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Study Of Optical Properties Of (PEO-PEG) Blends

دراسة الخصائص البصرية لمزيج من بوليمري بولي اثيلين اوكسايد وبولي اثيلين كلايكول (PEO-PEG)

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Abstract

The study it includes the recording of the spectrum of absorbance and transmittance for (PEO) solutions and the blend solution (PEO – PEG) , at the temperature (30 ºC). and calculating the absorption coefficient and other optical constants. These samples have been prepared in different weight concentrations (0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8 g/mL) % as solution for (PEO),then the additives added as (0.25 g) and (0.5 g) of (PEG)respectively, also samples prepared by liquids mixing method before and after adding (PEG) polymer. Optical properties such as (absorbance and refractive index) have been measured, then from those properties other properties were calculated such as (transmittance, reflectance, absorption coefficient of electromagnetic waves, natural lifetime, coefficient of fineness, molar reflectance, critical angle and Brewster angle). All those properties have been measured for two cases before and after addition at temperature (30 ºC).

the values of absorbance increase when concentration increase , the refractive index values of pure polymer and its additives are increasing with the increase of the concentrations of these polymer , Noting that the increment of absorption coefficient values under the influence of addition caused by increasing density of the solutions as a result of the increased concentrations, that led to the increase of light absorbed because the interaction of the electromagnetic wave and the large molecules of the polymer increases with concentration, Since the natural lifetime is inversely proportional to the absorption coefficient , so lifetime decreases under the influence of adding (PEG) polymer , The results show that decreasing in the values of transmittance with all concentrations , It's a clear from Figure below the values of reflectance are increases with increasing concentration before and after the addition , the results showed increase the values of molar reflectance after the addition of (PEG) derivative polymer, This Figures shows that the coefficient of the finesse of basic polymer and its blend has the same behavior to their reflectance, the Brewster angle shown to have the same behavior of refractive index. the critical angle values of PEO and its polymeric blend decrease with the increase of the concentration.

Keywords: (PEO),(PEO- PEG) , optical properties

الخلاصة

هذه الدراسة تتضمن تسجيل طيف الامتصاصية والنفاذية لمزيج من محلول (PEO) والمحلول المضاف (PEO - PEG) عند درجة حرارة (30 درجة مئوية). وتم حساب معامل الامتصاص والثوابت البصرية الأخرى. تم إعداد هذه العينات لعدة تراكيز مختلفة (0,1 -0,2 - 0,3 - 0,4 -0,5 -0,6 - 0,7 - 0,8غم / مل) ٪ من بوليمر (PEO) كمحلول ثم إضافة بوليمر (PEG) بتراكيز (0.25 غم) و (0.5 غم) على التوالي، وأيضا العينات عدت بطريقة مزج السوائل قبل وبعد إضافة بوليمر (PEG) وقد تم قياس الخصائص البصرية مثل (الامتصاصية ومعامل الانكسار)، ثم من هذه الخصائص تم حساب الخصائص الأخرى مثل (النفاذية ، الانعكاسية ، معامل امتصاص الموجات الكهرومغناطيسية ، العمر الزمني الطبيعي، معامل الرقة ، الانعكاس المولاري ، الزاوية الحرجة وزاوية بروستر). وقد تم قياس كل هذه الخصائص لحالتين قبل وبعد الإضافة في درجة حرارة (30 درجة مئوية) . إن قيم الامتصاصية تزداد عند زيادة التركيز كذلك قيم معامل الانكسار للبوليمر النقي والمواد المضافة لها تتزايد مع زيادة تركيز البوليمر، ونلاحظ زيادة في قيم معامل الامتصاص تحت تأثير الإضافة الناجمة عن زيادة كثافة المحلول نتيجة لزيادة التركيز، والتي أدت إلى زيادة امتصاص الضوء لأن التفاعل بين الموجات الكهرومغناطيسية والجزيئات الكبيرة يزداد مع زيادة التركيز ،كذلك العمر الزمني الطبيعي يتناسب عكسيا مع معامل الامتصاص، لذلك يقل العمر

الزمني الطبيعي تحت تأثير إضافة بوليمر (PEG) ، وأظهرت النتائج انخفاض قيم النفاذية لجميع التراكيز، يبدو واضحا من الأشكال أدناه إن قيم الانعكاسية تزداد مع زيادة التركيز قبل وبعد إضافة بوليمر (PEG) ، وأظهرت الأشكال بان معامل الرقة للبوليمر الأساس والمزيج تسلك نفس سلوك الانعكاسية وان سلوك زاوية بروستر نفس سلوك معامل الانكسار.وان قيم الزاوية الحرجة لبوليمر (PEO) والبوليمرات المضافة تقل مع زيادة التركيز.

