Study Structural and Optical properties of PVA films at different thickness

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Abstract

Polyvinyl alcohol (PVA) films with different thicknesses were prepared by casting method. The thickness of the prepared films were (35, 55, 75 and 100) µm. The optical transmission (T%) was measured in the wavelength rang of (200 – 1100)nm, The effect of thickness increasing on optical properties such as transmittance, refractive index, extinction coefficient in addition of the Real and Imaginary part of dielectric constant was studied. This study reveals that all these parameters affected by the increasing of the thickness, and also found that the optical energy gap has been increased with the increasing of the thickness.

Key Words: PVA, optical properties, X-ray diffraction.

دراسة الخصائص التركيبية والبصرية لأغشية بولي فينايل الكحول عند الأسماك المختلفة.

الخلاصة:

حضرت أغشية بولي فينيل الكحول بأسماك مختلفة باستعمال طريقة الصب. سمك الغشاء كان (٣٥،٥٥، ٧٥ و ١٠٠) مايكروميتر. تم دراسة الخصائص البصرية بمدى الأطوال الموجية (٢٠٠ – ١١٠٠) نانومتر، كان تأثير زيادة السمك على الخواص البصرية مثل النفاذية، معامل الانعكاس، معامل الخمود و ثابت العزل بجزيئه الحقيقي والخيالي. توصلت هذه الدراسة الى ان كافة هذه المعاملات قد تأثرت بزيادة السمك، كذلك وجد بان فجوة الطاقة البصرية ازدادت بزيادة السمك.

الكلمات المفتاحية: بولي فينيل الكحول، الخصائص البصرية ، حيود الأشعة السينية.

Introduction

The study on optical and structural properties of polymer films have increased enormously for their extensive application in optical and electronic devices [1,2]. Moreover these polymers are traditionally considered as an excellent host material for composites [3]. The polyvinyle alcohol (PVA) is a thermoplastic polymer with many having avery high dielectric strength, good charge storage capacity [1-5].

PVA films are easily prepared by a casting evaporation technique from aqueous polymer solution, thus avoiding the use of organic solvents. The resultant films are clear, homogeneous and resistant to tear. However, the water solubility of film reduces its usefulness in transdermal delivery systems. Heat – treating the film reduces water solubility, but also renders the film brittle and difficult to handle [6]. Various research groups studied the effect of doping on optical, structural and mechanical properties [1, 3,5, 7], but no study about effect different thickness of pure PVA films.

Thickness dependent changes in the optical properties can be caused by changes in the self – absorption , local film morphology in the region of light emission and optical interference i.e., micro cavity effects [8]. The aim of this study effect changing of thickness on PVA films using casting method and measuring some optical and structural properties.

Experimental

Casting method is used to prepare films of poly(Vinyl alcohol) in different thickness, were prepared by dissolving PVA (molecular weight 70000 g/mol) in deionized water thoroughly stirred using a magnetic stirrer with heating (40 ˚C) for about one hour until PVA was completely dissolved. The solution was poured into flat glass plate dishes, Homogenous films were obtained after drying in an oven for one hour at 50 ˚C. The film thickness was measured with the help of a Digital Caliper Vernier (a micrometer type 2610 A, Germany) and was found to be in (35,55,75,100)±1 µm.

Absorption and transmittance measurements were carried out using double beam UV/VIS sepectrometer (shimadzu japan) in the wave length (200-1100)nm. X-ray diffraction (XRD)analysis of the samples were performed using an automated powder X-ray diffract meter system (type 6000) with Cu target (λ=1.5406 ˚A).

Results and discussion

The XRD patterns of the PVA polymer are shown in Fig. (1) can be seen from these XRD patterns that a broad peak appeared around (18.60° - 20.01°) which is the characteristic peak for PVA. Where the full width half maximum intensity were reduce with increase thickness. The intensity of PVA films increase with thickness increase.

