# Influence of Molecular Weight and Concentration of Poly Vinyl Alcohol (PVA) Films on Optical Properties

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**Abstract**:

In this research polyvinyl alcohol (PVA) films was prepared by casting method at room temperature, the influence of different weights (0.25 , 0.5 , 0.75 ,1 )g for different molecular weight of PVA( 14000 g/mol and 160000 g/mol) was studied . The absorption and transmission were recorded by using UV-Visible spectrophotometer and used to calculate some of optical properties investigated including: Reflectance spectra, Energy gap, Absorption coefficient, Refractive index, Extinction coefficient and Real part, imaginary part of dielectric constants. From results it can be concluded that optical characterization is increase as increasing of concentration and decreasing of molecular weight.

**Key Words**: Optical Properties, Polymer Films, PVA, Effect of Molecular Weight, Effect of Concentration.

**تأثير الوزن الجزيئي والتركيز على الخصائص الفيزيائية لاغشية بولي فينيل الكحول**

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**الخلاصة :**

في هذا البحث تم تحضير غشاء بولي فينيل الكحول (PVA) بطريقة الصب في درجة حرارة الغرفة ، درست تأثيرات عدة اوزان ( 0.25,0.5,0.75,1) غرام من بولي فينيل الكحول ولعدة اوزان جزيئية (160000, 14000) غرام /مول . سجلت الامتصاصية والنفاذية باستخدام جهازالمطياف UV-Visible spectrophotometer واستخدمت لحساب بعض الخصائص البصرية منها طيف الانعكاسية ، فجوة الطاقة ،معامل الامتصاص ، معامل الانكسار ، معامل الخمود ، والجزء الخيالي والحقيقي لثابت العزل . اوضحت النتائج ان الخصائص البصرية تزداد بزيادة التركيز ونقصان الوزن الجزيئي .

## 1- Introduction

Polymers may either be naturally occurring or purely synthetic. There are a large number of synthetic polymers consisting of various families: adhesives, fibers, elastomers, plastics, etc. Each family itself has subgroups. Enzymes, nucleic acids, and proteins are polymers of biological origin. Polymers (macromolecules) are long chain molecules with high molecular weight, built-up by the repetition of simple chemical units called monomers and typically connected by covalent chemical bonds. The process of combining many monomers into a covalently bonded chain to form a big polymer called polymerization [Ebewele, 2000].

Polyvinyl alcohol (PVA) is synthetic polymer, odorless, tasteless, translucent, white or cream colored granular powder. It is soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents. PVA is emulsifying and adhesive properties. It is nontoxic, fully degradable, innocuous, non-carcinogenic and have good biocompatible properties, its excellent film forming with outstanding chemical stability [Eliassaf, 1972, Ebewele 2000,Saxena, 2004, Tripathi *et al*, 2009]. PVA manufactured by polymerizing vinyl acetate and hydrolyzing the resultant polymer to produce the alcohol. Because PVA is synthesized from polyvinyl acetate, a variety of different grades of PVA is available that varies in molecular weight and hydrolysis level. These two factors are the major determinants of the performance properties of PVA. Molecular weight is a measure of polymer chain length and is typically reported as a 4% aqueous solution viscosity [Sekisui,2011].

Alwash (2010) studied the direct transition for PVA at 25$^{\circ}$C and found energy gap is equal to 5.45 eV and the optical activation energy ΔE at 25 $^{0}$C for PVA is 5.8 $cm^{-1}$.. Hashim *et al* (2012) studied the optical properties of PVA pure and (PVA-CaO) Composites concluded the allowed indirect energy gap is 5.18 eV for pure PVA . Yousif *et al* (2012) recorded the energy gap of PVA is 5.48 eV at 25 $^{\circ}$C . Attia and Abd El-kader (2013) studied the optical properties of PVA and calculated the absorption edge equal 4.86 eV and refractive index 1.68.. Kramadhati and Thyagarajan (2013) recorded the PVA absorption edge is 5eV and direct band gap is equal to 5.3 eV and indirect band gap is 5.1 eV . Mustafa (2013) find the PVA absorption edge is 0.38 eV and energy gap of allowed indirect transitions is 5.05 eV and energy gap of forbidden indirect transitions is 4.92eV . Abdallh *et al* (2013) found that the $E_g$ for allowed direct transition is 5.9 eV.

The study includes measurement of optical spectra: absorption, transmission, absorption coefficient, refractive index, reflectance, extinction coefficient, optical band gap and complex dielectric constant for different concentrations also, finesse and optical conductivity.

**2- Theoretical Optical Properties**

The relationship between incident intensity and penetrating light intensity is given by eq. (1) [Valeur (2001) ,Bower (2002)] :

$I=I_o e^{-\alpha t}$ ………. (1)

Where t is the thickness in centimeter (cm) and α is the absorption coefficient ($cm^{-1}$),

$\alpha\, t = 2.303 \log I/I_o$……….(2)

where the amount of $\log I/I_o$ represents the absorbance (A).

The absorption coefficient can be calculated by:

$\alpha = 2.303\ (A/t)$ ………. (3)

If the amount of absorption coefficient is $\alpha \geq 10^4\ cm^{-1}$, the electronic transitions are direct.

