition and $r = 3$ for forbidden indirect transition.

The extinction coefficient indicates how much light absorbs at a certain wavelength. It is useful to have an estimation of this coefficient for following which spectrophotometer when purifying it, [14, 15]. The extinction coefficient (k) was calculated using the following:

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

The Refractive index (n), the index refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen [14, 16].

The reflectivity can be calculated from the refractive index and the incidence angle with the Fresnel equations, which for normal incidence reduces to [16]:

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

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

The complex dielectric function of material, denoted as [14]

$$\epsilon^* = \epsilon_1 + i\epsilon_2 \quad (7)$$

Describes a materials response to an applied electric field, ϵ_1 determines the degree to which the material polarize in response to an applied field, the following equation [14, 17].

$$\epsilon_1 = n^2 - k^2 \quad (8)$$

Real part

While ϵ_2 controls the relative phase of this response with respect to the applied field in the following equation [14, 17]:

$$\epsilon_2 = 2nk$$

(9) Imaginary part

4- Results and Discussions:

The wavelength scans of the phenol red solutions showed three absorbance maxima at (256 nm), (430-435) nm and (555-560) nm at intensity (0.215), (0.401) and (0.092), respectively. As shown in figure (3) matched with Surre J. et al [18].

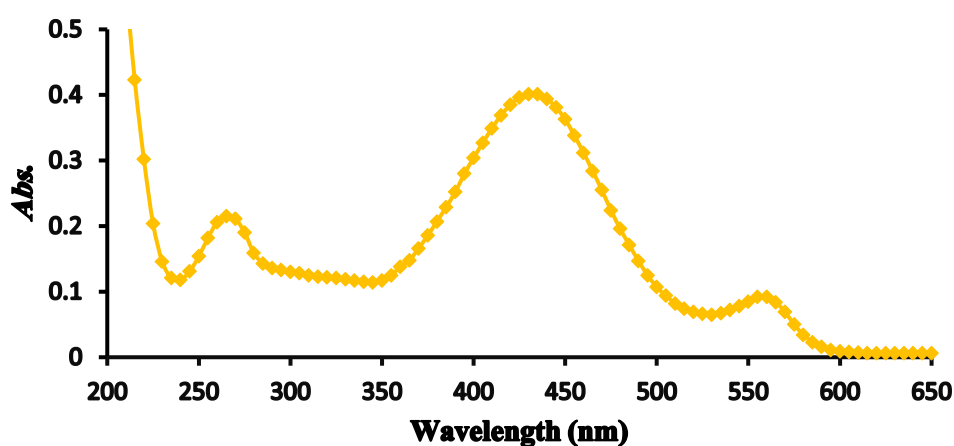


Fig. (3): Absorbance spectra of pure Phenol red solution.

The UV-VIS spectrum of absorption for pure PVA and Phenol red/ PVA with different ratio of phenol red dye solution (5, 10, 15, 20 and 25) ml is illustrated in figure (4) with range wavelength (200-650) nm. The maximum wavelength of absorption spectrum for PolyVinyl Alcohol (PVA) polymer at (275-280) nm with intensity (0.140). The result is matched with the result obtained by researcher [10].

The absorption spectra at (275-280) nm of pure (PVA) film may be attributed to $n-\pi^*$ transition of the hydroxyl group in the polymeric macromolecule [10]. The maximum intensity absorption wavelength for Phenol red / PVA films increased by increase the ratio of phenol red dye.

The conclusion from this figure is that: firstly; the absorption intensity is continuously increased with the increasing of the ratio of phenol red dye. Secondly; the absorption wavelength of phenol red in the two peak is increased toward longer wavelength about (10 nm) as shown in table (1).