The average particle size can be calculated using the first sphere approximation of Deby – Scherrer formula [9,10] :

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where D is the average diameter of the crystals, λ is the wave length of X –ray radiation, and **β** is the full width at half maximum intensity, It is evident that the average value of particle size for PVA in colloidal form is equal to 38.5 nm and 42.5 nm (see table 1).

The optical transmission spectra as a function of wave length in the range of (200-1100) nm , Its shown in Fig. (2). We can observe from this figure that the transmittance decreases with increasing the thickness. Thais may be attributed to the creation of levels at the energy band by increasing thickness thickness and this leads to the shift of peak smaller energies[11].

The optical absorption coefficient of PVA is very important because it provides information about the band structure of solids by using the following equation[12]:

$$\alpha h\nu = B\,(h\nu - E_g)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where B is a constant, hν is the photon energy, E_g is the optical energy gap and α is the absorption coefficient. The in direct allowed band gap was determined by plotting $(\alpha h\nu)^{1/2}$ as faction of photon energy as shown in fig. (3), the graph is a straight line and the value of E_g is obtained by extrapolating the liner portion of the graph to intercept the photon energy axis. The value of optical energy band gap found to be decreasing from 5.25 eV to 4.8 eV as the film thickness increases from (35 to 100) µm, the values of E_g is listed in table (1). In general, the density of localized state in the film increases with film thickness which leads to decrease in the band gap. This material has potential applications in waveguides, nano fibrous composite membrane, solid polymer electrolyte, fuel cells and intergrateed optics [7].

The refraction index n value provides the optical properties of the film and it is related by the fallowing equation [13].

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{1-R^2} - K^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where R is Reflectance and K is extinction coefficient as shown from fig. (4), the refractive index decrease as the wave length increase until 300 nm and then become nearly constant with increasing wave length. The value of refractive index within the constant range was 1.19 to 1.24 as the thickness percentage increase. The extinction coefficient (K) is directly proportional to the absorption coefficient as see in relation [11]:

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

It can be notice that the extinction coefficient increased as the film thickness increase, Fig. (5) shows the variation the extinction coefficient with wave length at different thickness films.

The real (ε1) and imaginary (ε2) parts of the dielectric constant related to the (n) and (K) values. The (ε1) and (ε2) values were calculated using the from [12] :

$$\varepsilon 1 = n^2 - K^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

While ε_1 is mainly depends on the K values, therefore notice the behavior of ε_1 is similar to the refractive index because of the smaller value of K^2 comparison of while ε_2 is mainly depends on the K values, Which are related to the variation of absorption coefficient [12]:

$$\varepsilon^2 = 2nk \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

It is found that ε_1 increases as the film thickness increase, and the ε_2 is decreases as the film thickness increase.

The real and imaginary parts of the dielectric constant indicate the same pattern and the values of real part and higher than imaginary part. The dielectric constants consists of real part ε_1 and imaginary part ε_2 , the variations of them with photon energy were determined and shown in figure (6) and (7).

The optical conductance (σ) is obtained using the relation [12, 13] :

$$\sigma = \frac{\propto nc}{4\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where (c) is the velocity of light in the space, n is refractive index and α is the absorption coefficient. Fig. (8) shows the variation of optical conductivity of PVA films as function of photon energy. The conductivity of PVA is constant up to (5 eV) of photon energy at thickness (35 and 55) µm, after that it increases with increase in photon energy, but the conductivity at thickness (75, 100)µm the conductivity is constant up to (4.5 eV), after that it increases with increase in photon energy. The PVA thickness caused the increase the increase in optical conductivity, which is due to high absorbance of polymer electrolyte films.

Conclusion

The PV A films have been prepared successfully by casting method, The study of effect films thickness has a great effect on optical properties. Transmittance and optical band gap decreases with the increasing, but the refractive index and extinction coefficient were increased.

Table (1) Show values of Energy gap and Grin size for PVA films at different thickness.

