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Optical and Dielectrical Properties of (PEG-CMC) Films Prepared by Drop Casting Method

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ABSTRACT

Films of PEG after and before doped by carboxymethyle cellulose CMC were deposed on glass substrates by drop casting method. The absorbance and transmittance spectra have been recorded for all the deposited films in order to study the optical constants such as, refractive index, extinction coefficient, optical conductivity, real and imaginary parts of the dielectric constant, these additives effect all the parameters under study and enhance their value especially the optical absorption. The values of absorption coefficient refer to allowed direct transition.

Keywords**:** Optical Properties; Energy Gap; PEG and CMC

1. INTRODUCTION

Polyethylene Glycol (PEG 6000) is a water-soluble and waxy solid that is used extensively in the several industries such as rubber, textile, paper, metal, wood, pharmaceutical, cosmetics and coating. PEG recognizes by many characteristic such as, highly compatible to various kinds of organic compounds, high boiling point, easy control of the degree of condensation, controllable hygroscopic property, less toxicity and less skin irritation [1].

Sodium carboxymethyl cellulose (Na-CMC) or cellulose gum is a cellulose derivative with carboxymethyl groups ($-CH_2-COOH$) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. CMC used as a lubricant in nonvolatile eye drops and artificial tears [2].

2. THEORETICAL PART

The study of the optical properties of polymers increases our knowledge of the type of polymer internal structure, nature of the bonds and expands the potential scope of polymer application. Polymers provide remarkable advantages in optical applications over common inorganic glasses, especially with respect to their light weight, impact and shatter resistance [3,4].

2. 1. Absorbance

Absorbance defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o) [5].

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

The light absorbance coefficient (α_{op}) and films absorption coefficient are given by the equation [6]:

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

where (d) represent a thickness of film.

The ratio (I / I_o) called (Transmittance) (T_r) , so can be defined as the ratio of the intensity of the transmitting rays (I) through the film to the intensity of the incident rays (I_o) on it as follows , and connected by absorbance as [7]:

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

2. 2. Nature Lifetime (T_L)

In the near – UV regions, the following expression can be used for estimating the nature life time of the excited states [8,9]:

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

where $\alpha_{op}(\max)$ is optical absorption coefficient of electromagnetic waves.

2. 3. Refractive Index (n)

The refractive index can be defined as a ratio between the speed of light in vacuum (c), to its speed of light in medium (v) and given by the relation [10]:

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

The value of refractive index was calculated by using equation depending on the reflectance and extinction coefficient (K) as in the following equation [11,12].

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

If extinction coefficient (K) equal to zero, then 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. 4. Reflectance (R)

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 .The reflectance can be represented depending on the value of refractive index by the relation [13]:

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

Reflectance also can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [14]:

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

Since the index of refraction of air is very nearly unity .Thus, the higher the index of refraction of the solid, the greater is the reflectivity. For typical silicate glasses, the reflectivity is approximately (0.05).

2. 5. Molar Reflectance (R_m)

It's a relation between the density of material and molecular weight, and measured by (m^3 / mole) unit, and given by [15]:

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

So can be defined as the multiplication relation between the specific reflectance and molecular weight.

2. 6. Extinction Coefficient (K)

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 depends on the density of free electrons in the material and on the structure nature [16]:

$$n^* = n - iK \qquad \text{……...……...…….. .(14)}$$

where:
n : the real part of refractive index.
n*: complex refractive index which it depends on the material type, crystal structure (grain size), crystal defects, stress in crystal and extinction coefficient, so given by following equation [17]:

$$K = \alpha_{op} \lambda / 4\pi \qquad \text{………………..….(15)}$$

where λ is the wavelength of incident photon rays.

