Structural and optical properties for PVA- PEG-MnCl₂ composites

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Abstract

Polymer films of PEG and PVA and their blend with different concentrations of MnCl₂ (0, 2, 4, 6 and 10 %.wt) were study using casting technique. The X-ray spectra of pure PEG, PVA and PVA:PEG films and with addition of 2% concentrations from (MnCl₂) show amorphous structures. The results for FTIR show the interaction between the filler and polymer blend results in decreasing crystallinity with rich amorphous phase. This amorphous nature confirms the complexation between the filler and the polymer blend. The optical properties of (PVA:PEG/MnCl₂) contain the recording of absorbance (A) and explain that the absorption coefficient (α), refractive index (n), extinction coefficient (kₒ) and the dielectric constants (real and imaginary part) increase with increasing the concentration of Composite (PVA:PEG/MnCl₂). The optical energy gap for electrons transitions both are direct and indirect allowed.

الخواص التركيبيه والبصريه للمتراكب بولي فينال الكحول وبولي اثلين كلايكول المطعم

بكلوريد المنغنيز

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الخلاصة

اغشيه بولي فينال الكحول- بولي اثلين كلايكول البوليمرية و المطعمة بتراكيز مختلفة من كلوريد المنغنيز (2,4,6,8,10) % قد حضرت بطرية السحب. كانت نتائج فحوصات الائشعه السينية للاغشيه النقية واضافة 2% من كلوريد المنغنيز عشوائية. نتائج فحوصات الاشعة تحت الحمراء بينت التفاعل بين المادة البوليمريه والمطعمة وكذلك زيادة التبلور. وهذه العشوائيه بسبب التداخل بين المادة البولمرية والمادة المدعمة، الخواص البصرية تضمنت دراسة الامتصاصية وتوضيح معامل الامتصاص ومعمل الانكسار ومعامل الخمود وثابت العزل الحقيقي والخيالي تزداد بزياده تراكيز الماده المطعمة. فجوة الطاقة للالكترونات الانتقالية كانت من نوع المباشرة والغير مباشرة المسموحة.

Introduction

Polymer blends play an important role because of their relatively simple preparation methods and diverse resulting properties [1]. Interest in studying polymer blends has considerably increased due to their significant industrial applications [2]. Blends with improved characteristics are produced by blending two or more polymers in order to combine their properties for certain purposes. Polyvinyl alcohol (PVA) is the most widely produced water soluble

synthetic polymer over a wide range of temperatures depending on its degree of hydrolysis, molecular weight and tendency to hydrogen bond in aqueous solutions [3]. Moreover, PVA is also nontoxic, potential material having high dielectric strength, good charge storage capacity and dopant dependent electrical and optical properties [4]. PVA has been found to have a wide range of applications in the industrial sector and it has been attractive in different areas of science and technology [5, 6].

Polyethylene glycol (PEG) Chemical formula is [H $(OCH_2CH_2)_nOH$]. Solubility all grades of polyethylene glycol are soluble in water. Polyethylene glycols are used in great variety of applications because of their chemical structure, their low toxicity, their solubility in water and their lubricating properties. They provide flexibility in choosing properties to meet the requirements of many different applications. In the rubber industry, they serve as heat transfer agents, mold release agents, rubber compounders, lubricants, and pigment carriers [7-10].

Filler additives were added to polymer or polymer blend to improve and modify its properties. Transition metals have influence on the structural, optical, morphological and thermal properties of polymer blend. Manganese is well known as a magneto active multivalent element. Thus, its halides can be used as fillers to modify the electric conduction and the optical absorption of PVV:PEG. On the other hand, $MnCl_2$ is considered as a good candidate for one- or two-dimensional phenomena [11].
Most of the early works on metal/polymer composites are patented and little systematic investigation has been carried out in this field, especially on the particulate composite systems.

In the present work, PEG:PVA blend doped with different concentrations of $MnCl_2$ have been prepared by casting method. The structural and optical characteristics of the prepared composites were studied with on their physical properties.

Experimental part
The materials used in the present work were Poly-vinyl al alcohol (PVA) and Poly-ethylene glycol (PEG) with addition of different concentrations from ($MnCl_2$). Equal weights of PVA and PEG with ratio 50: 50 wt% for one gm of PVA and one gm of PEG was first dissolved in the common solvent (30 mL of distilled water) and then both the polymers were homogeneously mixed using a magnetic stirrer at the constant temperature at 50˚C for 12 hours. Complete homogeneous solution was casted on Teflon petri dishes and left for the evaporation of the solvent. The resulting PVA:PEG films were dried up to 4 days at room temperature in the desiccators to remove the traces of solvent, and then lifted out of the petri dish for further analysis. On the other hand, $MnCl_2$ was dissolved in double distilled water in the same condition. The resulting solution of $MnCl_2$ particles were added to the polymer blend PVA:PEG solution with mass fraction (0, 2, 4, 6, 8, 10) wt%. with temperature of 100 ^oC . The resulting solution was then cast to glass slides and leave over it for about 72 h. After drying, the films were peeled from Petridish (it has diameter 5cm) and then left to dry. The thickness of films were in ranging from 150 to 200 nm were obtained and kept in vacuum desiccators until use.

NICOLET FTIR 6700 spectrometer was used to record the FTIR spectra in the range 400 - 4000 cm^{-1} to study the functional groups of the samples. The absorbance Spectrum was recorded of

the wavelength range (200 - 1100) nm by using the double-beam spectrophotometer (UV- 1800 shimedza).

The absorption coefficient (α) was calculated in the fundamental absorption region from the following equation [12]:

$$\alpha = 2.303 A/d \qquad (1)$$

where (A) is absorbance and (d) is the thickness of sample.