1. Introduction

Studies on optical properties of polymer have widely applications in electronic devices and optical devices like solar cells, fuel cells, solid state batteries. and also exhibits promising medical technological applications .[1] Ion-conducting solid polymer electrolytes are arguably the most attractive materials today because of their potential applications in various electrochemical devices, such as dye-sensitized solar cells, super capacitors, rechargeable batteries, sensors, etc. [2] In recent years, the electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarization properties . The optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix.[3]

2. Experimental

2-1 Materials and Method

The materials used in this study divided into basic (PEO) and its additive (PEG) and the (PEO- PEG) blends were prepared by liquids mixing method ,the appropriate concentrations of blends were (0.1 ,0.2 ,0.3 ,0.4 ,0.5 ,0.6 ,0.7 ,0.8 g/mL) % are dissolved in (250 mL of Dimethylformamide (DMF) under stirring with heat 30C °for 120 min).

2-2 Optical meter

The absorbance and transmittance for solutions were measured by using a device measuring the spectrum, made by (Shemadzo) company, Japan, type (Double-Beam Spectrophotometer (UV-1800)) Where the range of wavelengths is (190-1100) nm. A computer programmer make scanned for all wavelengths and gave the value of wavelength that occurs in it a greatest absorption.

Refractive index was measured by using digital refractometer, type (Abbe-13743), made by (ZEISS) company as where this device measures the refractive index of solutions at the ranges between (1.3–1.7). The device has been calibrated to take measurements with distilled water and compared with Tables and the percentage error in the device was (± 0.001).

2.3 Theoretical calculations

2-3-1 Absorbance

Absorbance defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o) [4].

$$A = I_A / I_o \quad \text{.........................(1)}$$

The optical absorbance coefficient (α_{op}) of solution and film is given by the equation [5]:

$$\alpha_{op}=2.303A/d \quad \text{............ (2)}$$

Where (d) represent a thickness of sample.

The ratio (I / I_o) called (Transmittance), (T_r) connected with absorbance by equation [6]:

$$T_r = e^{-2.303A} \quad \text{................................. (3)}$$

2-3-2 Nature Lifetime (T_L)

The nature lifetime of the excited states can be determine by using expression [7,8]:

$$T_L = \frac{10^{-4}}{\alpha_{op}(max)} \quad \text{.......................... (4)}$$

Where ($\alpha_{op}(max)$) is optical absorption coefficient of electromagnetic waves. In the near (UV) region.

2-3-3 Refractive Index (n)

The refractive index can be given by the equation [9]:

$$n = \frac{c}{\nu} \quad \text{........................ (5)}$$

Where defined as a ratio between the speed of light in a vacuum (c), to the speed of light in a medium (ν) .

The values of refractive index were measured practically then applied in equation depending on the reflectance and the extinction coefficient (K_n) as shown in the following equations [10,11]:

$$R = \frac{(n-1)^2 + K_{n2}}{(n+1)^2 + K_{n2}} \quad \text{......................................(6)}$$

If the extinction coefficient equal zero, then the equation (6) will be:

$$R = \frac{(n-1)^2 + 0}{(n+1)^2 + 0} \quad \text{.......................................(7)}$$

$$\sqrt{R}\; n + \sqrt{R} = n - 1 \quad \text{..............................(8)}$$

$$1 + \sqrt{R} = n\;(1 - \sqrt{R}) \quad \text{..............................(9)}$$

Then, refractive index will become:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad \text{...................................(10)}$$

2-3-4 Reflectance (R)

The reflectance can be represented depending on the value of refractive index by the equation [12]:

$$R = \left[\frac{n-1}{n+1}\right]^2 \quad \text{.............................. (11)}$$

Reflectance also can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [11]:

$$R + T + A = 1 \quad \text{..(12)}$$

When light radiation passes from one medium into another having a different index of refraction, some of the light is scattered at the interface between the two media even if both are transparent

Since the index of refraction of air is very nearly unity. Thus, higher index of refraction of the solid, greater is the reflectivity. For typical silicate glasses, the reflectivity is approximately (0.05). Just as the index of refraction of a solid depends on the wavelength of the incident light, so the reflectivity varies with wavelength. Reflection losses for lenses and other optical instruments are minimized significantly by coating the reflecting surface with very thin layers of dielectric materials such as magnesium fluoride (MgF_2) [12].

2-3-5 Molar Reflectance (R_m)

Molar Reflectance can be represented by equation [13]:

$$R_m = \frac{n^2-1}{n^2+1}\frac{M_v}{\rho} \qquad \text{……….………….………} (13)$$

It's a relation between the molecular weight and density of the material. Its measured by (m^3 / mole) unit . So can be defined as the multiplication relation between the specific reflectance and molecular weight.

2-3-6 Extinction Coefficient (K_n)

Extinction coefficient (K_n) given by following equation [14]:

$$K_n = \alpha_{op} \lambda / 4\pi \qquad \text{.. …..…..………………..….}(14)$$

Where (λ) is the wavelength of incident photon.

It represents the imaginary part of complex refractive index (n^*):

The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in a material, where it values depend on the density of free electrons in the material and also on the structure nature [14]:

$$n^* = n - i K_n \qquad \text{……. ……….…………...…….. .}(15)$$

Where:

n : the real part of refractive index.

n*: complex refractive index which depends on the material type, crystal structure (particle size), crystal defects and stress in the crystal.