2. 7. Coefficient of Finesse (F)

It is a measure of the sharpness of the interference fringes, and defined as follows [18]:

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

2. 8. Critical Angle (θ_c)

The critical angle is defined as the angle of incidence which provides an angle of refraction of (90-degrees) , and given by following equation [19]:

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

2. 9. Brewster Aangle (θ_B)

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, with no reflection. When un polarized light is incident at this angle, the light that is reflected from the surface is therefore perfectly polarized. This special angle of incidence is named after the Scottish physicist Sir David Brewster (1781–1868), and given by follow equation [20]:

$$\theta_B = \tan^{-1}(n) \quad (18)$$

2. 10. The Electronic Transitions

The electronic transitions can be classified into two types:

1. Direct Transition

This transition happens in semiconductors when the bottom of (C.B.) be exactly over the top of (V.B.), which means they have the same value of wave vector i.e. ($\Delta K = 0$) in this state the absorption appeared when ($h\upsilon = E_g^{opt.}$) in this transition type required of the Law's conservation in energy and momentum. These direct transitions have two types [21]:

a. Direct allowed transition:

This transition happens between the top points in the (V.B.) to the bottom point in the (C.B.).

b. Direct forbidden transitions:

This transition happens between near top points of (V.B.) and bottom points of (C.B.), The absorption coefficient for this transitions type given by [21]:

$$\alpha h\upsilon = B\,(h\upsilon - E_g^{opt.})^r \quad \text{............ (19)}$$

where: E_g: energy gap between direct transition, B: constant depended on type of material, υ: frequency of incident photon, r: exponential constant, its value depended on type of transition, ($r = 1/2$) for the allowed direct transition and ($r = 3/2$) for the forbidden direct transition.

2. Indirect Transitions

In these transitions type, the bottom of (C.B.) is not over the top of (V.B.), in curve (E-K), the electron transits from (V.B.) to (C.B.) not perpendicularly where the value of the wave vector of electron is not equally before and after transition of electron. ($\Delta K \neq 0$), this transition type happens with helpful of particle is called "Phonon", for conservation of the energy and momentum law. There are two types of indirect transitions [21]:

a. Allowed indirect transitions:

These transitions happened between the top of (V.B.) and the bottom of (C.B.) which is found in different region of (K-space).

b. Forbidden indirect transitions:

These transitions happened between near points in the top of (V.B.) and near points in the bottom of (C.B.), the absorption coefficient for transition with a phonon absorption is given by [21]:

$$\alpha h\upsilon = B\,(h\upsilon - E_g^{\,opt.} \pm E_{ph.})^r \qquad \ldots\ldots\ldots\ldots\ldots \quad (20)$$

where E_g: energy gap for indirect transitions, $E_{ph.}$: energy of phonon, is (+) when phonon absorption and (-) when phonon emission, (r = 2) for the allowed indirect transition and (r = 3) for the forbidden indirect transition.

3. EXPERIMENTAL PART

3. 1. Optical Measurements

The main purpose of studying the optical properties of the PEG (Mw. 6000 Dalton) films after and before adding CMC (Mw.800000 Dalton) polymer as blends is to identify the effect of adding this material on the optical properties of PEG. The research covers the recording of the spectrum of absorbance and transmittance for the PEG films at the room temperature and calculating the absorption coefficient, extinction coefficient and other optical constants.

3. 2. Absorbance

Figure (1) displays the optical absorption spectrum of (PEG-CMC) blend films as a function of the wavelength of concentration (0.8 g/mL)% over the spectral range of (200-1100) nm. From the Figure we can be shown that absorbance for all films have a high values at wavelength between (200-210) nm, the absorbance decreases with the increasing of wavelength. Adding CMC to PEG leads to increase the intensity of the peak. The increase of absorbance with the increase of CMC concentration can be explained by the fact CMC absorbed the incident light on them, in other words ions absorb the incident light by the free electrons [22].