The refractive index is explained in terms of real and imaginary parts. The real part of the refractive index (n) or simply the refractive index which describes the oscillations of the incident radiation in the crystal, while the imaginary part (k) known as the extinction coefficient which describes the attenuation of the incident radiation as it propagates in the crystal. The values of (n) and (k) can be determined from the absorption coefficient α and reflection (R) spectra.

The refractive index (n) is the written in terms of reflectance of the surface as [13]:

$$n = ((4R/(R-1)^2 - k^2))^{1/2} - (R+1)/(R-1) \qquad (2)$$

while the extinction coefficient k is related to the absorption coefficient α by:

$$K = \alpha \lambda /4\pi \qquad (3)$$

The forbidden energy gap of indirect transition both allowed, forbidden calculated according to the relationship [14]:

$$\alpha h v = \beta (h v - E_g)^m \qquad (4)$$

hv: is the energy of photon, β :is proportionality constant, E_g: is optical energy gap of the transition.

The optical dielectric constant ε can be expressed as a complex equation in the form $\varepsilon = \varepsilon_r - i\varepsilon_i$, where ε_r is the real part generally relates to dispersion, while ε_i is the imaginary part provides a measure of the dissipative rate of the wave in the medium. The real and imaginary parts of the complex dielectric constant are related to the refractive index and the extinction coefficient as [15]:

$$\varepsilon_r = n^2 - k^2 \qquad (5)$$

$$\varepsilon_i = 2nk \qquad (6)$$

Results and discussion
 Structure properties
    Fig. 1 presents the X-ray spectra of pure PEG and PVA and their blend with different concentrations of $MnCl_2$ in the range $2\theta = 10\text{-}65^o$. Pure PEG, PVA and PVA:PEG films and with addition of 2% concentrations from ($MnCl_2$) show amorphous structures.
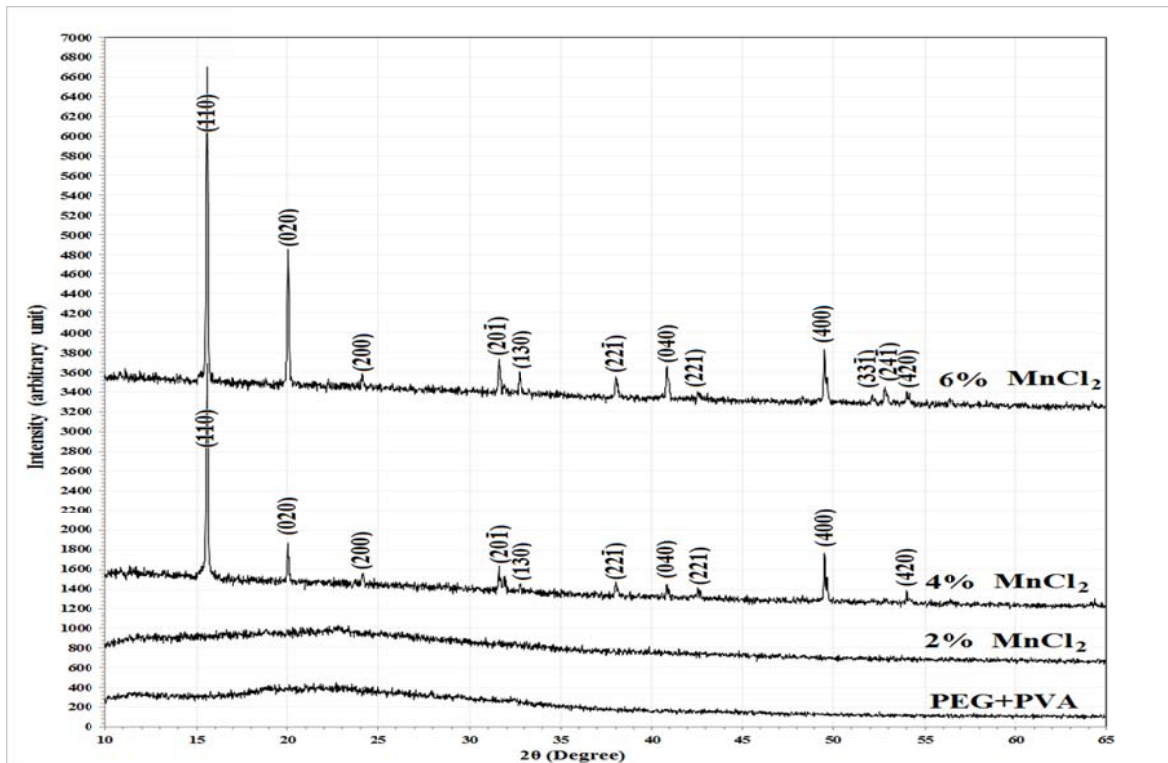
Fig. 1: X-ray diffraction scans of various MnCl₂ filling levels for PVA/PEG films.

After adding $MnCl_2$, it was observed that the tendency of apparently diminution of crystallinity with the increase of $MnCl_2$ content in blend sample implies a decrease of the number of hydrogen bonds that are formed between PEG and PVA if present [16]. Also, this might be a result of dilution effect of Mn^{2+} when mixed with polymer, which suppress recrystallization of broken blend polymer chains and inhibit crystal growth. The two peaks at $2\theta = 15.59$ and 20.02, have been found to be increased in intensity and decreased broadness in for $wt \geq 8\%$. which revealed that there is distortion in crystal structure of the blend. This results reveal the increase in amorphous nature the films which revealed that there is distortion in crystal structure of the blend.

Moreover, there are no new peaks appeared for $MnCl_2$. This indicates the complete dissolution of the filler in amorphous regions of the polymers [16].

From all previously mentioned results, the interaction between the filler and polymer blend results in decreasing crystallinity with rich amorphous phase. This amorphous nature confirms the complexation between the filler and the polymer blend.