2-3-7 Coefficient of Finesse (F)

Coefficient of Finesse can be represented by equation [8]:

$$F = \frac{4R}{(1-R)^2} \qquad \text{…..…………….………....…} (16)$$

It is a measure of the sharpness of the interference fringes

2-3-8 Critical Angle (θ_c)

Critical Angle can be represented by equation [61]:

$$\theta_c = \mathrm{Sin}^{-1}(1/n) \qquad \text{……………..…..} (17)$$

Which is defined as the angle of incidence which provides an angle of refraction of (90-degree) .

2-3-9 Brewster Angle (θ_B)

The refractive index can be represented by equation [15] :

$$\frac{\text{Sin }\theta}{\text{Sin }\varphi} = n \qquad \text{......... .... (18)}$$

Because the rotaiontial angle is (90^o) therefore we get :

$$\text{Sin }\varphi = \text{Cos }\theta$$

$$\frac{\text{Sin }\theta}{\text{Sin }\varphi} = \frac{\text{Sin }\theta}{\text{Cos }\theta} = n \qquad \text{...................... (19)}$$

$$n = \tan\theta \qquad \text{........................... (20)}$$

$$\theta_B = \tan^{-1}(n) \qquad \text{................................ (21)}$$

Where θ_B Brewster Angle

Brewster's angle (also known as the polarization angle) is an angle of incidence at which light with a particular polarization is perfectly transmitted through a transparent dielectric surface. When a polarized light is incident at this angle, the light that is reflected from the surface and therefore perfectly polarized. This special angle of incidence is named by Scottish physicist Sir David Brewster (1781–1868) .

3. Results and Discussion:

3.1 Optical Properties:

3-1-1 Absorbance Spectrum

Absorbance measurements of (PEO) before and after adding (PEG) polymers were plotted against different wavelengths in the range between (290-340) nm , as shown in figure (1). This figure shows that the absorbance of pure polymer and its additive are increasing with the increase of the concentrations of these polymers .

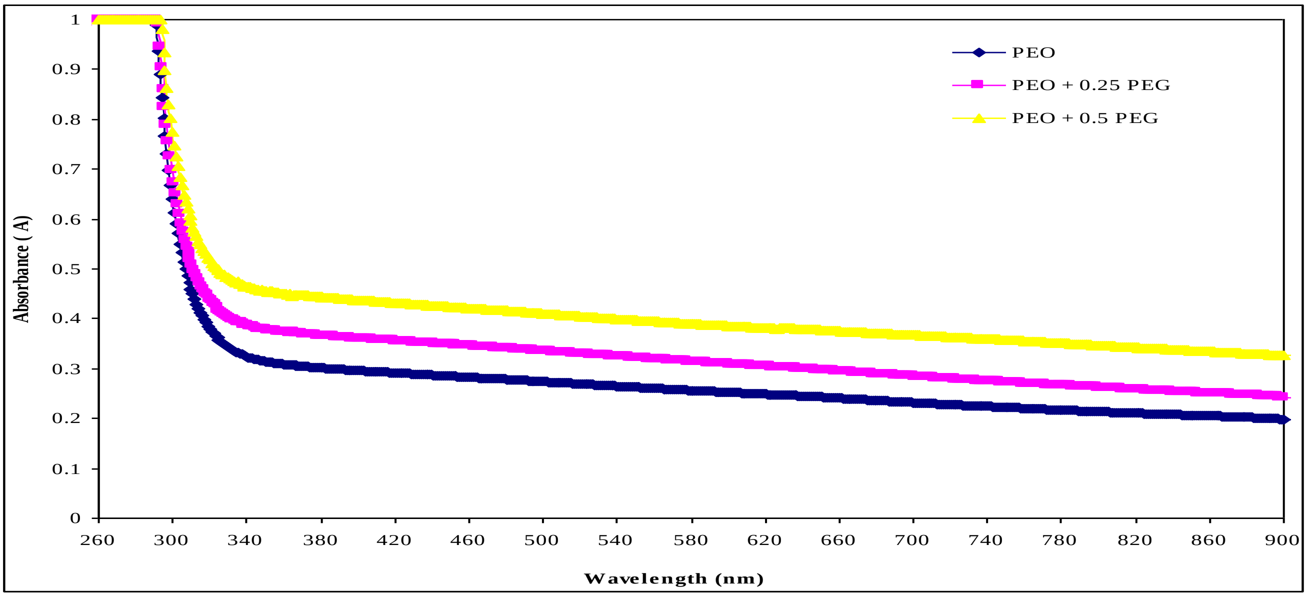

Figure (1): Absorbance VS different wavelengths for (PEO + PEG).