Thickness (µm)	Energy gap (eV)	Grin size (nm)
35	5.25	38.5
55	5.05	52.4
75	5	46.3
100	4.8	42.5

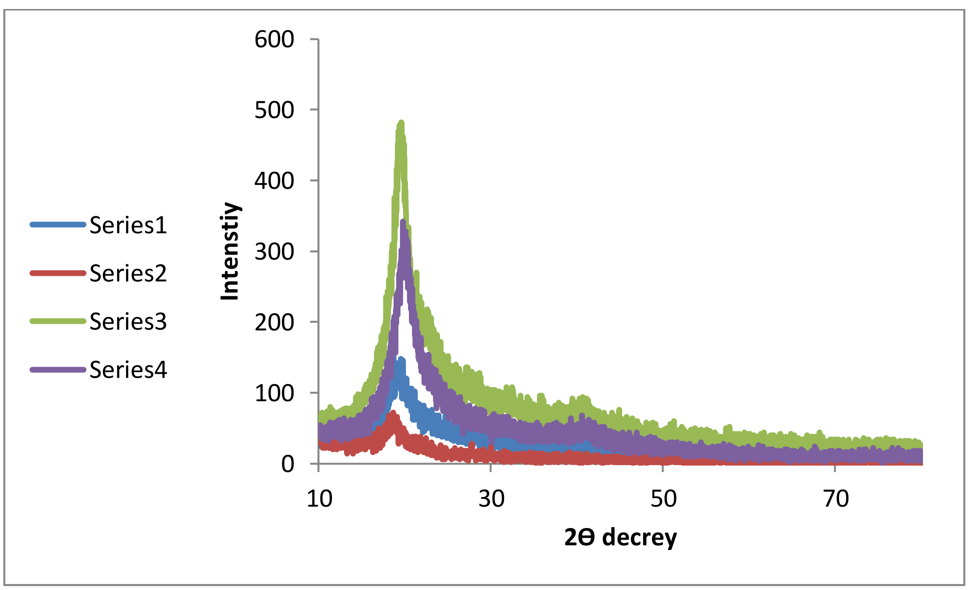

Fig (1) X-ray diffraction of PVA films for different thickness.