Fig. 2 depicts the IR spectra of PVA, PEG and PVA/PEG. The main PEG:PVA characterizing frequencies are observed. FTIR spectroscopy of blend films were carried out to detect peak shifts, which may be due to the interaction, like hydrogen bonding, between two polymers.
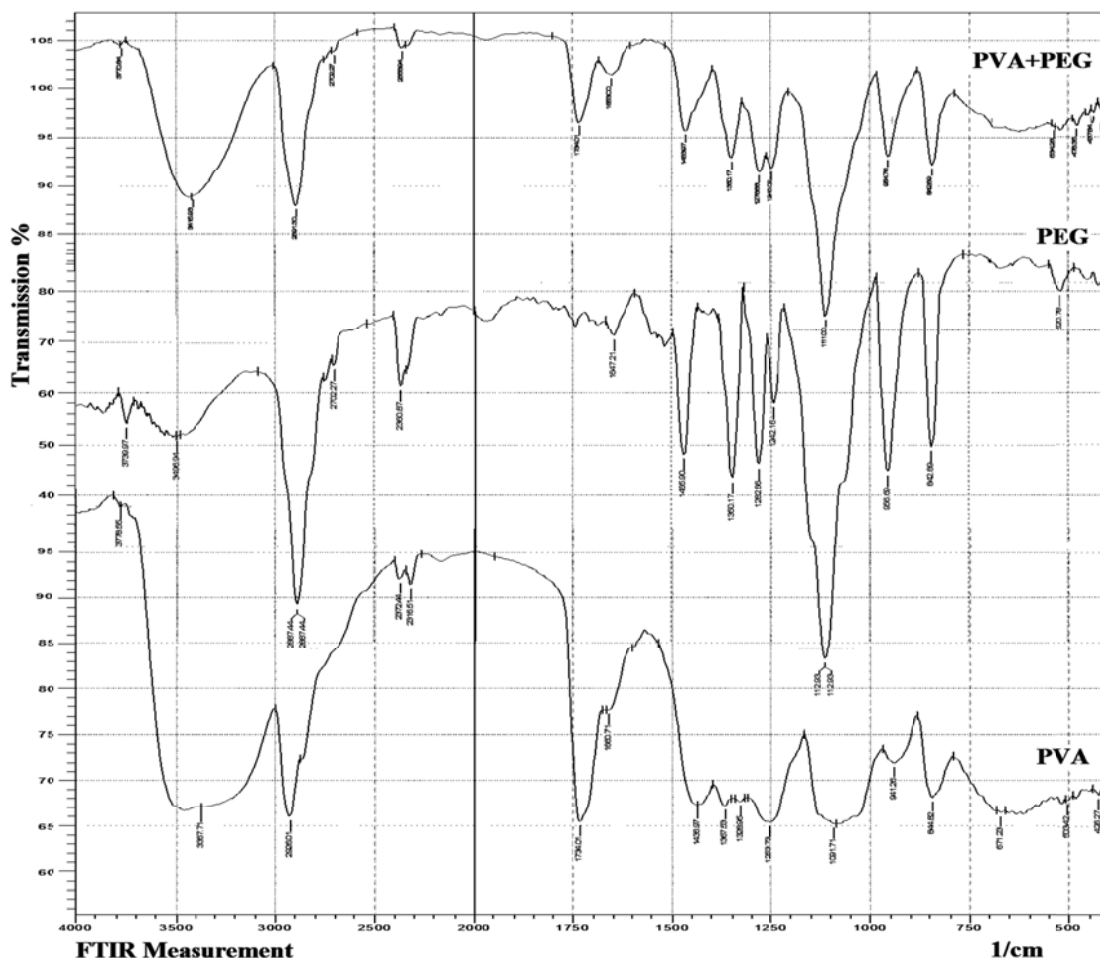
Fig. 2: FTIR transmission spectra of PVA, PEG and PVA/PEG.

For pure PVA, the characteristic absorption bands at about 3367 are assigned to O-H stretching and bending vibration of hydroxyl group. The band corresponding to methylene group (CH_2) asymmetric stretching vibration occurs at about 2926 cm^{-1}. The vibrational band at about 1734 cm^{-1} corresponds to C=O stretching of PVA. The band at about 844 cm^{-1} is assigned to stretching mode of CH_2. The band at about 1093 cm^{-1} corresponds to C-O stretching of acetyl group present on the PVA backbone. The absorption band at 941 cm^{-1} is assigned to CH_2 stretching.

For pure PEG, main characteristic bands of PEG can be observed. A sharp band at 2887 cm^{-1} is attributed to CH_2 stretching of methylene group. The bands at around 1464 cm^{-1} and 1350 cm^{-1} represent CH_2 scissoring and CH_2 asymmetric bending, respectively. The relatively small band at around 1282 cm^{-1} is assigned to CH_2 symmetric twisting, C-O-C stretching mode has sharp band at 1112 cm^{-1} out-of-plane rings C-H bending mode at 956 cm^{-1}.

The changes in absorption of the functional groups causes change in force constant of donor and acceptor groups and due to this change in frequency of stretching, deformation of these groups occurs. It has been already reported that PEO is a proton accepting polymer (ether group), which is necessary for the formation of hydrogen bond between two polymers[17, 18].