Figures (1) represent the relation between the absorbance of pure polymer and its blend with (PEG) additives polymer against various concentrations. We can note from this figures, the values of absorbance increase when concentration increase because the absorbance is directly proportional with concentration according to the Lambert-Beer law. Furthermore the values of absorbance increase after the addition of (PEG) polymer , this is because the addition led to increase the values of concentration in same volume, then increase the number of particles that absorb the energy of incident light according to the Lambert-Beer law. this is agreement with [16,17] .
Fig. (2) represent the absorbance vs molar concentrations of PEO before and after adding (PEG)

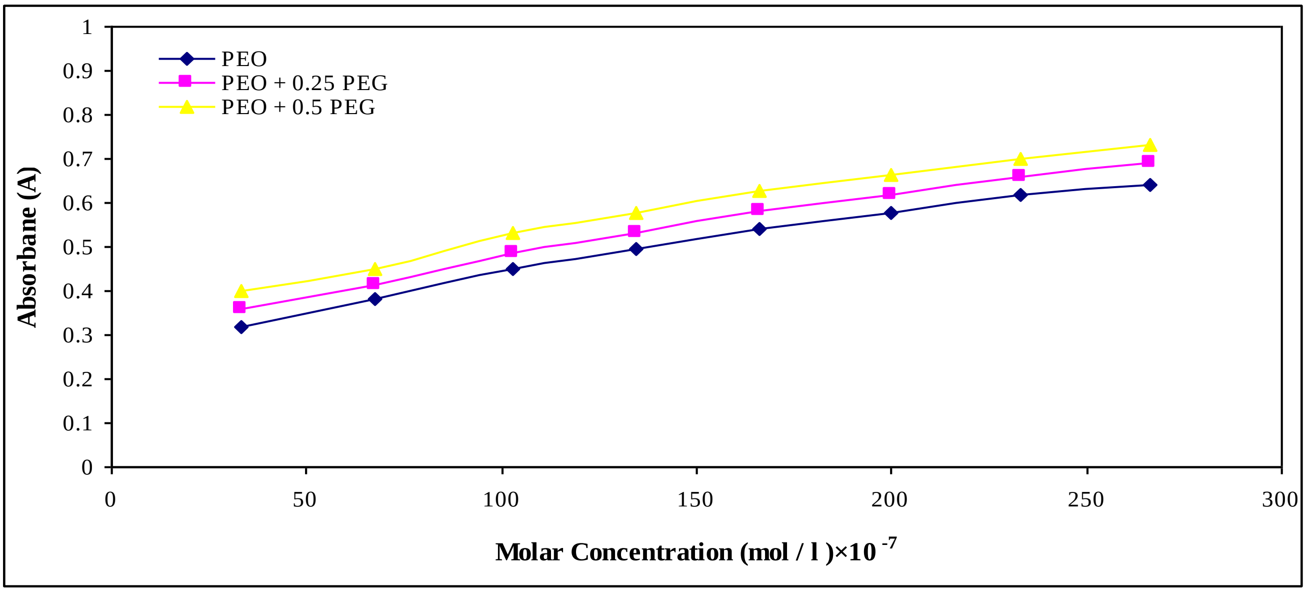

Fig. (2): Absorbance vs molar concentrations of PEO before and after adding (PEG)

3-1-2 Refractive Index

The measured values of refractive index of (PEO) before and after adding (PEG) polymer are shown in figure (3). This figure shows that the refractive index values of pure polymer and its additive are increasing linearly with the increase of the concentrations of these polymer. This increment with concentrations are clearly satisfied, because refractive index is a function of density, since the density increase uniformly by increasing concentrations, the refractive index of these polymer blends also have uniformly increment. this is agreement with [16,18,19] .

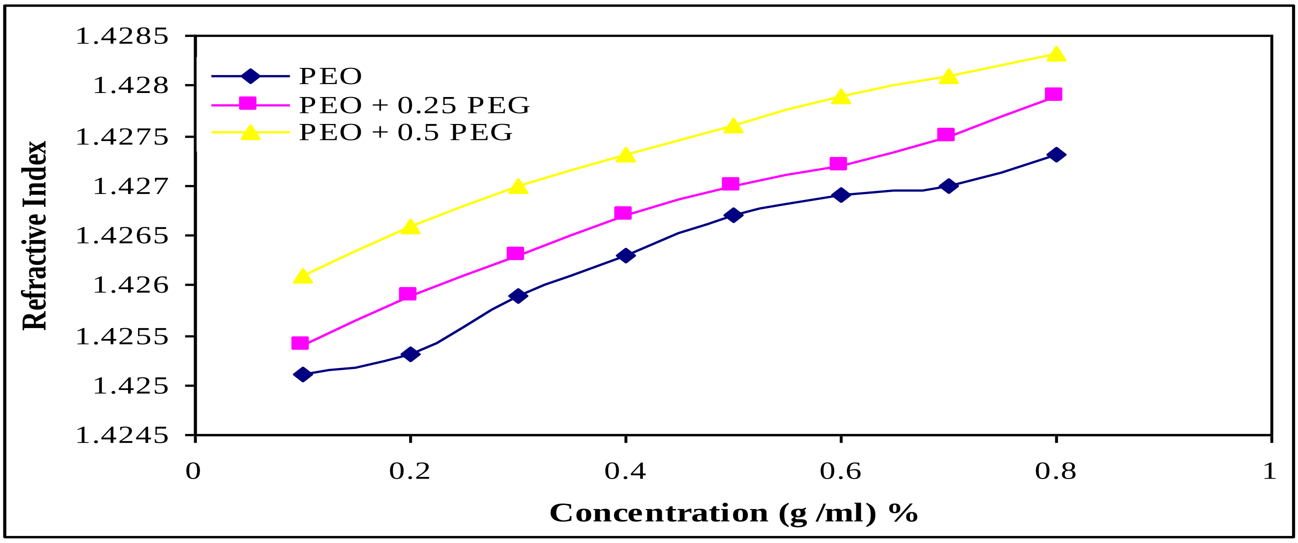

Fig. (3): Refractive index vs concentrations of PEO before and after adding (PEG)