Table (1): The maximum wavelength and absorbance of PVA and Phenol red dye solution with different volume ratio

| Sample | Peak | λ_{\max} (nm) | A_{\max} |
|---------------------------------|-------------|---|------------------------------|
| Phenol Red | 1 | 265 | 0.215 |
| | 2 | 435 | 0.401 |
| | | 430 | 0.401 |
| | 3 | 560 | 0.092 |
| | | 565 | 0.092 |
| PVA | 1 | 280 | 0.41 |
| | | 275 | 0.14 |
| PVA + phenol Red +(5ml) | 1 | 275 | 0.478 |
| | 2 | 435-440 | 0.392 |
| | 3 | 570 | 0.377 |
| PVA + phenol Red +(10ml) | 1 | 275 | 0.379 |
| | 2 | 435 | 0.376 |
| | 3 | 570-575 | 0.272 |
| PVA + phenol Red +(15ml) | 1 | 275 | 0.48 |
| | 2 | 570 | 0.344 |
| | 3 | 435 | 0.517 |
| PVA + phenol Red +(20ml) | 1 | 275 | 0.541 |
| | 2 | 435 | 0.62 |
| | 3 | 570 | 0.366 |
| PVA + phenol Red +(25ml) | 1 | 275 | 0.507 |
| | 2 | 435 | 0.601 |
| | 3 | 570 | 0.383 |

It is clear that the transmittance for pure PVA much larger than phenol red/PVA films in UV region, the transmittance spectra is inverse the absorption spectra matched with Surre J. et al [18].

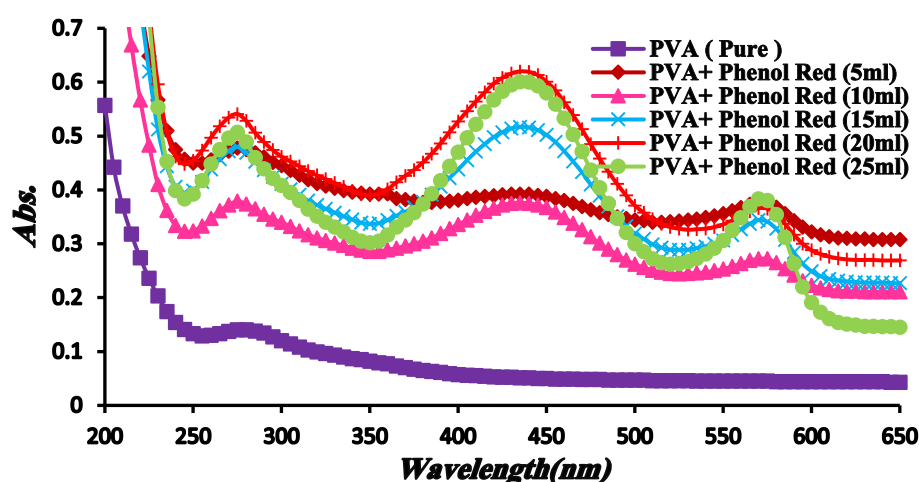


Fig. (4): Absorbance spectra of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

The eq. (2) is used to calculate the value of absorption coefficient, the absorption coefficient is used to indicate the nature of electronic transitions. It's obvious from Fig. (6), the values of absorption coefficient is less than ($\alpha < 10^4 \text{ cm}^{-1}$) so that indirect electronic transition is clearly investigated. The value of energy gap can be determined for allowed transition calculated by using eq. (3) as shown in Fig. (7) and table (2) shown the energy band gap for indirect allowed is decreased with increased the doping ratio of phenol red , this behavior attributed to creation of new levels in the band gap, lead to facilitate the crossing of electrons from the valence band to these local levels to the conduction band [19].