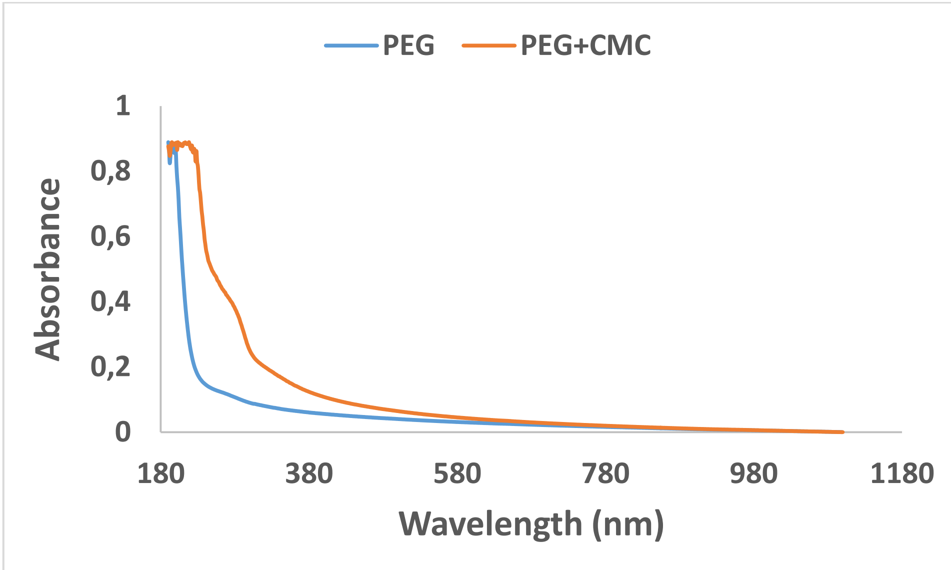

Fig. 1. The absorbance vs wavelength for PEG and (PEG-CMC) films.

3. 3. Transmittance

Figure (2) represent the optical transmittance spectra for all PEG and (PEG-CMC) films before and after adding different weights of CMC with film thicknesses. From the plots it can be noticed that the transmittance values increases with the increasing of the wavelength due to the decrease in absorbance values because the transmittance is inversely proportional with absorbance, also Figure shows that pure PEG polymer has greater transmittance than (PEG-CMC) films [23].

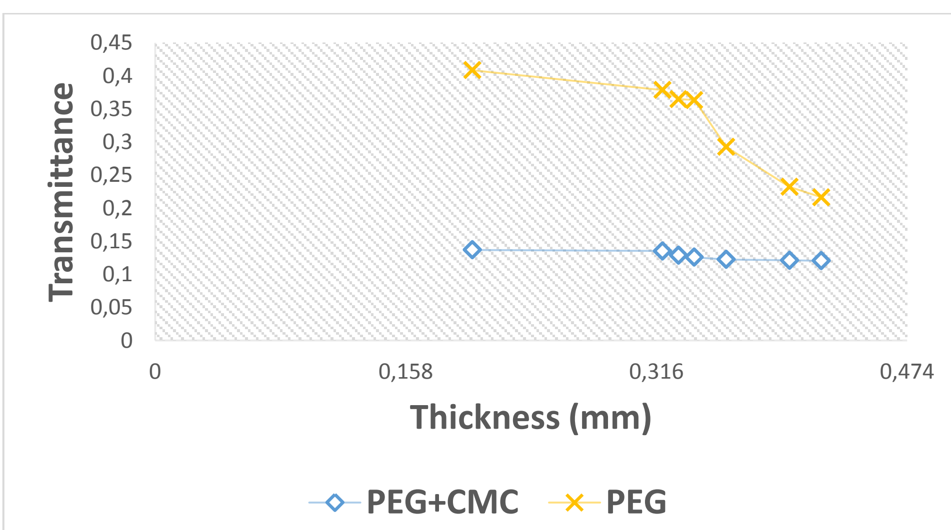

Fig. 2. The transmittance vs thicknesses for PEG and (PEG-CMC) films.