The amount of optical energy gap from this region can be evaluated by the relation**.**

$\alpha = \alpha_o(h\upsilon - E_g)^r / h\upsilon$ ………(4)

Where hυ is the photon energy, $\alpha_o$ is the proportional constant, $E_g$is the allowed or forbidden energy gap of direct transition and r is a constant depending on the type of the electronic transitions. r takes the value (1/2) for allowed direct transition and (3/2) for forbidden direct transition.

The energy is dependence on absorption coefficient as illustrate in the from:

When the amount of absorption coefficient ($\alpha < 10^4$ cm-1)

$\alpha = \alpha_o(h\upsilon - E_g \pm E_p)^r / h\upsilon$ ……….(5)

Where ($E_g$) is the minimum energy gap, ($E_p$) is the phonon, (+) absorbed (-) emitted, (r) take the value (2) for allowed indirect transition and (3) for forbidden indirect transition .

By plotting $(\alpha h\upsilon)^{1/2}$ versus (hυ) for fixed (r)value, the extrapolation of the liner part could be used to define $E_g$ .

The refraction index consists of real and imaginary parts (*N* = *nik*), the relation between reflectivity and refractive index is given by eq. (6) [Valeur (2001) ,Bower (2002)]:

$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}$ ………..(6)

Where *k* is the extinction coefficient. The absorbance and transmittance can be calculated by the following equation:

$R + A + T = 1$…………(7)

The refractive index can be expressed by eq. (8)

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

The extinction coefficient can be calculated by using eq. (9):

$K = \frac{\alpha\lambda}{4\pi}$ ………………(9)

Where $\lambda$ is the wavelength of the incident ray.

The relation between the complex dielectric constant and the complex refractive index *N* is expressed by:

$\varepsilon = N^2$ ……………… (10)

It can be concluded that:

$(n\text{-}ik)^2 = \varepsilon_1\text{-}i\varepsilon_2$ ……………… (11)

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

$\varepsilon_1 = n^2 - k^2,\ \varepsilon_2 = 2nk$ …………(12)

Also, the finesse coefficient is given by:

$F = \frac{4R}{(1-R)^2}$ …….(13)

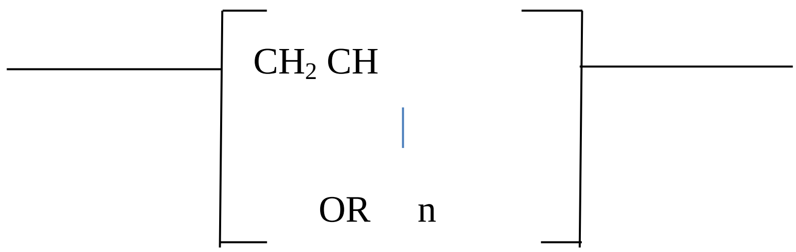
the optical conductivity can be found by using the following eq.

$\sigma_{opt} = \frac{nc\alpha}{4\pi}$ ………(14)

Where (n) is refractive index ,(c) is light velocity , (α) is absorption coefficient

## 3- Materials and Methods

The chemical structure of PVA shown in fig.(1) with Mw(14000) g/mol natural granular viscosity of 4% aqueous solution 4-6 cp obtained from DBH Chemical LTD Pooled England and Mw (160000) g/mol viscosity 27-33 cp obtained from HIMEDIA CO. India .




where R = H or $COCH_3$

**Fig 1: Chemical structure of PVA polymer [Saxena, 2004] .**

PVA solution was prepared by dissolving (0.25, 0.5,0.75 and 1)g of PVA powder with 10 ml distilled water , stirred for 3to 4 hours at room temperature ( 25 -35 $^{o}$C ) to ensure for fully dissolving. Forming the PVA films by casting the solution in glass petridish and allowed to evaporate slowly at room temperature for (24-48 hours ). To find concentration of PVA films for each weight (0.25.0.5,0.75 and 1)g taken according to eq.(15) and the data shown in table (1).

m = C V Mw ………….(15)

where m is weight of polymer(g) , C is concentration (mol/liter) , V is volume of solvent (liter) , Mw is molecular weight (g/mol) .

UV-Visible absorption and transmission spectra for PVA films are obtained by T80 UV-VIS spectrometer PG instruments Ltd.

Also, the thickness of these samples illustrated in table (1) was taken by using digital micrometer .

By using eq. (15) we calculate the concentration for different weights and different Mw of PVA see table 1.

**Table (1) No. of samples with their weights, concentration and thickness**

| No. of Sample | Mw of PVA ( g/mol) | Weight (g) | Concentration (C) (mol/l) | Thickness (t) (mm) |
|---|---|---|---|---|
| 1 | 160000 | 0.25 | $1.562x10^{-4}$ | 0.0518 |
| 2 | 14000 | 0.25 | $1.785x10^{-3}$ | 0.0692 |
| 3 | 160000 | 0.5 | $3.125x10^{-4}$ | 0.0898 |
| 4 | 14000 | 0.5 | $3.57x10^{-3}$ | 0.0863 |
| 5 | 160000 | 0.75 | $4.687x10^{-4}$ | 0.1028 |
| 6 | 14000 | 0.75 | $5.357x10^{-3}$ | 0.1164 |
| 7 | 160000 | 1 | $6.25x10^{-4}$ | 0.2105 |
| 8 | 14000 | 1 | $7.142x10^{-3}$ | 0.281 |

## 4- Results and Discussion

The UV- VIS absorption spectra for all films are illustrated in fig (2),the maximum wavelength of absorption spectrum of PVA polymer with two molecular weight is at 280 nm, and this is matched with results obtained by (Abdullah and Hussen (2011) and Hashim *et al*,2012). Also their results showed a peak intensity of absorbance are ( 0.01,0.4) appear at ( 280 nm) respectively .