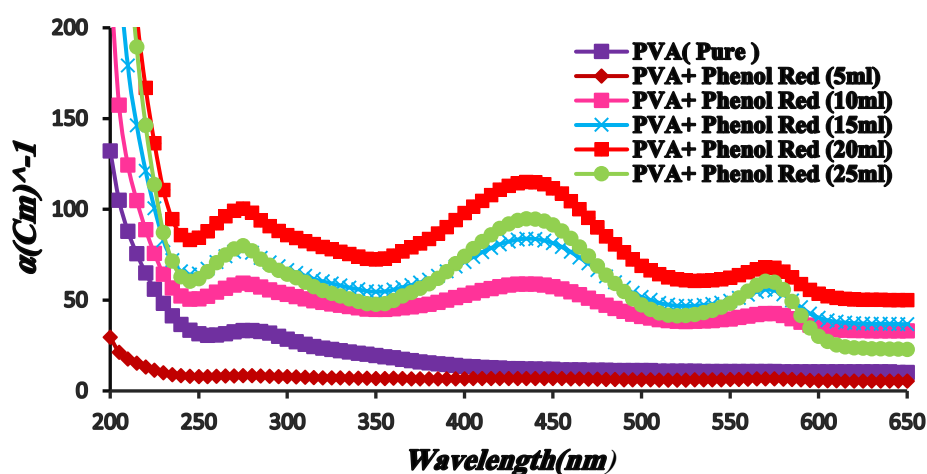


Fig. (5): Absorption coefficient of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

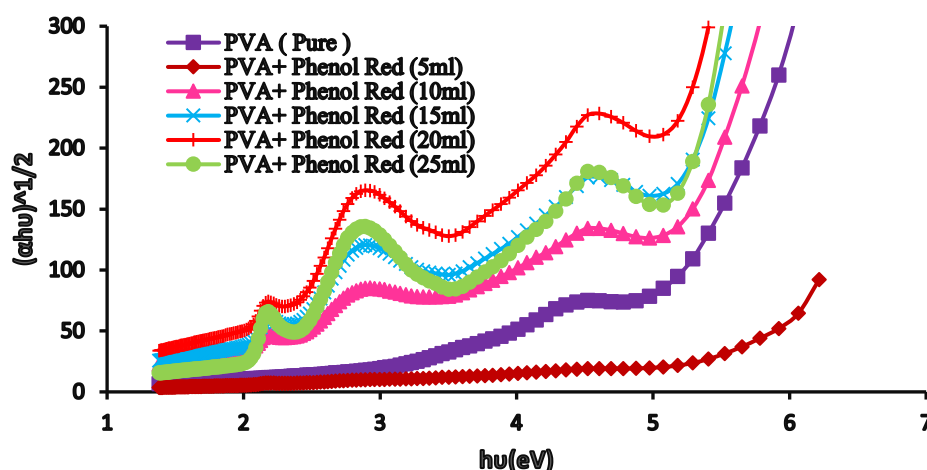


Fig. (6): The allowed indirect transition of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

Table (2) Optical properties of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution

| Parameters | Pure PVA | Phenol red | PVA+ phenol red | | | | |
|----------------------|----------|------------|----------------------------|-------|-------|-------|-------|
| | | | Doping ratio of phenol red | | | | |
| | | | 5 | 10 | 15 | 20 | 25 |
| $\lambda(\text{nm})$ | 275-280 | 275 | 275 | 275 | 275 | 275 | 275 |
| intensity | 0.14 | 0.401 | 0.392 | 0.376 | 0.517 | 0.620 | 0.601 |
| Allowed energy (eV) | 5.00 | 5.40 | 4.80 | 4.80 | 4.80 | 4.55 | 4.40 |

Reflection spectrum calculated from eq. (5) and shown in Fig. (7) Reflection for pure PVA is little at wavelength (280) nm and maximum reflection obtained for ratio (25 ml) at wavelength (275 nm) is (0.181). The reflection spectra is increased with increasing the volume ratio. Refractive indices have been calculated from eq. (6) and illustrated in Fig. (8). The maximum refractive obtained for ratio (25 ml) at wavelength (275 nm) is (2.48) from refractive spectrum.