3-2 Optical Calculations

From optical measurements, we can calculate other optical parameters as:

3-2-1 Absorption Coefficient of Electromagnetic Waves

The values of the absorption coefficient of light are obtained by creating a slope of a straight line between absorbance and molar concentration which refers to the values of the absorption coefficient as in table (1) illustrates the change in the values of the absorption coefficient for polymer solution of (PEO) before and after the addition of (PEG) polymer. Noting that the increment of absorption coefficient values under the influence of addition caused by increasing density of the solutions as a result of the increased concentrations, that led to the increase of light absorbed because the interaction of the electromagnetic wave and the large molecules of the polymer increases with concentration, according to the law of Lambert- Bear and thus increase the absorption coefficient. Table (1) shows that (PEO) polymer blend has higher value of absorption coefficient . this is agreement with [16,19] .

Table (1): Absorption coefficient of PEO and its additives.

Type of Polymer	Absorption Coefficient[α_{op}] (lit/mole.cm)
PEO	1.39×10^4
PEO + 0.25 PEG	1.43×10^4
PEO + 0.5 PEG	1.45×10^4

3-2-2 Natural Lifetime

In the near ultraviolet region the values of natural lifetime of (PEO) before and after adding (PEG) polymer, that causes excitation in the ultraviolet spectrum was obtained by using equation (4). Since the natural lifetime is inversely proportional to the absorption coefficient, so lifetime decreases under the influence of adding (PEG) polymer and this is illustrated in table (2). this is agreement with [19] .

Table (2): Natural lifetime of PEO and its additives.

Polymer Type	Natural Lifetime (s)
PEO	0.72×10^{-8}
PEO + 0.25 PEG	0.7×10^{-8}
PEO + 0.5 PEG	0.69×10^{-8}

3-2-3 Transmittance Spectrum

The values of transmittance of all concentrations of (PEO) before and after adding (PEG) polymer were calculated approximately by using equation (3). The results show that decreasing in the values of transmittance with all concentrations, this is because the values of absorbance is directly proportional to concentration and there are logarithmic relation between absorbance and transmittance.

Figure (4) shows that transmittance decrease with the increase of the added concentration, this is caused by added (PEG) polymer contains electrons in it is outer orbits can be absorb the electromagnetic energy of the incident light and transfer to higher energy levels, this process is not accompanied by emission of radiation because the traveled electron to higher levels have occupied vacant positions of energy bands, thus part of the incident light is absorbed by the substance and dose not penetrate through it. this is agreement with [19] .

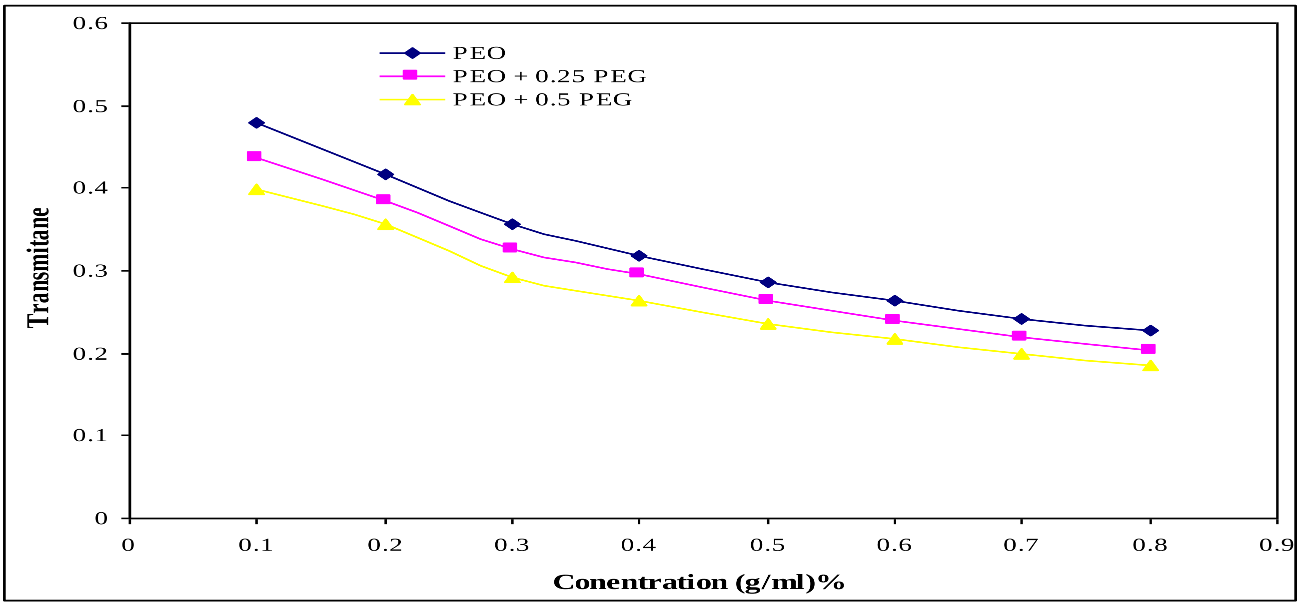

Fig. (4): Transmittance vs concentrations of PEO before and after adding (PEG)