Whereas in our study the intensity of absorption spectrum of PVA is increased with increasing concentration and decreasing molecular weight of polymer: 0.112 for 160000 and increased to be 0.392 for lower Mw 14000.

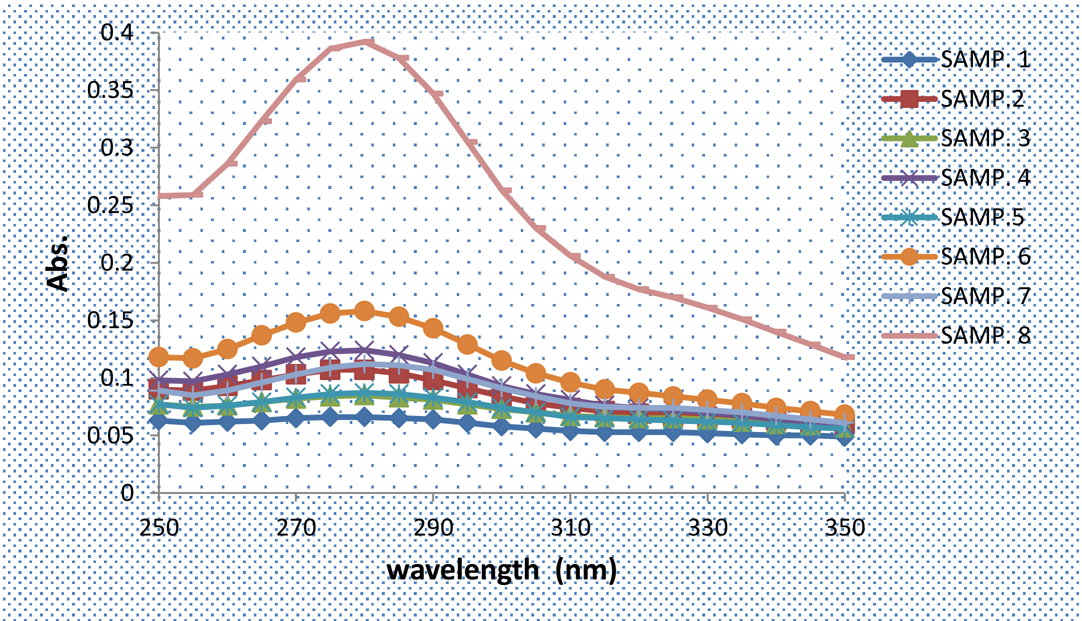



**Fig.(2): UV/VIS absorption spectrum for PVA films with different molecular weight and concentration.**

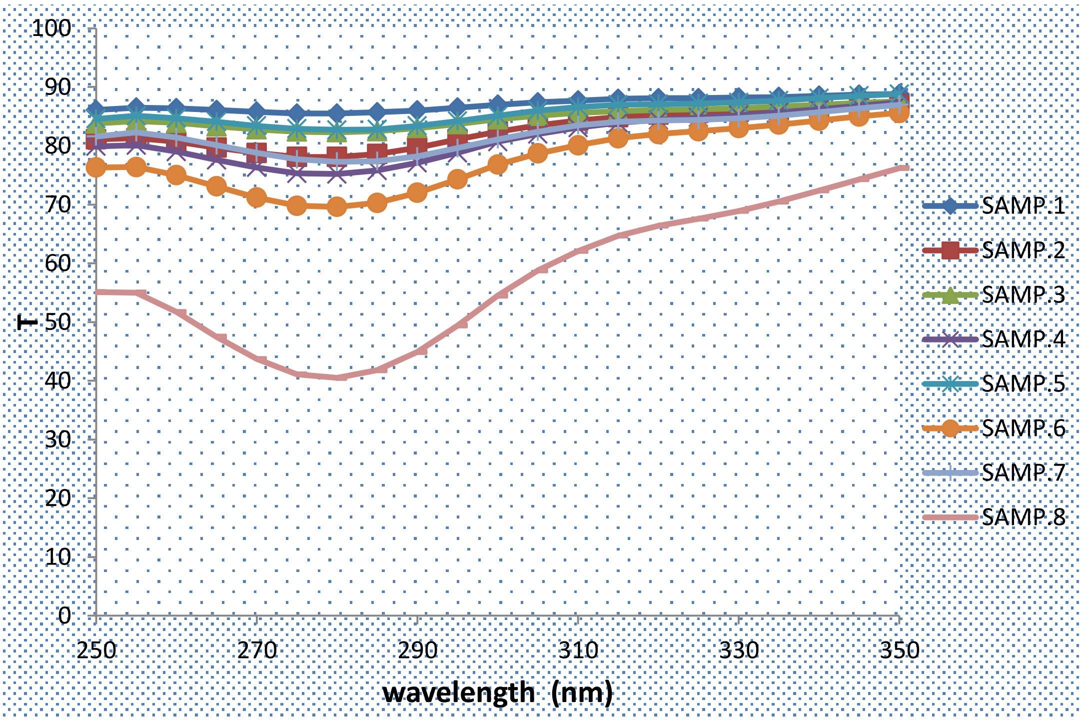