3. 4. Reflectance

Figure (3) represent the relation between the reflectance and thiknesses of the pure (PEG) and (PEG-CMC) films, there is a little change appear in the plot, then rapid reduction will appear in the range (200-380) nm. Also Figure shows that increasing thicknesses of the additive led to increase the reflectivity because of increased the blend density and high reflectivity to be in a certain range of the ultraviolet spectrum, and decreases with the increasing of wavelength in the visible region [24].

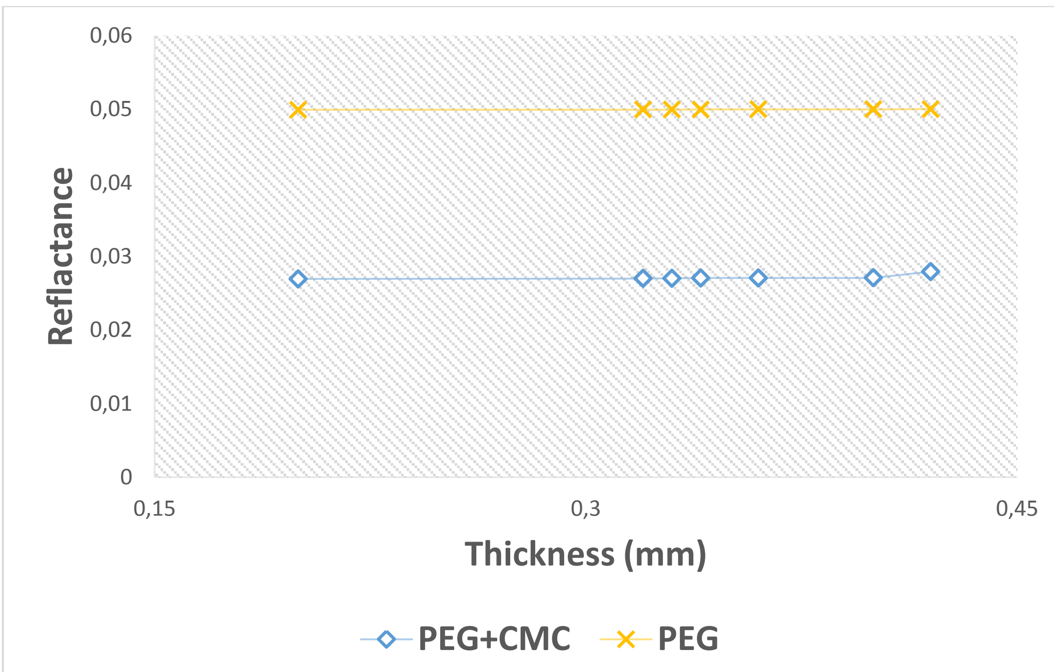

Fig. 3. Reflectance vs thicknesses for PEG and (PEG-CMC) films.

3. 5. Absorption Coefficient

Figure (4) shows the absorption coefficient as a function of photon energy for (PEG) and (PEG-CMC) films. It can be noticed that the absorption coefficient is a smallest at low energy, this means that the possibility of electron transition is little because the energy of the incident photon is not enough to move the electron from the valence band to the conduction band [25]. The value of the absorption coefficient increase with increasing the concentration of the additive whereas increase molecules that absorb incident energy and thus increases the value of the absorption coefficient. This behavior is similar to that given by [26].