3-2-4 Reflectance Spectrum

Reflectance of all samples was computed by using equation (11). The results of reflectance were plotted in the figure (5). It shows to have the same behavior of their refractive index, because reflectance equation has only one variable parameter, which is a refractive index. The uniformly increment of reflectance of (PEO) before and after adding (PEG) polymer. It's a clear from figure below the values of reflectance are increases with increasing concentration before and after the addition, the reason is due to increase the density of the solution as the reflectance is entirely dependent on density ,this is agreement with [19] .

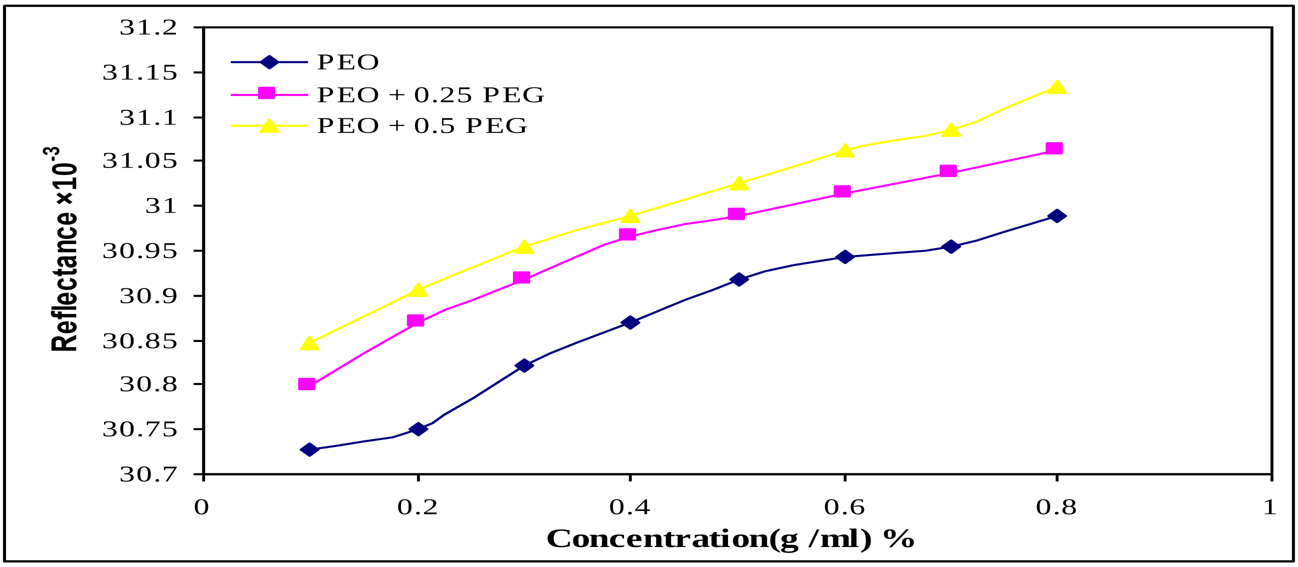

Fig. (5): Reflectance vs concentrations of PEO before and after adding (PEG)

3-2-5 Molar Reflectance

Molar reflectance values were calculated by using equation (13), the results showed increase the values of molar reflectance after the addition of (PEG) polymer, the reason is due to increase the values of viscosity average molecular weight under the influence of adding, because molar reflectance entirely depended on molecular weight and this is agreement with [19] .