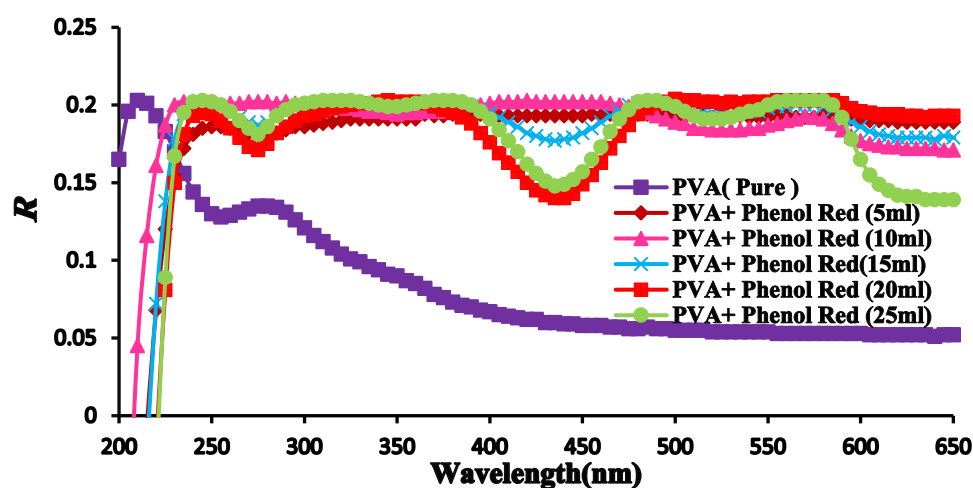


Fig. (7): Reflection spectrum of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

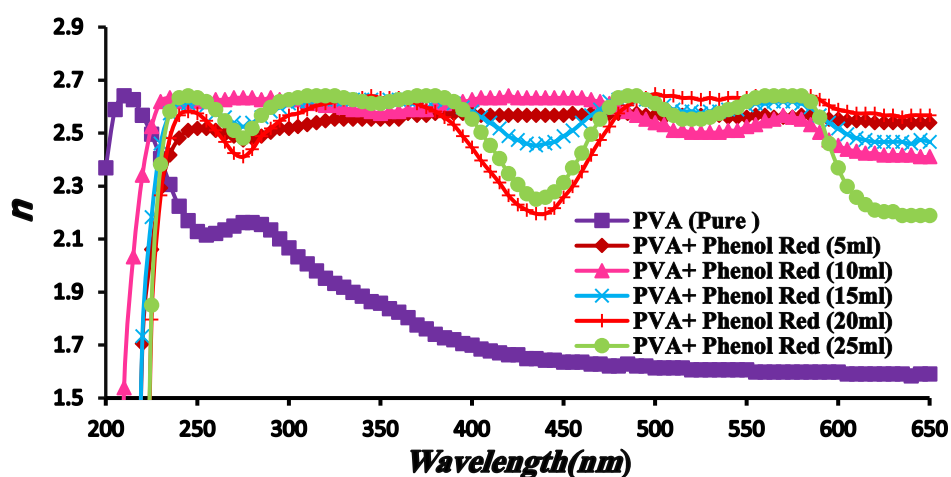


Fig. (8): Refractive index of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

The extinction coefficient that calculated from eq. (4) shown in fig.(9). Maximum extinction coefficient at wavelength (275 nm) is (0.00021) for ratio (20 ml) and decrease to be (0.00017) for ratio (25 ml) at the same wavelength.

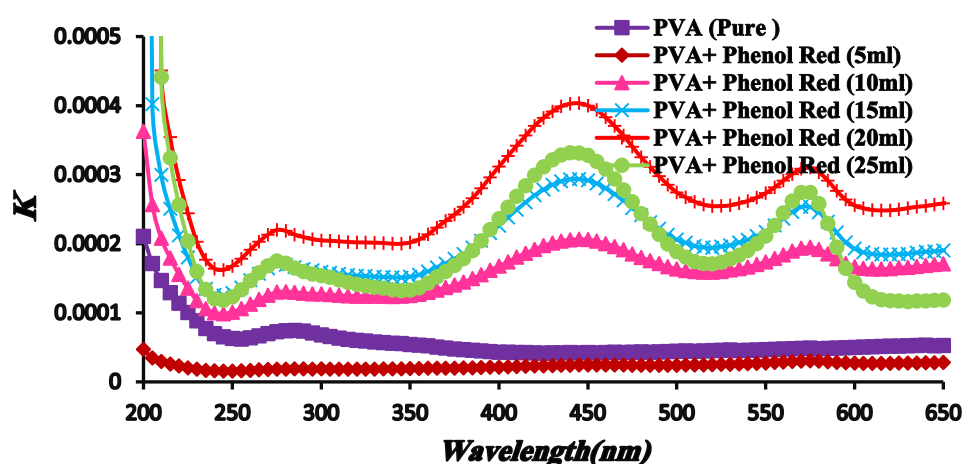


Fig. (9): Extinction coefficient of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

The real and imaginary dielectric constants determined from eqs. (8) and (9), respectively were determined and plotted as in Figs. (9) to (11), respectively. The maximum real dielectric constant obtained for ratio (25 ml) at wavelength (275 nm), imaginary dielectric constant obtained for ratio (20 ml) is (0.00103) and decrease to be (0.00086) for ratio (275 nm) at the same wavelength.