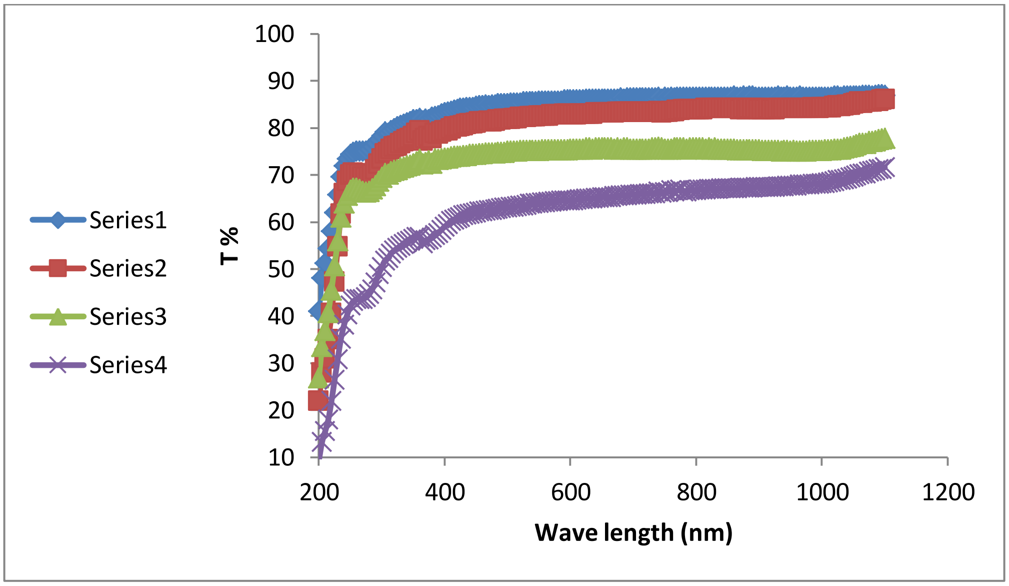

Fig. (2)Transmission versus wavelength for the as different thickness

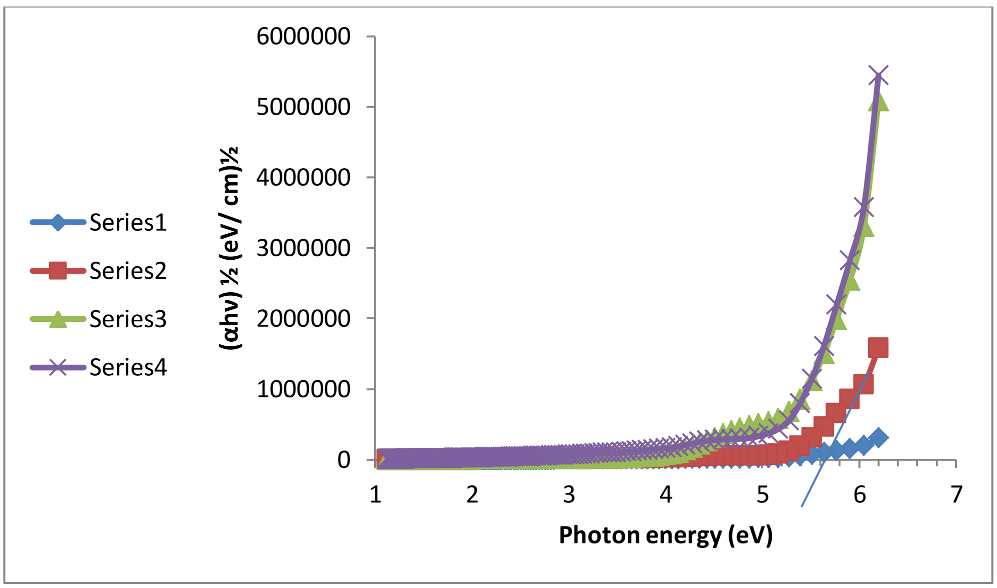

Fig. (3) $(\alpha h\nu)^{1/2}$ versus photon energy for PVA films at different thickness.

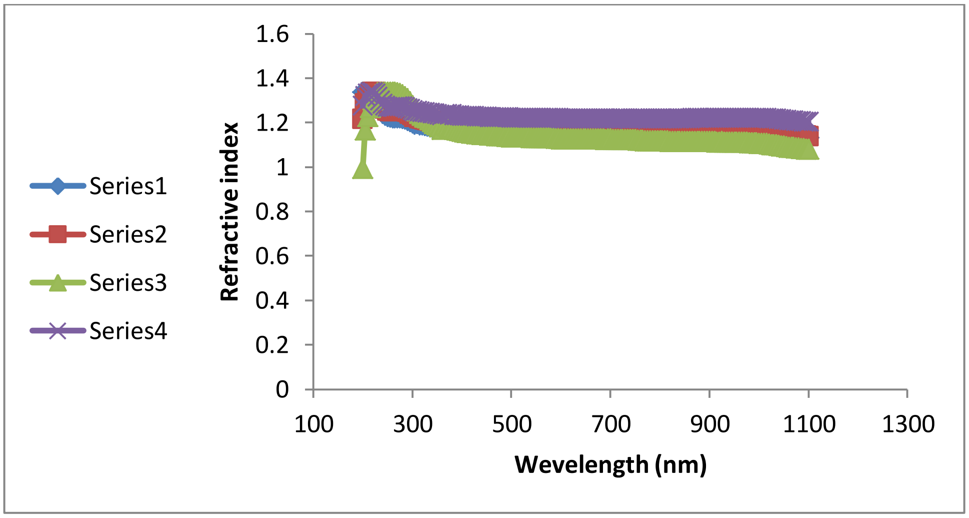

Fig. (4) Refractive index versus wavelength for the as deposited films.