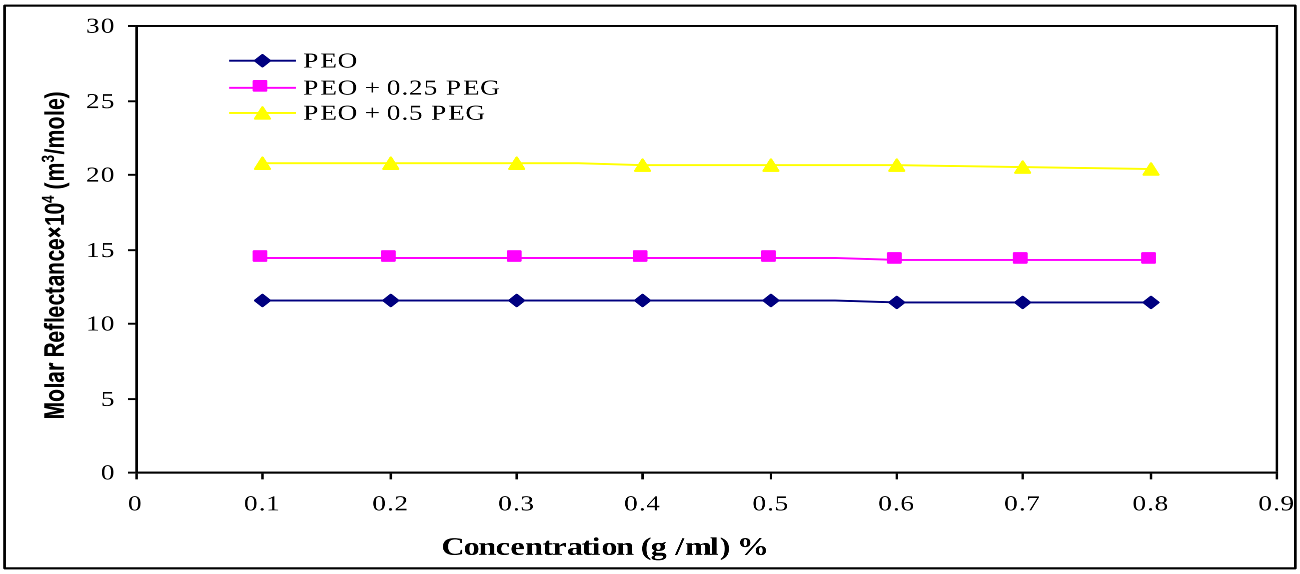

Fig. (6): Molar reflectance vs concentrations of PEO before and after adding (PEG)

3-2-6 Coefficient of Finesse

The coefficients of the finesse of (PEO) before and after adding (PEG) polymer were calculated by using equation (16), as shown in figures (7). This figures shows that the coefficient of the finesse of basic polymer and its blends has the same behavior to their reflectance, because this coefficient depends on reflectance, from another aspect the influences of adding lead to increase the values of finesse coefficient, this is because the increasing of reflected light as a result of increasing the density after addition, and this results is agreement with [19] .

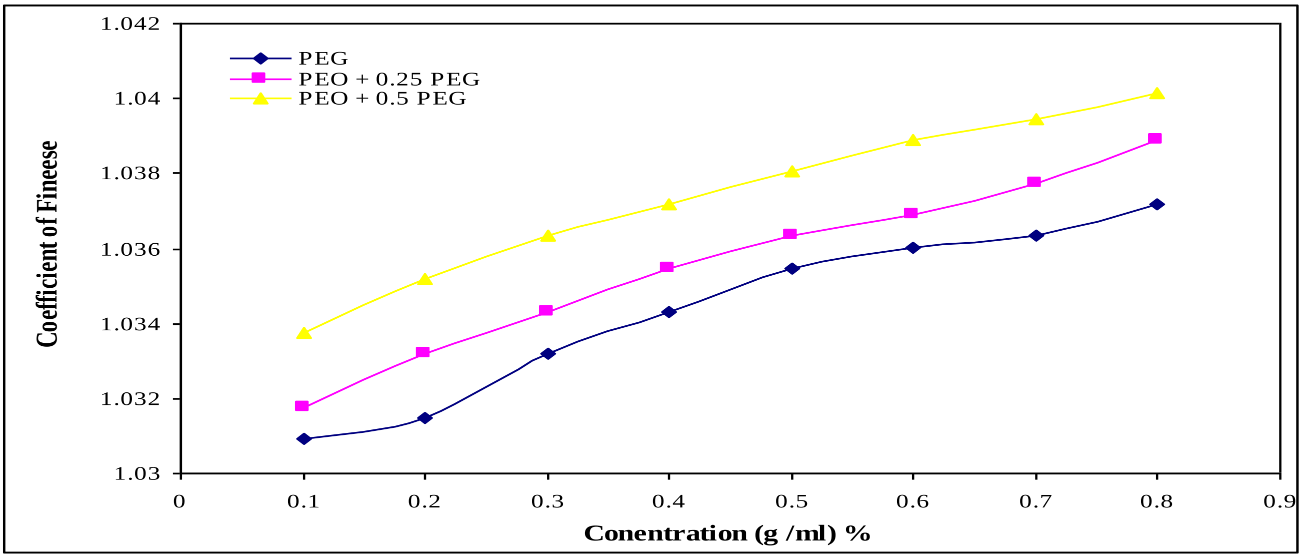

Fig. (7): coefficients of the finesse vs concentrations of PEO before and after adding (PEG)

3-2-7 Brewster and Critical Angles

The Brewster angles of (PEO)before and after adding (PEG)polymer were calculated by using equation (18), figure (8) shows that the brewster angle values for different concentration. It's a clear from the equation above that brewster angle shown to have the same behavior of refractive index.

The critical angle was calculated by using equation (17), figure (9) shows that the critical angle values of PEO and its polymeric blend decrease linearly with the increase of the concentration, because it is inversely proportional to their refractive index or it is a clear that as concentration increase, the density also increases therefore the incident rays will bend toward normal and causes critical angle to decrease and this is agreement with [19] .