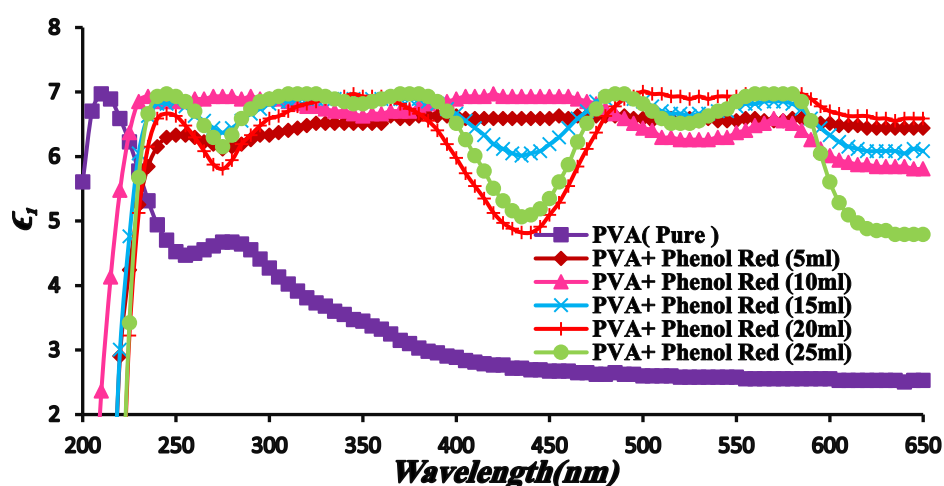


Fig. (10): Real dielectric constant of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

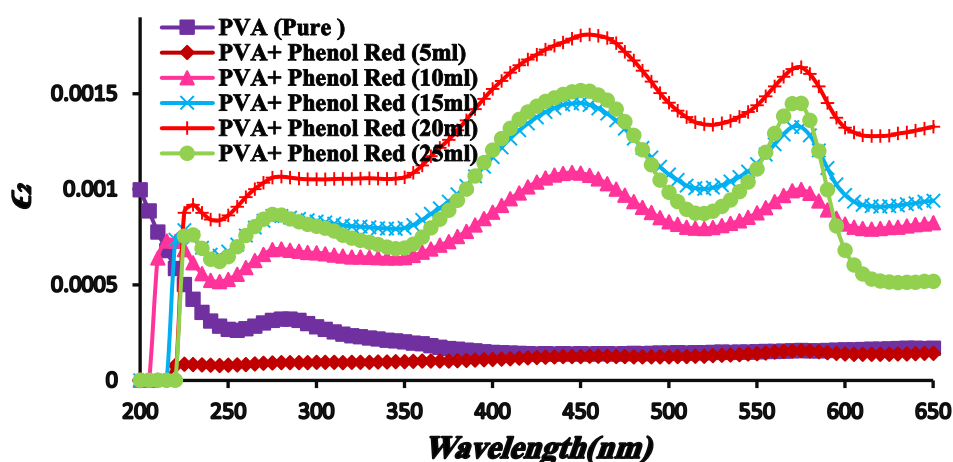


Fig. (11): Imaginary dielectric constant of pure PVA and Phenol red/ PVA films with several doping ratio of Phenol red solution.

Conclusion:

The absorption intensity is continuously increased with the increasing of the ratio of phenol red dye. Secondly; the absorption wavelength is increased toward longer wavelength about (10 nm). The energy band gap for indirect allowed is decreased with increased the doping ratio of phenol red , this behavior attributed to creation of new levels in the band gap, lead to facilitate the crossing of electrons from the valence band to these local levels to the conduction band.