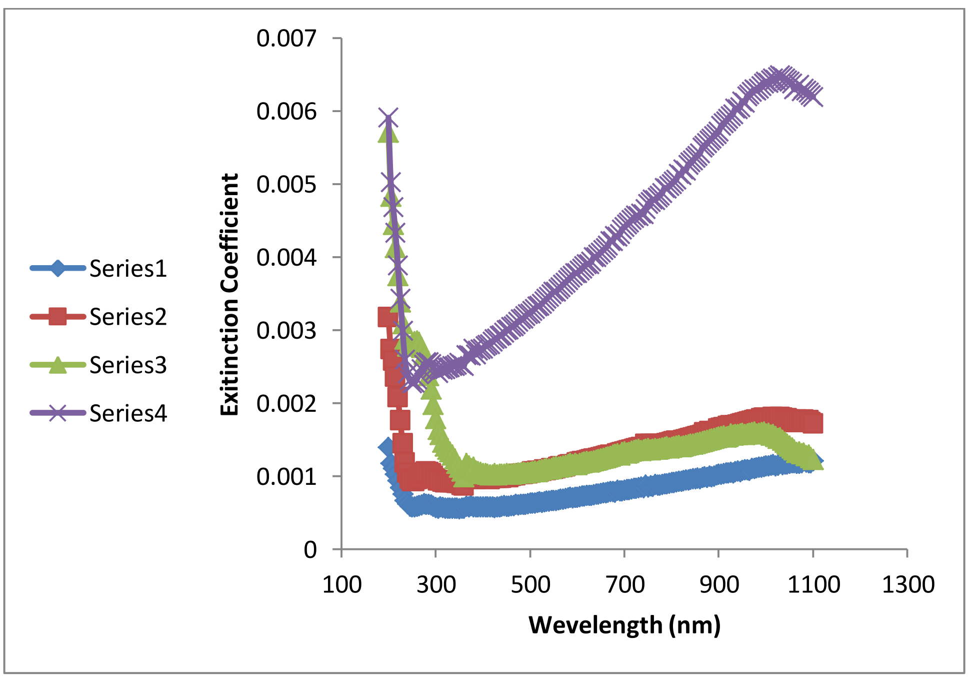

Fig. (5) Extinction coefficient versus wavelength for as deposited films.

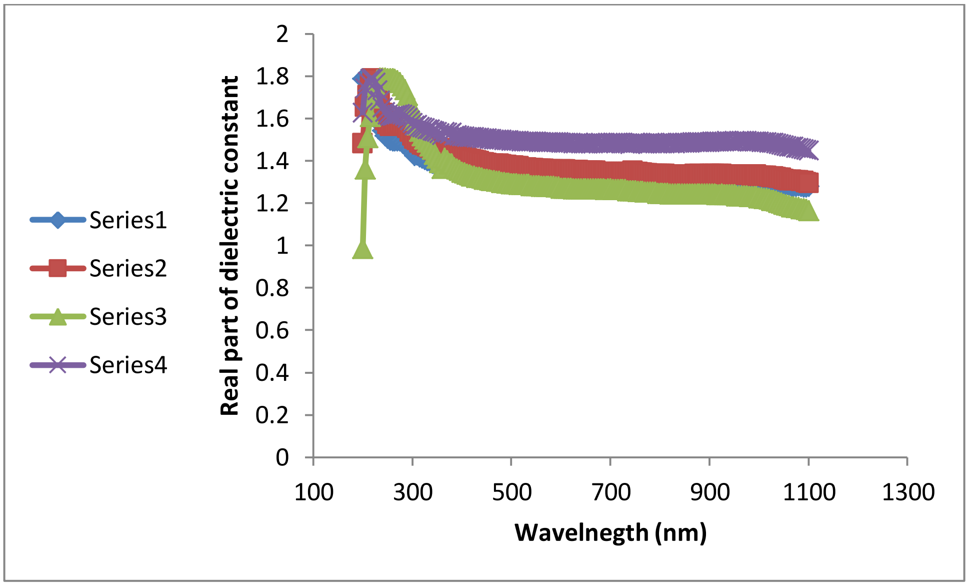

Fig. (6) Real part of Dielectric Constant of PVA films versus wavelength for different thickness films.