Fig.3 shows the spectra of PVA:PEG blend and the blend with 0, 2, 4, 6, 8, and 10 wt. % of $MnCl_2$. From the figure, the relative

intensities of some characteristic vibrational bands for those $MnCl_2$ blends are decreased. This indicates that the amorphous regions of the prepared samples are augmented with increasing the filler. The shifts of O-H stretching vibration from $3200 cm^{-1}$ to $3500 cm^{-1}$, the CH_2 stretching vibration from $2891 cm^{-1}$ to $2933 cm^{-1}$, C=O stretch from $1665 cm^{-1}$ to $1760 cm^{-1}$, C-C stretching, $947 cm^{-1}$ to $955 cm^{-1}$ and out-of-plane rings C-H bending mode from $966 cm^{-1}$ to $962 cm^{-1}$ were observed. These indicate the chemical interactions of $MnCl_2$ with the polymer blend these results are nearly in agreement with Abdelraze [19].
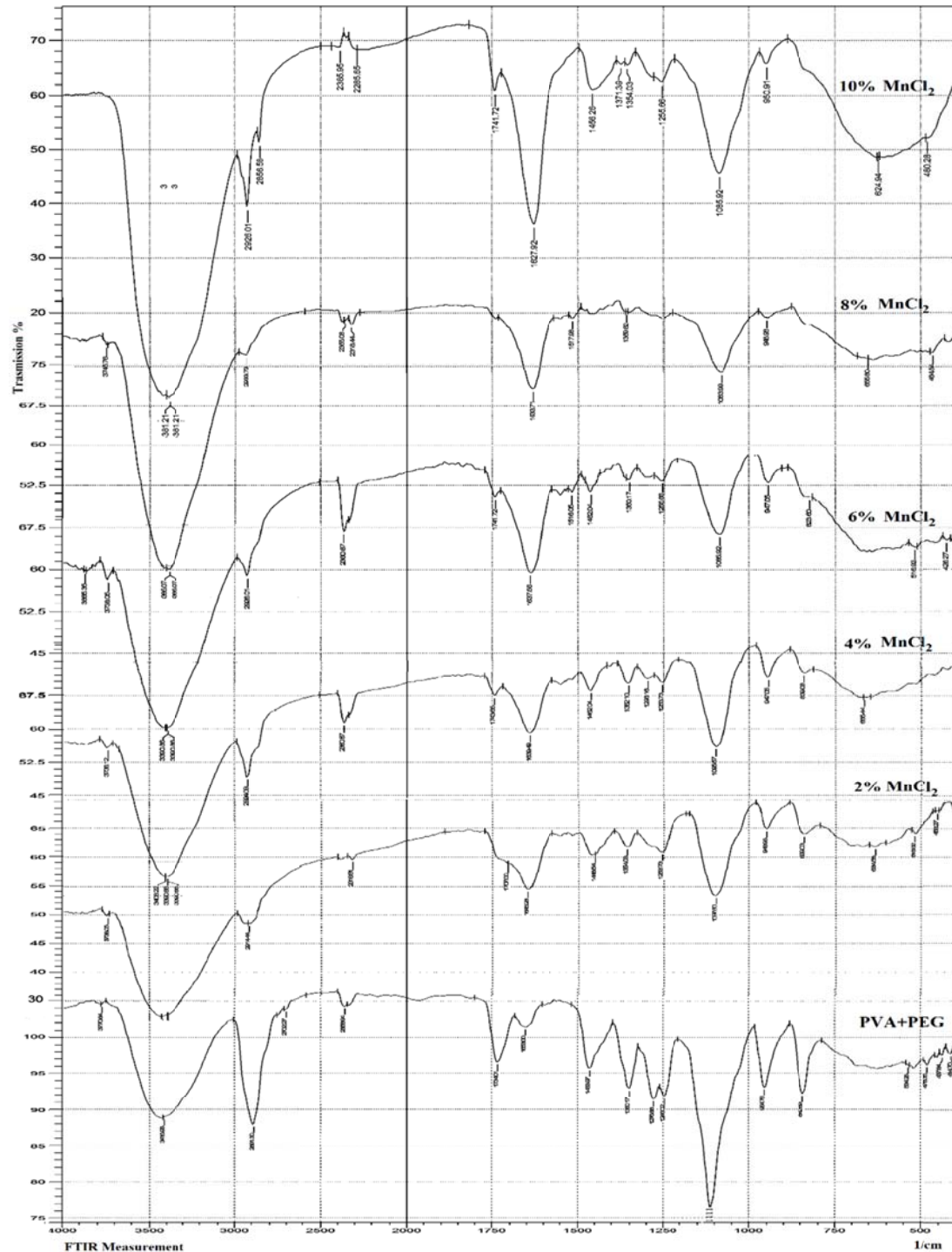

Fig. 3: FTIR transmission spectra of different concentration MnCl₂ in PVA/PEG.

The optical properties

The optical absorption method can be used for the investigation of the optically induced transitions. It provides information about the band structure and energy gap in crystalline and non-crystalline materials [20].