**Fig.(3) :Transmission spectrum for PVA films with different molecular weight and concentration**

Transmission spectra of PVA films for two molecular weight and concentration were shown in fig. (3). transmission decrease as increased of weights and decreasing of molecular weight .The minimum transmittance is (40.5) at wavelength (280 nm).

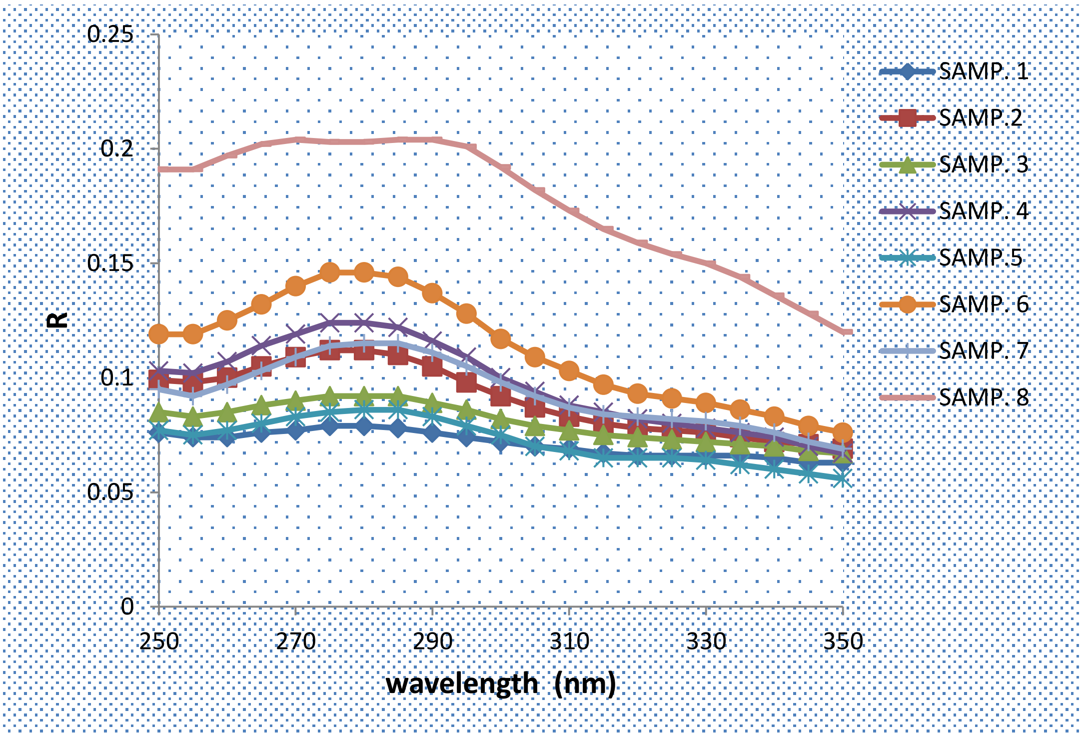
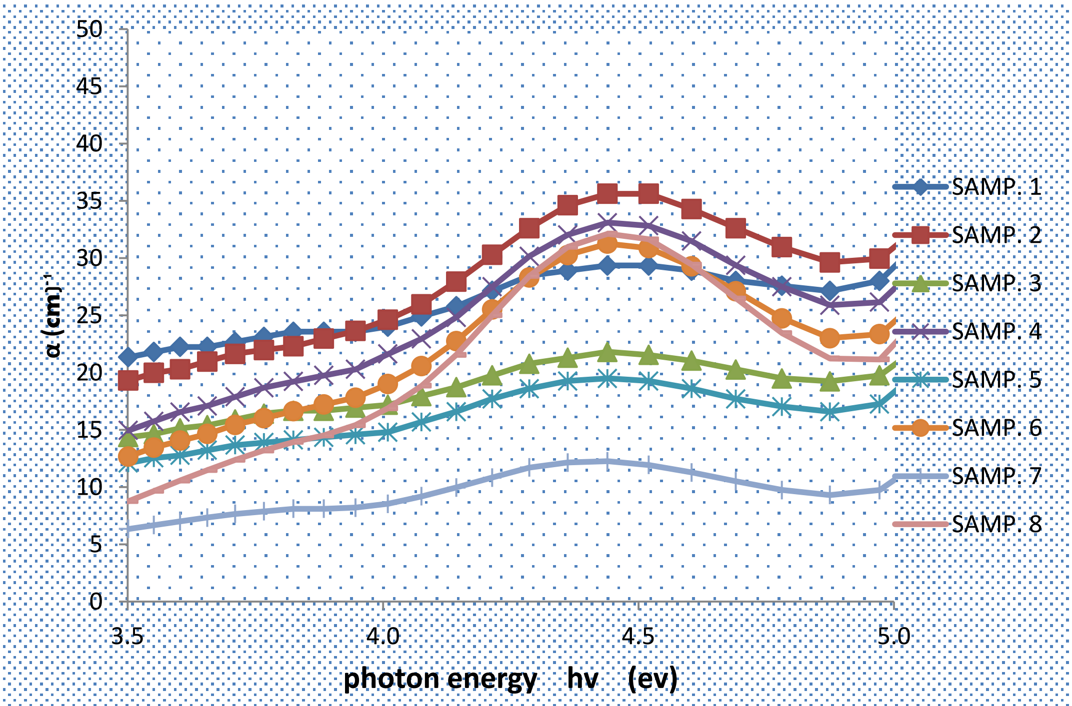