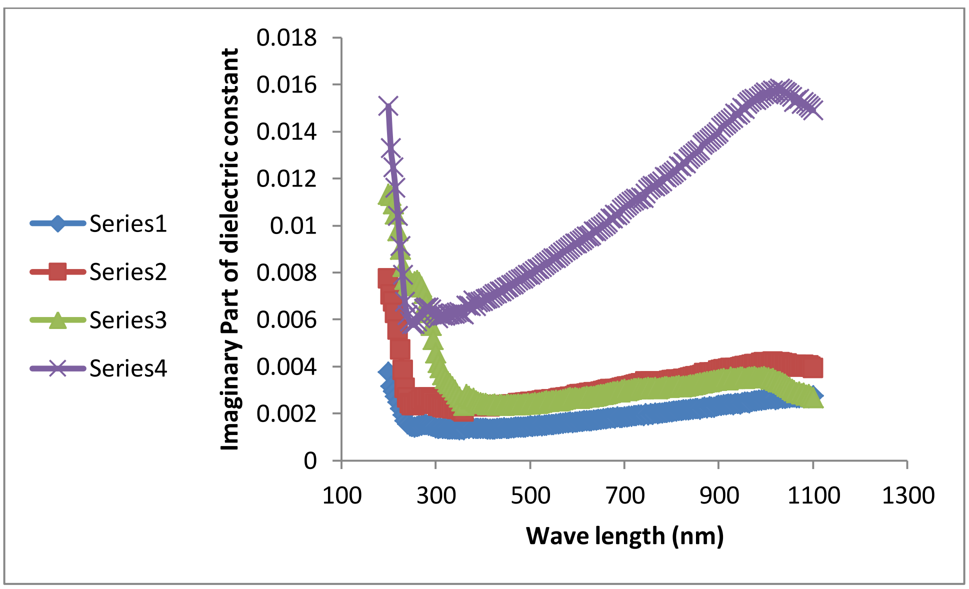

Fig.(7) Imaginary part Dielectric constant of PVA versus wavelength for different thickness films.

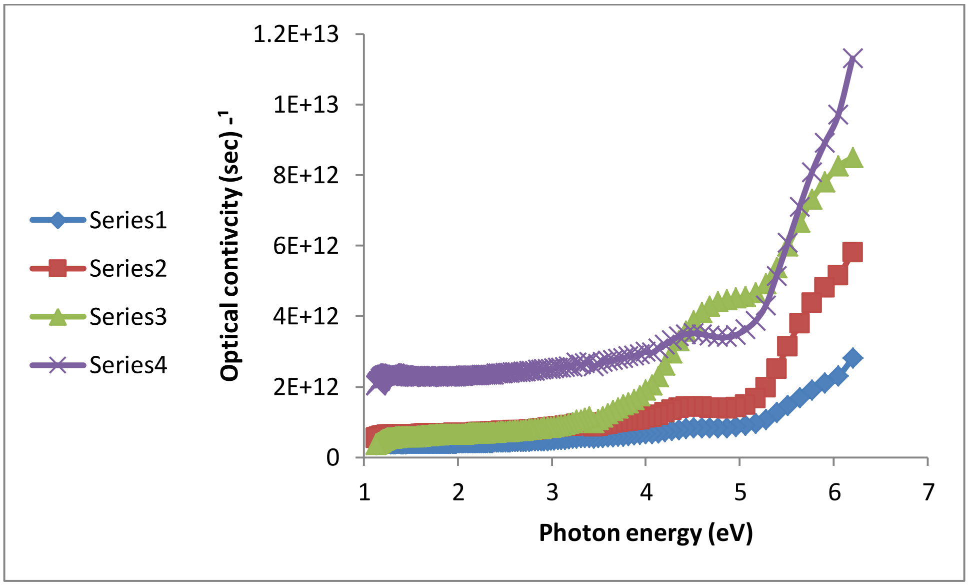

Fig.(8)Optical Conductivity of PVA versus Photon energy for different thickness films.

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