Fig. 4A and 4B show the absorption spectra of the Pure PVA and PEG and blended PEG:PVA polymer films with different content (0, 2, 4, 6, 8, and 10) from $MnCl_2$ material as a function of wavelength spectra in the range of 300-1100 nm respectively. From the spectra, we can see that peak height of PVA increases, band edge increases and the absorption band of PEG shifts towards shorter wavelengths. The value of absorption for PEG:PVA material will be between the values of absorptions for PVA and PEG materials. The absorption process induces an interaction between electromagnetism and the sample, which can be interpreted through variations in the absorption spectra. It can be seen from the figure that PVA, PEG and PEG:PVA films were almost non- absorbing for 350-1100 nm meaning no interaction of light is taking place in this wavelength region.
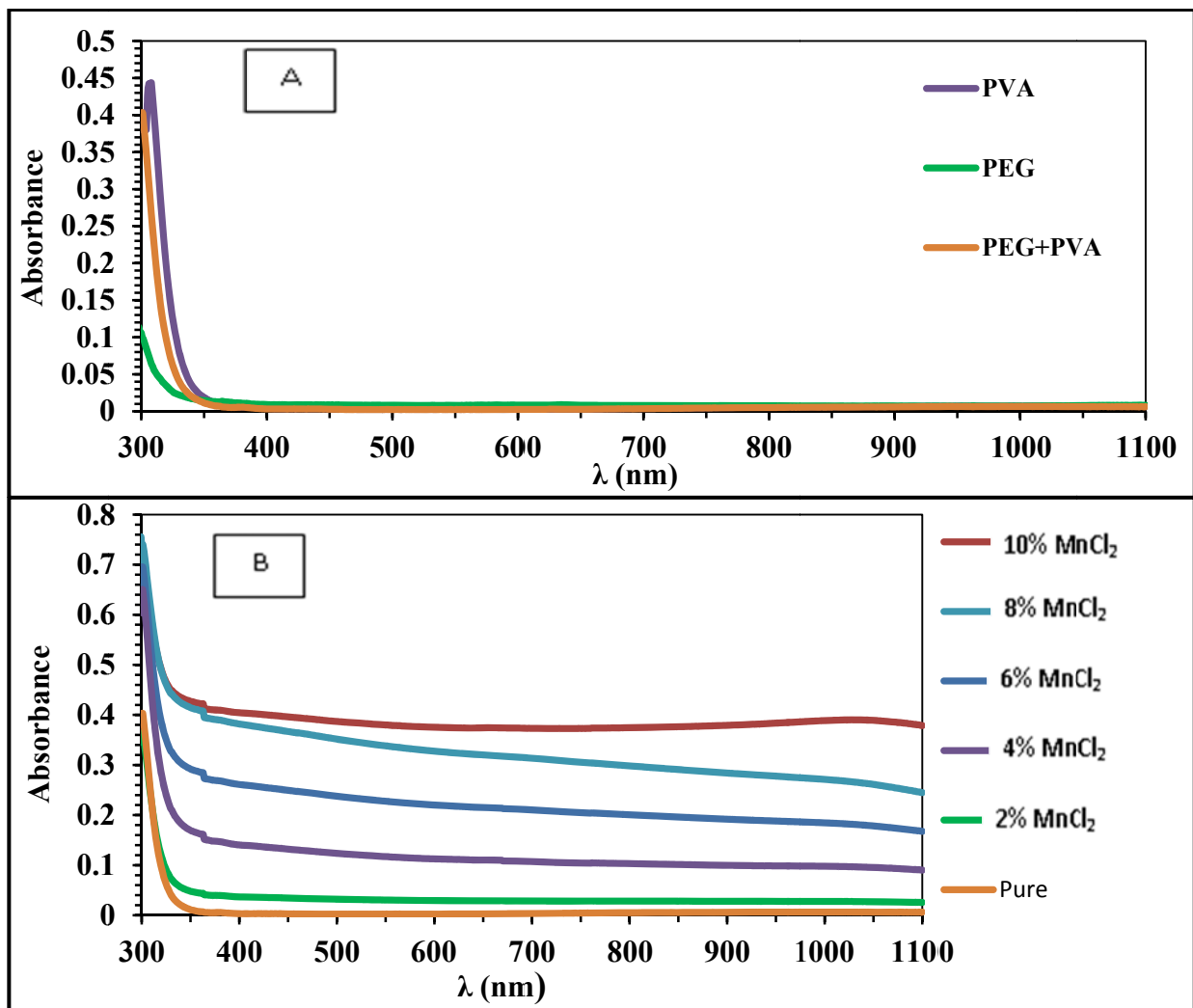

Fig. 4: A- Absorbance of PVA, PEG and PEG:PVA polymer composites.
B- Absorbance of PEG:PVA and PVA:PEG/MnCl₂ composites with different concentrations of MnCl₂.

From the spectra of Fig. 4B, we can see that peak height increases, band edge increases and the absorption band shifts towards longer wavelengths with increasing the weight percentage of $MnCl_2$. The adding of different amounts of $MnCl_2$ material to polymers blend does not change the chemical structure of the polymer material but new physical mixture is formed. From this figure, we note the intensity of the peak of absorption values were increase with increase of $MnCl_2$ material concentrations for all samples. This increase attributed to increase the number of carries charges which cause to increase the absorbance and this is due to absorb the incident light by free electrons [21]. When the wavelength decreases (at the neighborhood of the fundamental absorption edge), the interaction between incident photon and material will occur, and the photon will be absorbance [20].

The absorbance of composites were increased with the increase of concentration of ($MnCl_2$) material, this is due to ($MnCl_2$), absorbs the incident light [22-24]. At low wavelength, the change of absorption coefficient is large. This is indicates the large probability of electronic transitions are the absorption edge of the region [25]. This means that a great possibility for electron transitions consequently, the energy of incident photon is enough to move the electron from the valence band to the conduction band.