**Fig (4) :Reflection spectrum for PVA**




**films with different molecular weight and concentration**

The relationship between the reflectance and concentration is described in Fig.(4). The reflectance increases with increasing the concentration and decreasing the molecular weights.

**Fig.(5):Absorption coefficient for PVA films with different molecular weight and concentration.**

From fig (5), results shown that α is less than $10^4$ ($cm^{-1}$)that's indicate the electronic transition is indirect transition between connecting band and valance band .

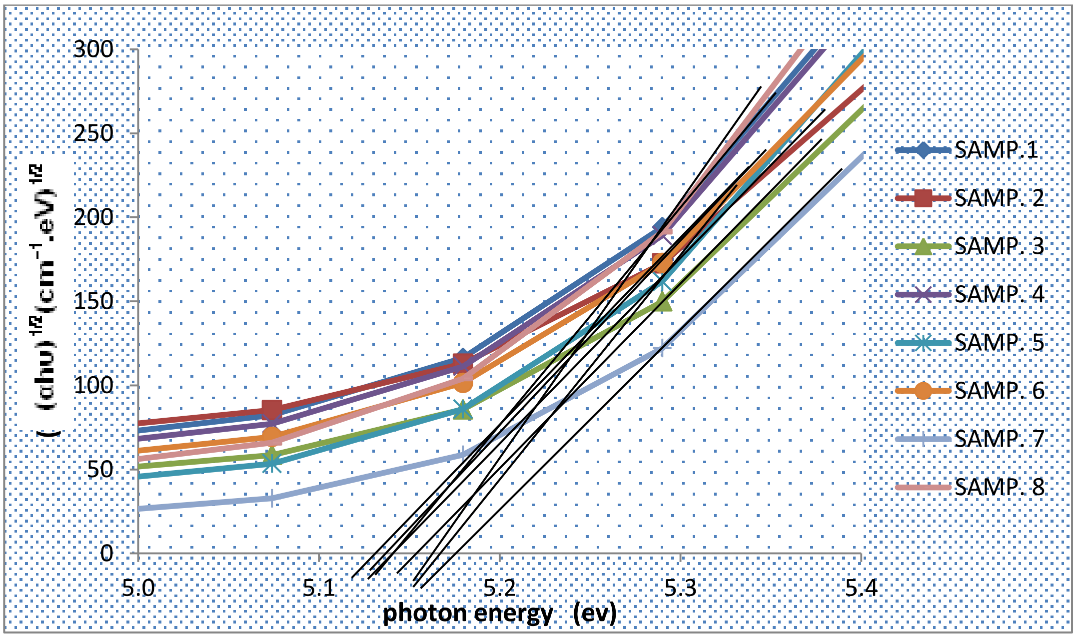



**Fig.(6) The allowed indirect transition for PVA with various photon energy.**

The relationships between $(\alpha h\upsilon)^{1/2}$ versus photon energy for the polyvinyl alcohol samples are shown in Fig.(6) for allowed indirect transition. It can be evaluated from extrapolating of linear region of the curve to a point of $(\alpha h\upsilon)^{1/2}$ versus hυ for PVA at different concentrations .

The indirect allowed energy gap are (5.13, 5.11, 5.14, 5.12, 5.12, 5.11, 5.16, 5.15) eV for the weights [0.25g (160000),0.25g(14000),0.5g (160000),0.5g (14000), 0.75g (160000),0.75g (14000) ,1g(160000) ,1g (14000) ] , respectively .