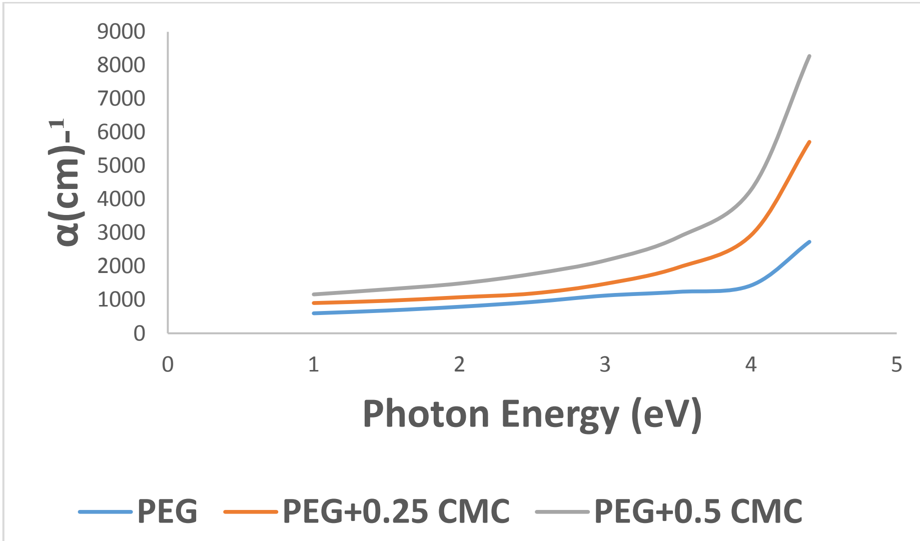

Fig. 4. Absorption coefficient vs photon energy for PEG and (PEG-CMC) films.

3. 6. Optical Energy Gap

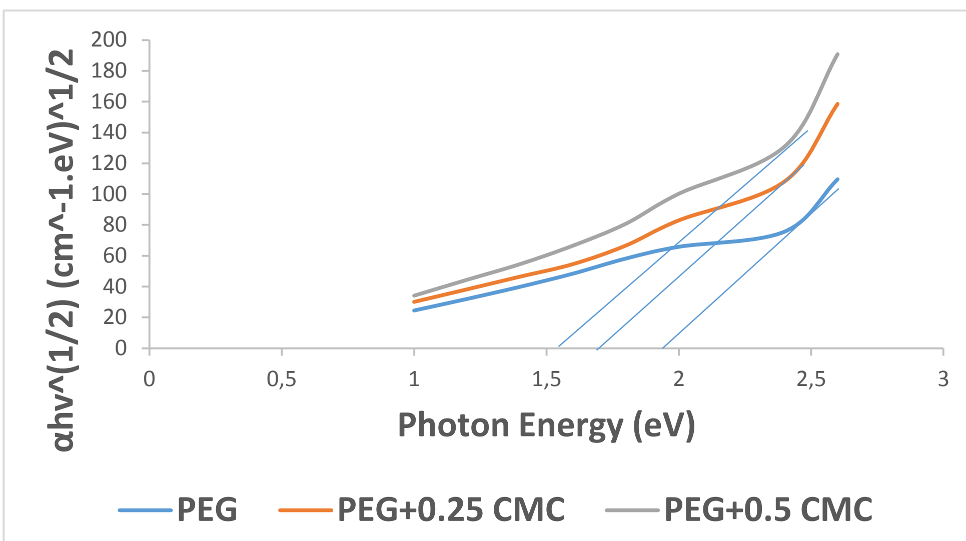

Fig. 5. Absorption coefficient vs photon energy for PEG and (PEG-CMC) films.

The experimental values of $(\alpha h\nu)^{1/2}$ plotted against (hν) of (PEG) and (PEG-CMC) blend films as shown in Figure (5). Extrapolating the straight line of the plot $(\alpha h\nu)^{1/2}$ versus (hν) for zero absorption coefficient values (α = 0) give the energy band gap value for the allowed indirect transition. It appears from Figure the values of optical energy gap decrease with the increasing of the weight percentage of the CMC added. This result attributed to the creation of onsite levels in the forbidden energy gap [27]. From Figure it can be noticed that the energy gap for pure PEG films equal to (1.95 eV), and its value after adding (0.25g) CMC equal to (1.84 eV), and for (0.5g) CMC become (1.55 eV).