The change of the extinction coefficient as a function of the wavelength, is shown in Figs. 5A and 5B for PVA, PEG, PEG:PVA and PVA: PEG with different concentration of $MnCl_2$ respectively. It can be noted that (k) has low value at low concentration and increases with the increasing of the concentration of particles ($MnCl_2$) because of increasing of absorption coefficient (α) with the increase of weight percentages of $MnCl_2$ nanoparticles [26].
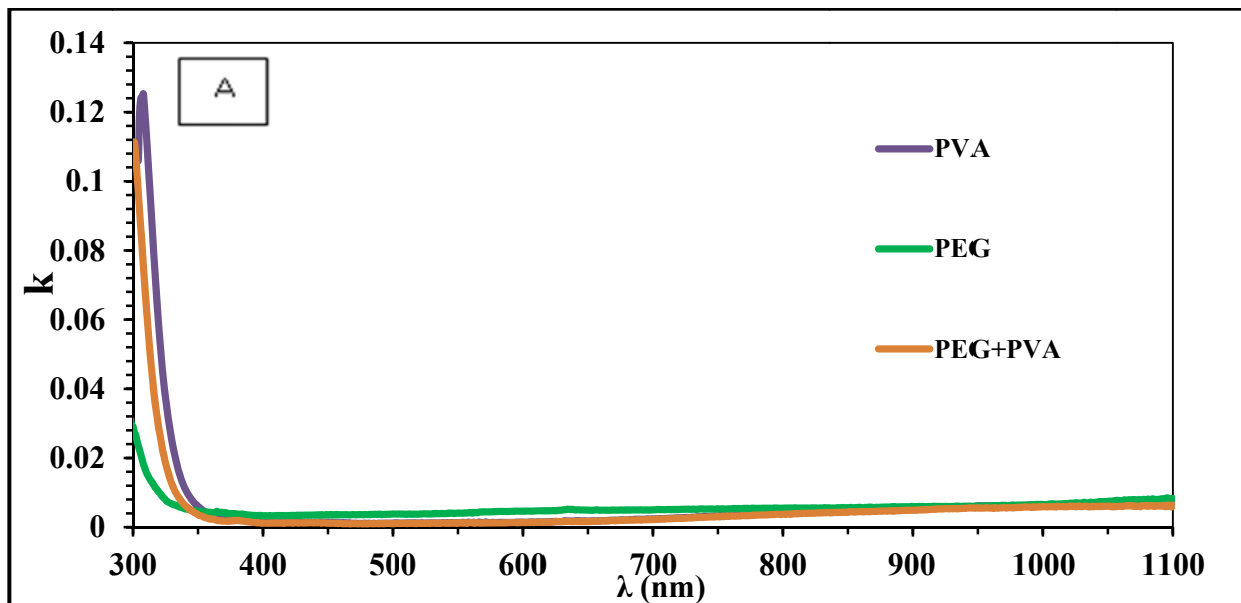

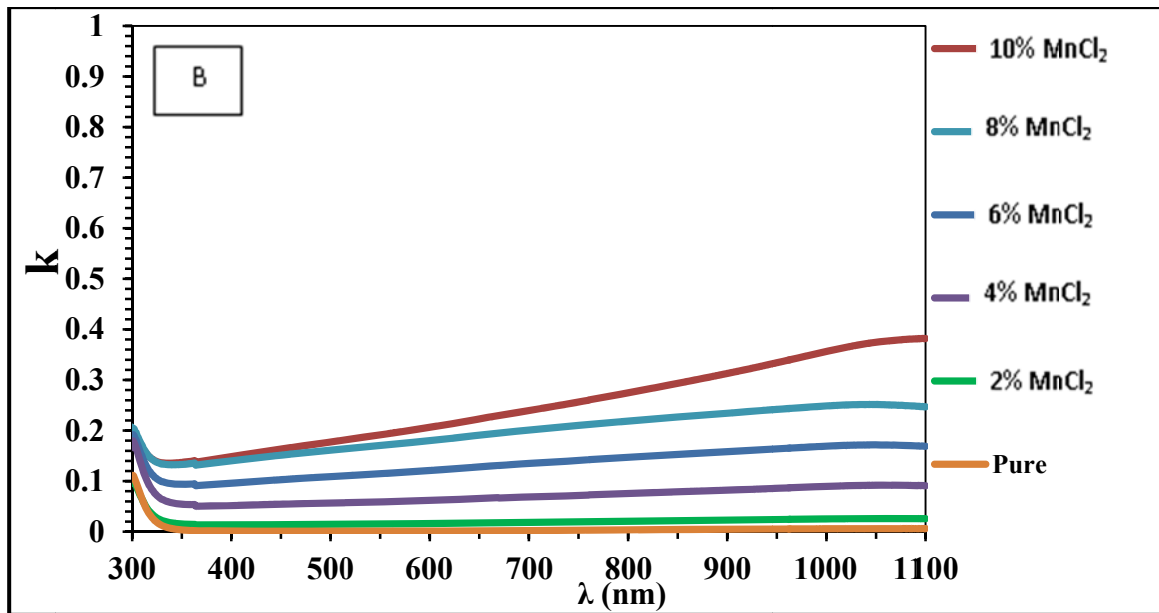*Fig. 5A: Extinction coefficient of PVA, PEG and PEG:PVA composites.*

Fig.5B: Extinction coefficient of PEG:PVA and PVA:PEG /MnCl₂) with different concentration of (MnCl₂).

Figs.6A and 6B shows the change of refractive index for PVA, PEG, PEG:PVA and PVA:PEG with adding different concentration of MnCl$_2$ composites as a function of wavelength, respectively.
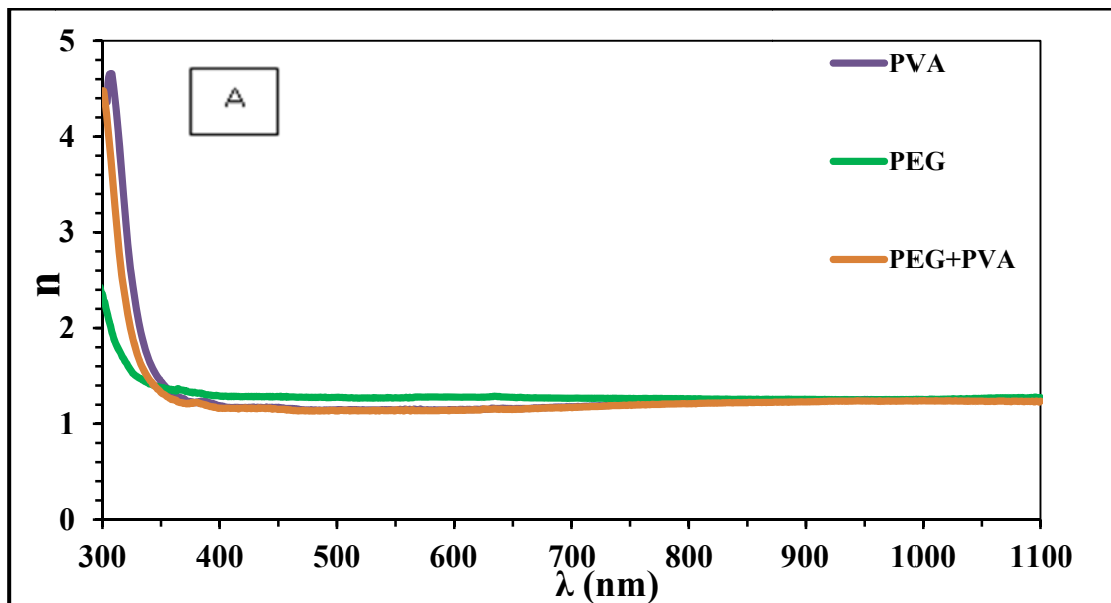