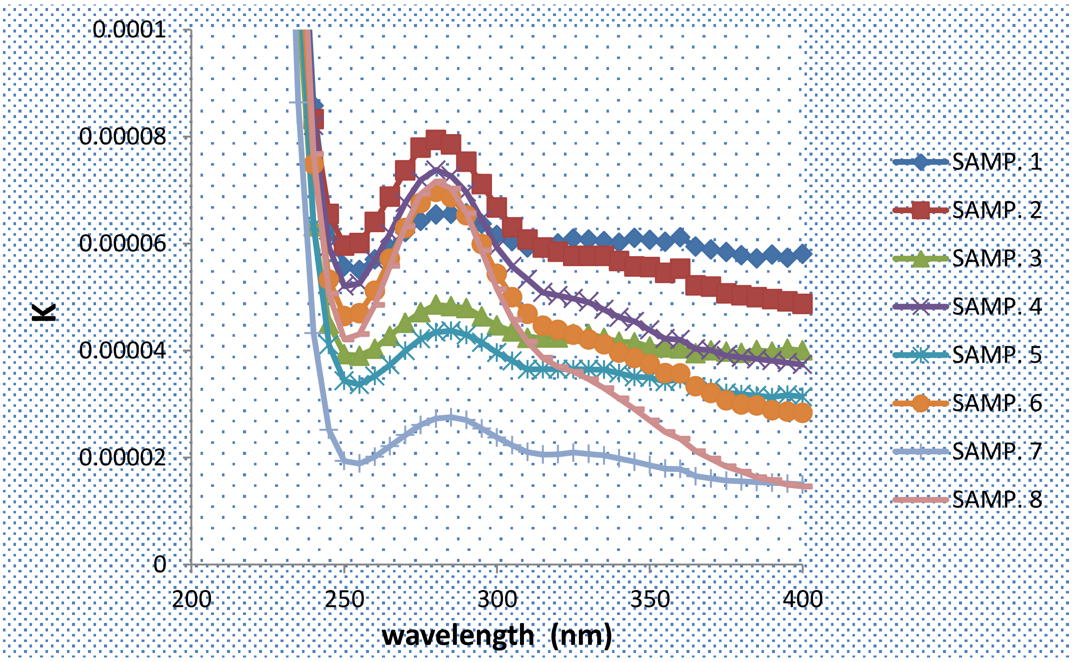



**Fig. (7). Extinction coefficient (K)for PVA films with different molecular weight and concentration.**

The change of extinction coefficient as a function of wavelength as shown in Fig.(7) The extinction coefficient peak at wavelength 280 nm are ranging between 7.938 x$10^{-05}$ for weight 0.25g and Mw 14000 to 2.7316 x$10^{-05}$ for weight 1g and Mw 160000 .

It was noted that k has lower value at high concentration and high Mw (160000), and this is attributed to increase in the absorption coefficient with increased of concentration . The extinction coefficient is high at the longest wavelengths and low concentration.

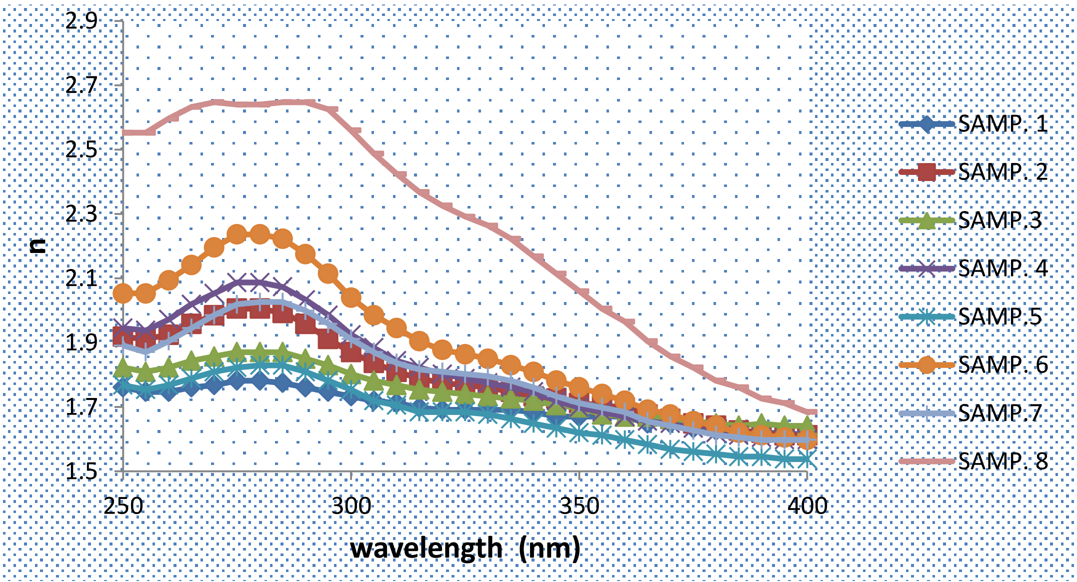



**Fig.(8). The refractive index (n)for PVA films with different molecular weight and concentration.**

Also refractive index is increase as increasing the weights and decreasing the molecular weights, the maximum n is 2.64 at 280 nm for Mw 14000 and weight 1 g , while the maximum n is 2.02 for Mw 160000 at the same wavelength and weight.

The real dielectric constant depends on $n^2$ and $k^2$, but the imaginary dielectric depends on k and n. The real and imaginary dielectric constant ($\varepsilon_1$ and $\varepsilon_2$) for PVA calculated from Eq.(12). Figs.(9 and 10) shows the changes of these constants with wavelengths. The values of the real dielectric constant are high with respect to the imaginary dielectric constant, because they are dependent on $n^2$ and $k^2$values.