References:

- 1) Tubbs R.K., Sequence Distribution of Partially Hydrolyzed Poly (vinyl acetate). *Journal of Polymer science*, 4, 623–629, 1966.
- 2) Demerlis C.C., Schoneker D.R., Review of the oral toxicity of polyvinyl alcohol (PVA), *Food Chem. Toxicol.*, 41, 319–326, 2003.
- 3) Kadajji V. G. and Betageri G. V., *Water Soluble Polymers for Pharmaceutical Applications*, *Polymers*, 3, 1972-2009, 2011.
- 4) Saxena S.K., *Polyvinyl Alcohol (PVA), Chemical and Technical Assessment 61st JECFA*, 1-3, FAO(2004).
- 5) Herbst W., Hunger K., *Industrial Organic Pigments Production, Properties, Applications*, Third, Completely Revised Edition. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 1-672, 2004.
- 6) Saha U., Mukherjea K.K., Development of a multifunctional biomimicking L-cysteine based oxovanadium (IV) complex: synthesis, DFT calculations, bromo-peroxidation and nuclease activity, *RSC Advances*. 5 (114): 94462–94473, 2015.
- 7) Liu Z., Liu J., Chen T., Phenol red immobilized PVA membrane for an optical pH sensor with two determination ranges and long-term stability, *Sensors and Actuators B* 107,,311–316, 2005.
- 8) Sreedhar S., Illyaskutty N., Sreedhanya S., Philip R., and Muneera C. I., An organic dye-polymer (phenol red-poly (vinyl alcohol)) composite architecture towards tunable -optical and -saturable absorption characteristics, *J. Appl. Phys.* 119, 193106, 2016.
- 9) Ganesh V., Shkir M., Yahia I.S., Parakkandy J.M., AlFaify S., Phenol red dyed Bis thiourea Zinc acetate crystal growth and characterization for electro-optic applications, *optic*, 158, 997-1005, 2018.
- 10) Jalil M.S., *Physical Properties, Antibacterial and antibiofilm Activities of PVA Polymer with Safranin Dye and Biosurfactant*, Ph.D Thesis, College of Science, Al-Mustansiriyah University, 2015.
- 11) Madhloom S.A., *physical properties and Antibacterial Activity of polymer with TiO₂ Nanoparticles*, Master Thesis, College of Science, Al-Nustansiriyah University, 2016.

- 12) Lin F., "Preparation and Characterization of Polymer TiO_2 Nanocomposites via In-situ Polymerization, M.S.C. Thesis, University of Waterloo, Applied Science in Chemical Engineering, 2006.
- 13) Fox M., Optical Properties of Solid", Great clarendon street, oxford OX2 6 DP, Oxford Univ. press, 2001.
- 14) Tauc, Amorphous and liquid semiconductors, Plenum press London and New York, 1974.
- 15) Alwan T. J., Refractive index dispersion optical properties of dye doped polystyrene films, Malaysian polymer journal, 5 (2), 204-213, 2010.
- 16) Saadallah H. F., Spectroscopic properties study of polymer film doped by dye laser organic type (C_{10}), M.Sc Thesis in College of Science, Mustansirya University, 2007.
- 17) Mahmoud T. H., Study of structural and optical properties of (CdO) thin film doped with (Sn) by thermal evaporation under vacuum technique, M.Sc Thesis in College of education, Ibn- AL- Haitham, Baghdad University, 2011.
- 18) Surre J., Canard I, Bourne P., Courbiere E., Francesch C.i, Chatellier S., Belkum A.V. and Ramjeet M., Enhanced detection of Carbapenemase-Producing Enterobacteriaceae by an optimized phenol red assay, Diagnostic Microbiology and Infectious Disease, S0732-8893(17)30279-1, 2017.
- 19) Mansour A.F., Mansour S.F., Abdo M.A., Improvement Structural and Optical Properties of ZnO / PVA Nanocomposites, IOSR Journal of Applied Physics, 7(2), 60-69, 2015.