3. 7. Refractive Index

Figure (6) shows that the change of refraction index for (PEG) and (PEG-CMC) films as a function of photon energy. This Figure shows that high values of the refractive index in ultraviolet region because of the high reflectance in this region, but in the visible region note that low values because of the little reflectance in this region.

We know that the refractive index depends mainly on reflectance according to the relation (11). For this reason we notice that the increasing of refractive index by increasing the concentration of CMC because the reflectance is increased, this behavior attribute to increase of the density with increase the concentration [28,29].

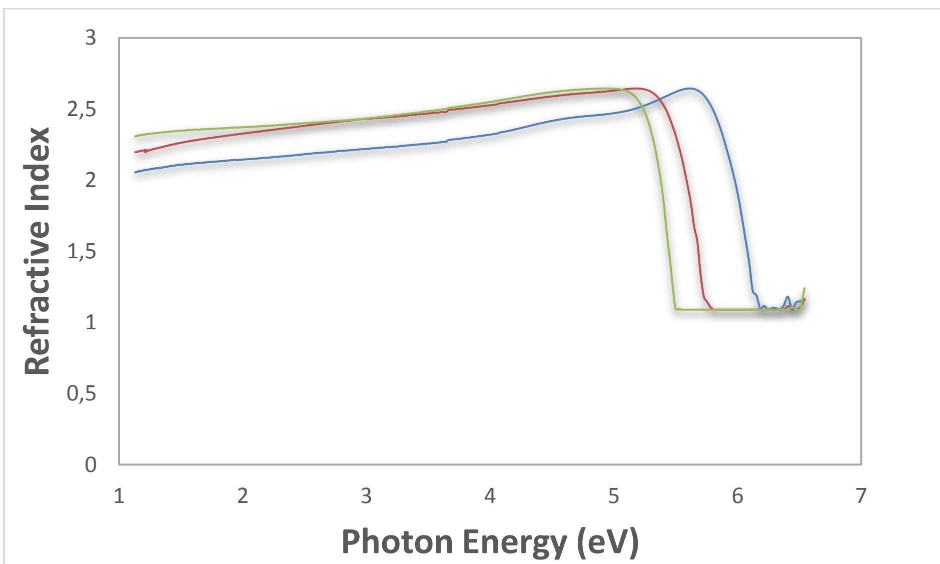

Fig. 6. Refractive vs photon energy for PEG and (PEG-CMC) films.

3. 8. Real and Imaginary Dielectric

The real and imaginary dielectric constant (ε_r, ε_i) for (PEG) and (PEG-CMC) films have been calculated from ($\varepsilon_r = n^2 - k^2$ and $\varepsilon_i = 2nk$) respectively. The Figures (7 and 8) show the change of (ε_r, ε_i) as a function of the photon energy . The real and imaginary parts of dielectric constant follow the same pattern as the refractive index and extinction coefficient respectively, and that is because the dependence of (ε_r) on refractive index and (ε_i) on the value of extinction coefficient and the value of real part are higher than the imaginary parts [30].