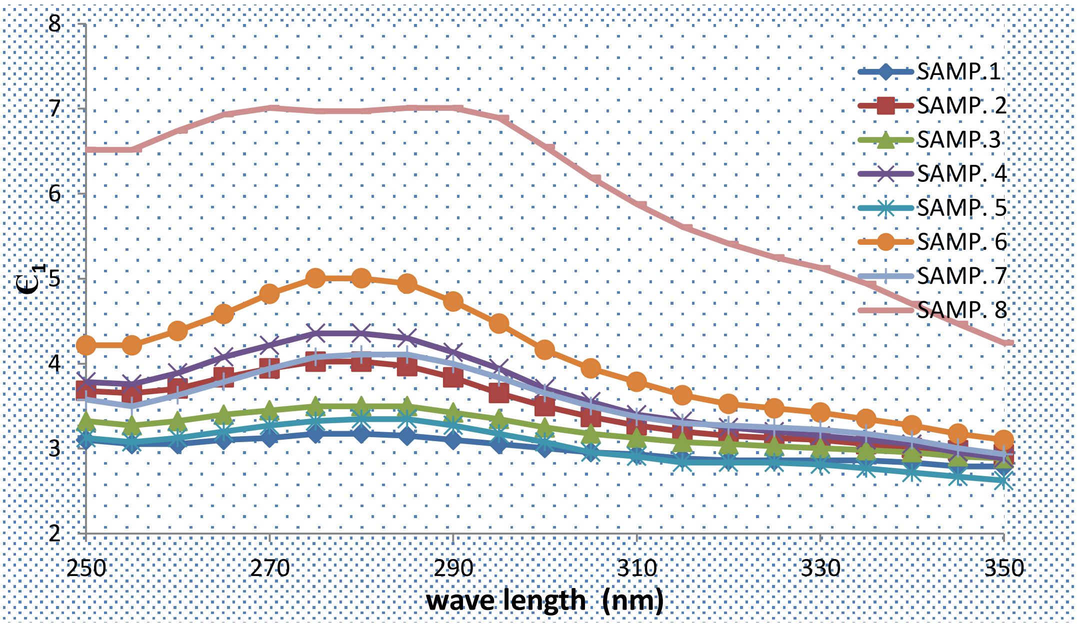



**Fig.(9) . The real dielectric constantfor PVA films with different molecular weight and concentration as a function of incident wavelength**

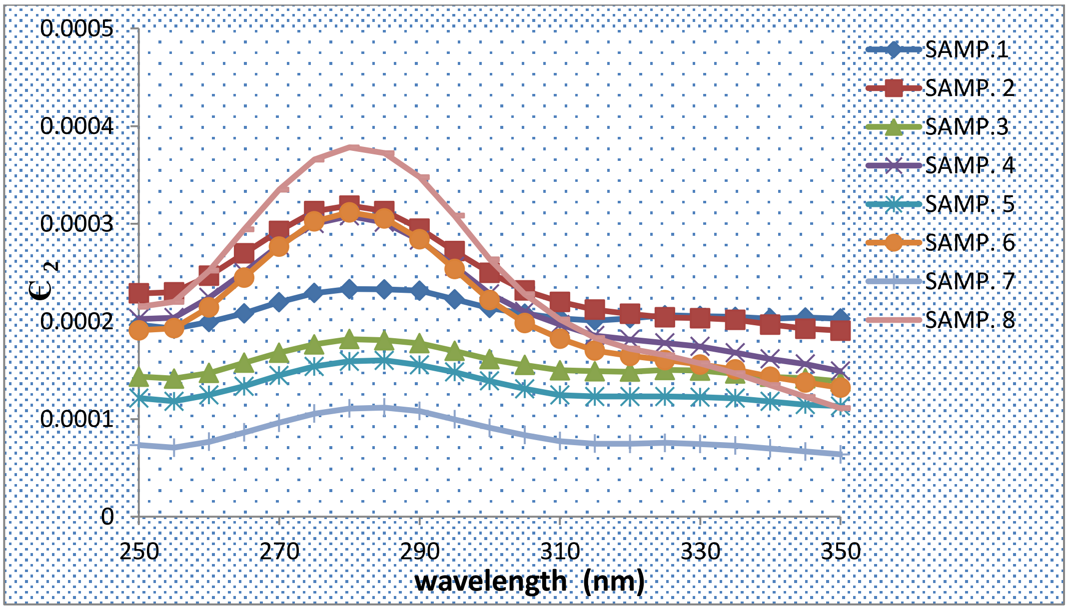



**Fig.(10). The imaginarydielectric constantfor PVA films with different molecular weight and concentration as a function of incident wavelength .**