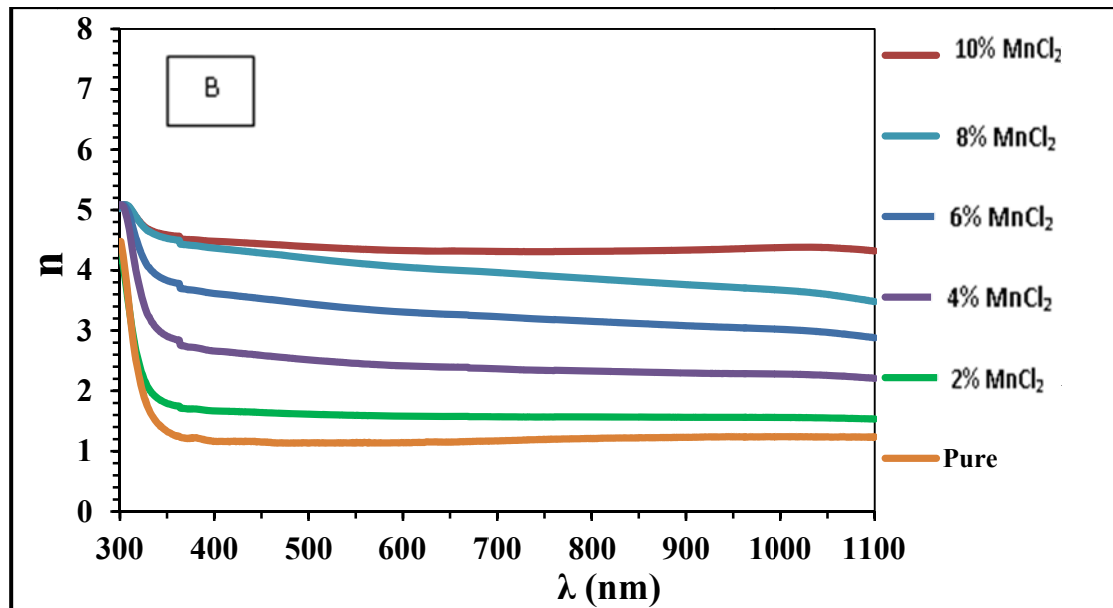*Fig. 6A: Refractive index of (PVA, PEG, and PEG:PVA) composites.*

Fig.6B: Refractive index of (PVA, and PVA:PEG /MnCl₂) composites with different concentration of (MnCl₂).

From Fig. 6A, we note that the refractive index value for PEG:PVA composite was between the refractive index values for (PVA) and (PEG) composites.

From Fig. 6B, we can see that the refractive index increases with increasing the weight percentages of the concentration of (MnCl₂) in the polymer composites. This reason is the increase of the (MnCl₂) concentration leading to increase of the density of the composites [27].