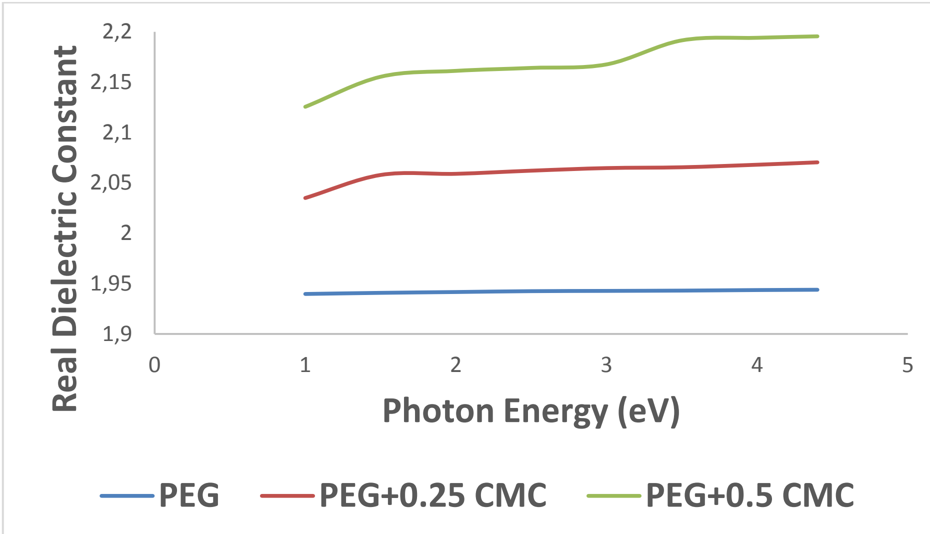

Fig. 7. Real dielectric constant vs photon energy for PEG and (PEG-CMC) films.

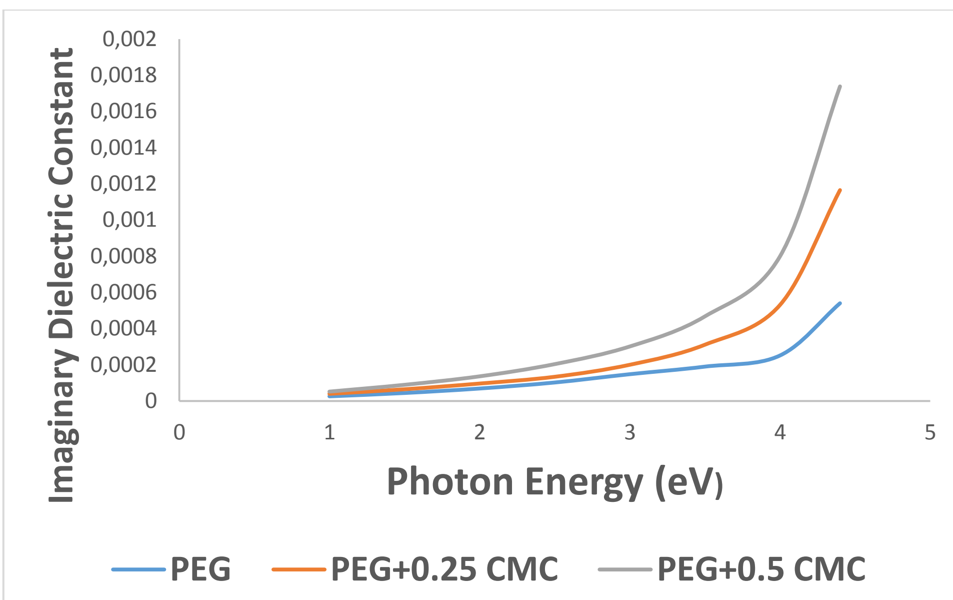

Fig. 8. Imaginary dielectric constant vs photon energy for PEG and (PEG-CMC) films.

The change of the extinction coefficient as a function of the photon energy for (PEG) and (PEG-CMC) films shown in Figure (8). It can be noticed that extinction coefficient increases with increasing the additive of the CMC, due to increased absorption coefficient because that the extinction coefficient depends mainly on absorption coefficient. The increasing of extinction coefficient at the high photon energy is due to the high absorbance of films in that region [28].