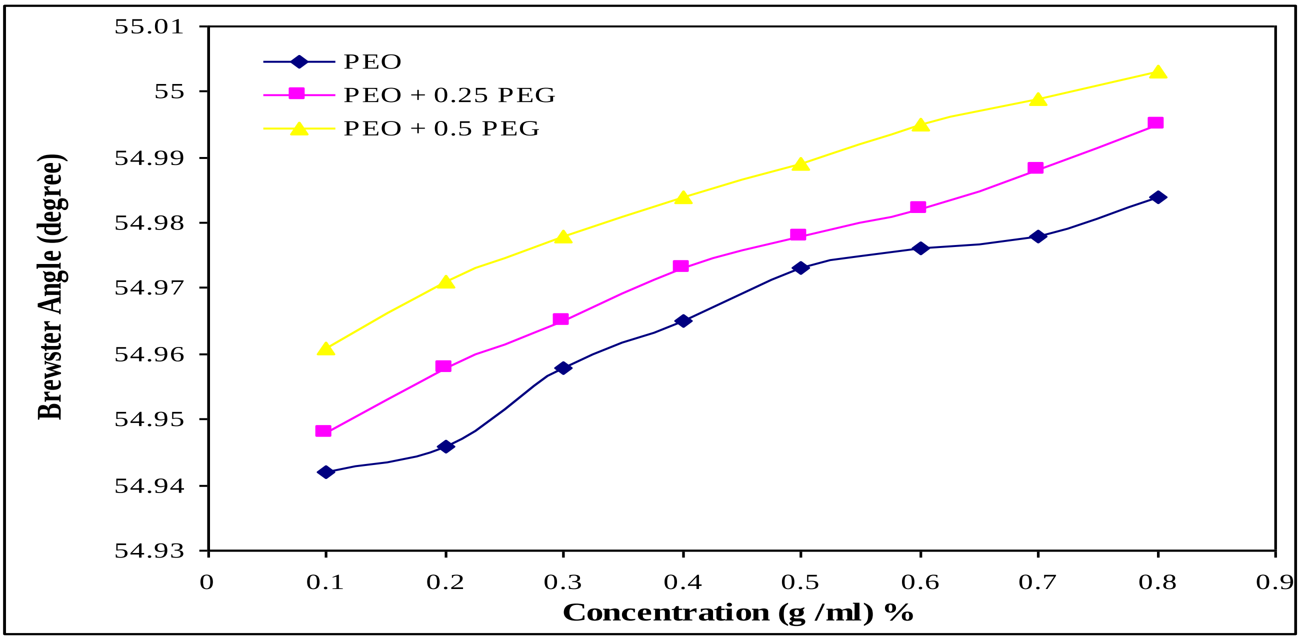

Fig. (8): Brewster angles vs concentrations of PEO before and after adding (PEG)

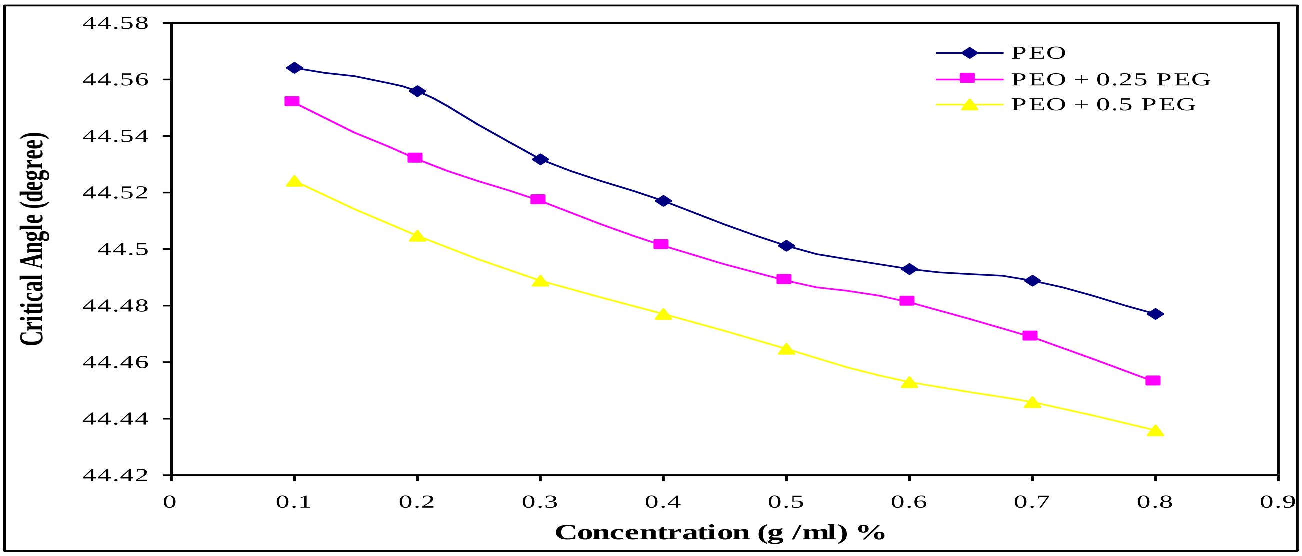

Fig. (9): critical angle vs concentrations of PEO before and after adding (PEG)

4. Conclusions

The summarized results from this work are the following:

1. It is found through the study that these polymers appear a continuous change in their physical properties (optical) as a result of adding (PEG) to (PEO) as the (PEO- PEG) led to the improvement of these properties.
2. The addition of (PEG) to (PEO) led to the improvement optical properties as increasing the all properties expect natural lifetime , transmittance spectrum and critical angle which decrease with increasing concentration .

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