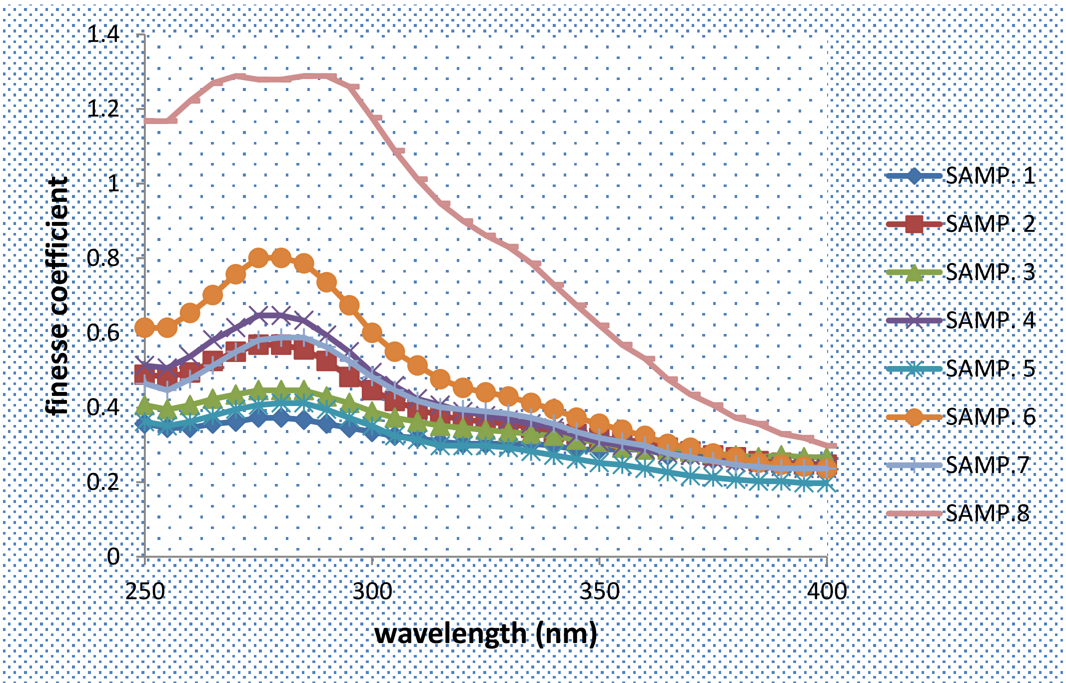



**Fig. (11). The finesse coefficient for PVA films with different molecular weight and concentration as a function of incident wavelength .**

Fig.11 shows the values of finesse coefficient against wavelengths at different concentrations of PVA. It was observed that F values decrease from1.278 for 1g Mw14000 to0.377 for 0.25 g Mw 160000 but the peak remain at 280 nm Also, the finesse coefficient increases with increasing in weights , concentration and decreasing the Mws because of weights additives that lead to changing in reflectance which F is dependent on R, as described in eq. (13).

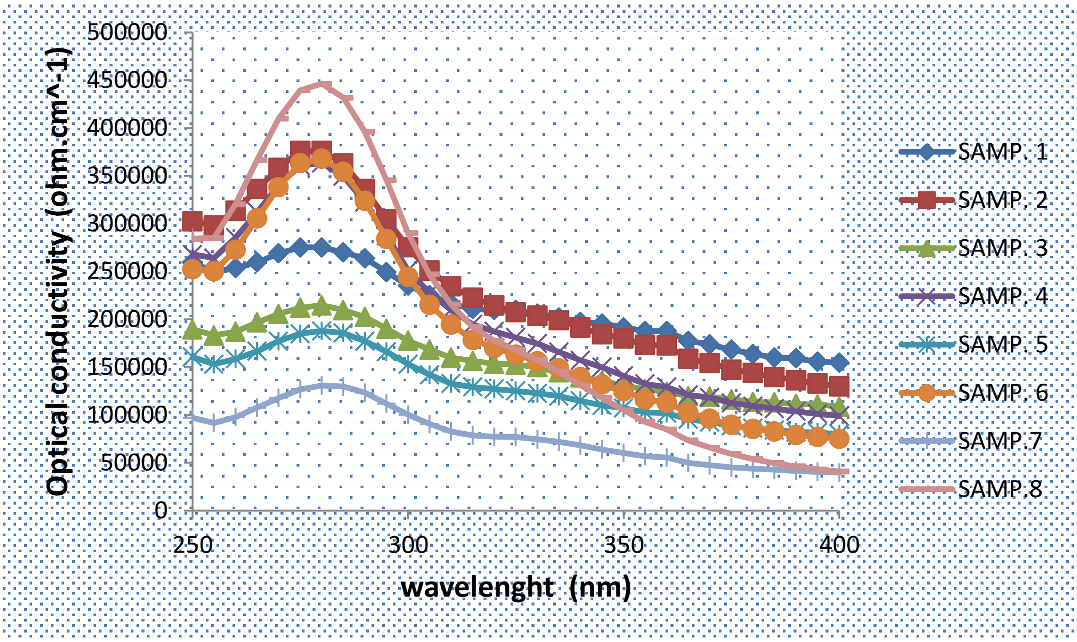



**Fig. (12). The optical conductivity for PVA films with different molecular weight and concentration as a function of incident wavelength .**

The optical conductivity is increase when reach to 250 nm and decreases suddenly after 310 nm of wavelength as shown in Fig. 11. It was observed an increase in optical conductivity as decreasing in Mw. This optical conductivity becomes constant after 390 nm.

**Conclusion :**

In this research the optical properties of PVA were studied for different weights (0.25,0.5,0.75,1) g, different concentration and different molecular weight (14000,160000) g/mol , the optical properties absorbance, absorption coefficient, as other constants are increase as increasing of concentration and decreasing of molecular weight , the value of absorption coefficient indicate the kind of energy gap shows that electronic transition is indirect transition for PVA

**Acknowledgment**

The authors thankfully acknowledges the physical department / College of Science /Almustansiriya University/ Baghdad/ Iraq, for their cooperation especially the head of department Pro.Dr. Ali al zaki .

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