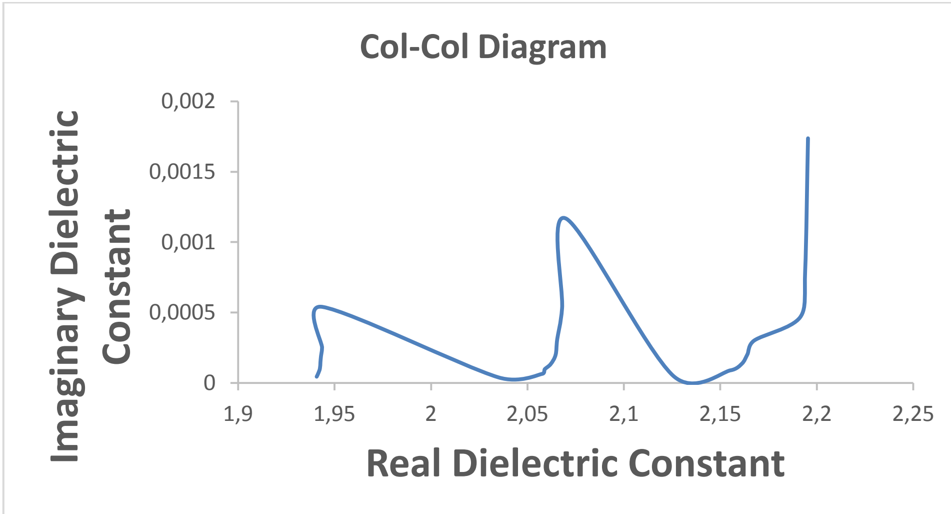

Fig. 9. Col-Col Diagram.

3. 9. Optical Conductivity

Figure (10) shows that the optical conductivity as a function of photon energy. It was observed that the optical conductivity increase at high photon energy is due to the high absorbance of sample also may be due to the electron excited by photon energy. This behavior is similar to that give by [30].

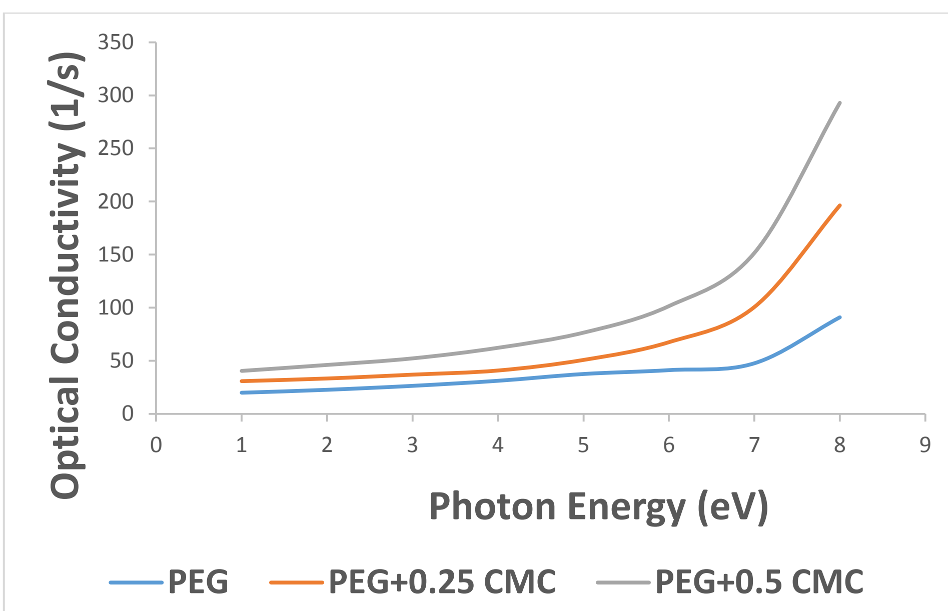

Fig. 10. Optical conductivity vs photon energy for PEG and (PEG-CMC) films.

4. CONCLUSIONS

1 - The new semiconductor films prepared by drop casting method with low energy gap.

2 - The higher absorption in (UV-region) makes the films good material for screening off (UV-portion) of electromagnetic spectrum, which is dangerous to human and animal health. These films can be used for eyeglass coating for protection from sunburn and in the saving of tires and any rubber types.

3 - Adding cellulose derivative polymer to PEG lead to increase reflectivity in (UV region), therefore it can be used as a coating for different types of glass to protect the level of solar radiation and reduce it.

4 - The decreasing in the value of energy gap gives a new semiconductor film.

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