The optical band gap of the Pure and blend samples was determined from the UV-Vis spectra. The values of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{2}$ were calculated and plotted against hν. The straight portion of the curve was then extrapolated and its intersection on the abscissa was determined as shown in the inset of figure. This value corresponds to the energy gap. Figs. 7A and 7B shows the relation between absorption edge $(\alpha h\nu)^{1/2}$ for (PVA, PEG, and PEG:PVA) and PVA:PEG with addition of (0, 2, 4, 6, 8, 10 wt% from MnCl₂) composites as a function of photon energy respectively. Fig. 8C show Indirect energy gap of PEG:PVA and PEG:PVA/MnCl₂ composites with different concentrations of MnCl₂.
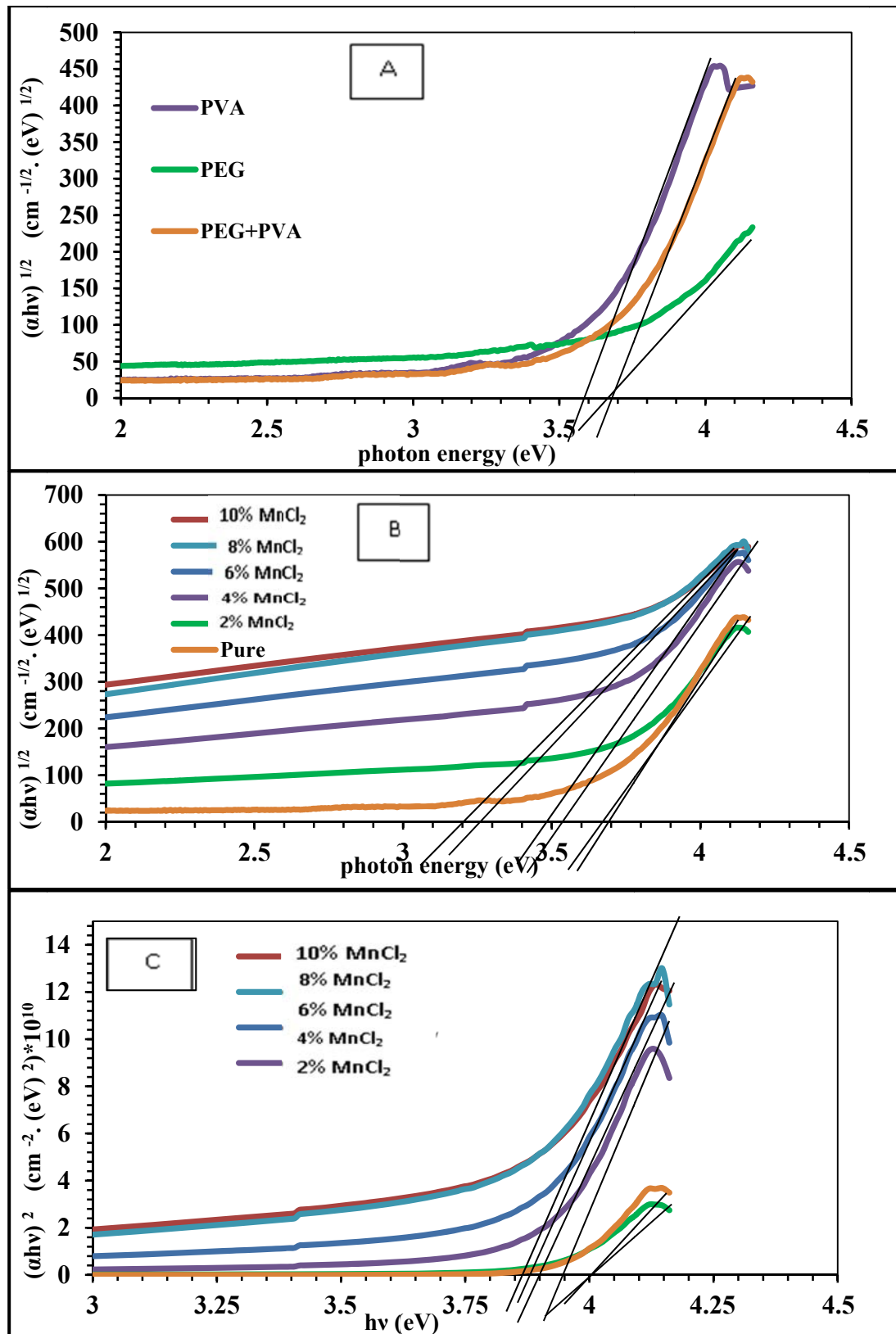
Fig.7: A- Energy gap of PVA, PEG, and PEG:PVA composites.
B- Direct Energy gap of PEG:PVA and PEG:PVA/MnCl₂ composites with different concentrations of MnCl₂.
C- Indirect Energy gap of PEG:PVA and PEG:PVA/MnCl₂ composites with different concentrations of MnCl₂.

The values of allowed direct and indirect energy gap are shown in Table 1.

Table 1: Energy gap for the allowed direct and indirect of (PVA:PEG-MnCl₂) composites.

MnCl$_2$ Concentration (wt.%)	Eg (eV)	
	Allowed Direct	Allowed Indirect
0	3.95	3.64
2	3.94	3.62
4	3.92	3.48
6	3.88	3.43
8	3.86	3.19
10	3.48	3.13

It is note that the energy gap (E_g) value for (PEG:PVA) composite was between the values of energy gap for (PVA) and (PEG). The obtained results showed that the energy gap (E_g) decreased with increase the (MnCl$_2$) concentration. This indicates that there are charge transfer complexes arose between the polymer blend and Mn-ions [19]. This behavior can be attributed to the fact that in heterogeneous composites, the electrical conduction depends on defect and impurities [due to the formation of defects created during the blending] and the interaction between the polymer chains and the formation of some bonds [28-30].

Figs. 8A and 8B shows the change of ε_r as a function of the wavelength for (PVA, PEG, and PEG:PVA) and (PEG:PVA and PVA:PEG/MnCl$_2$ composites respectively.
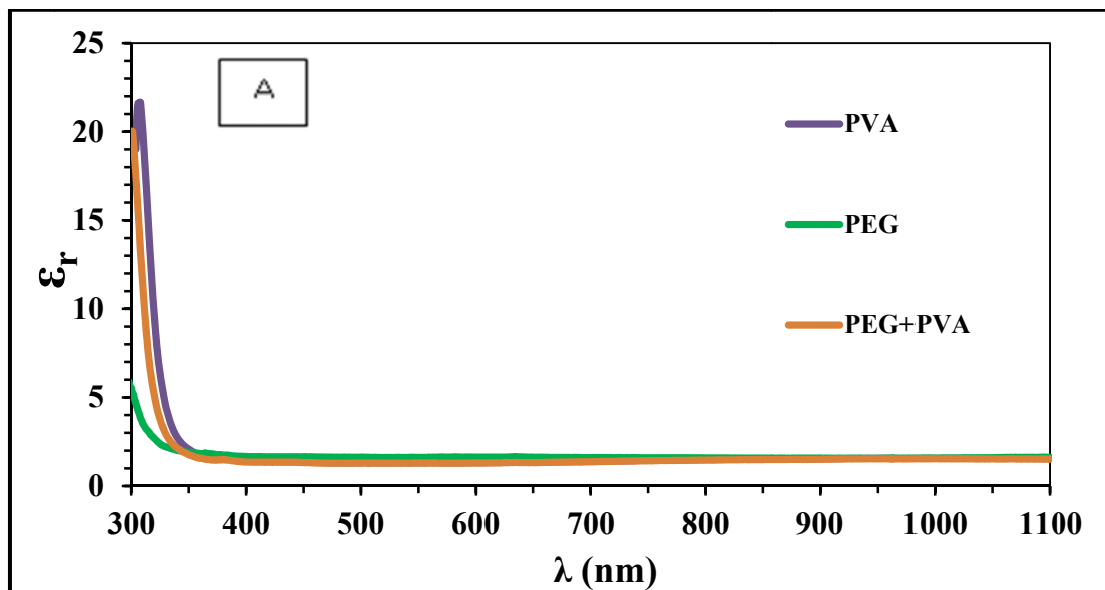

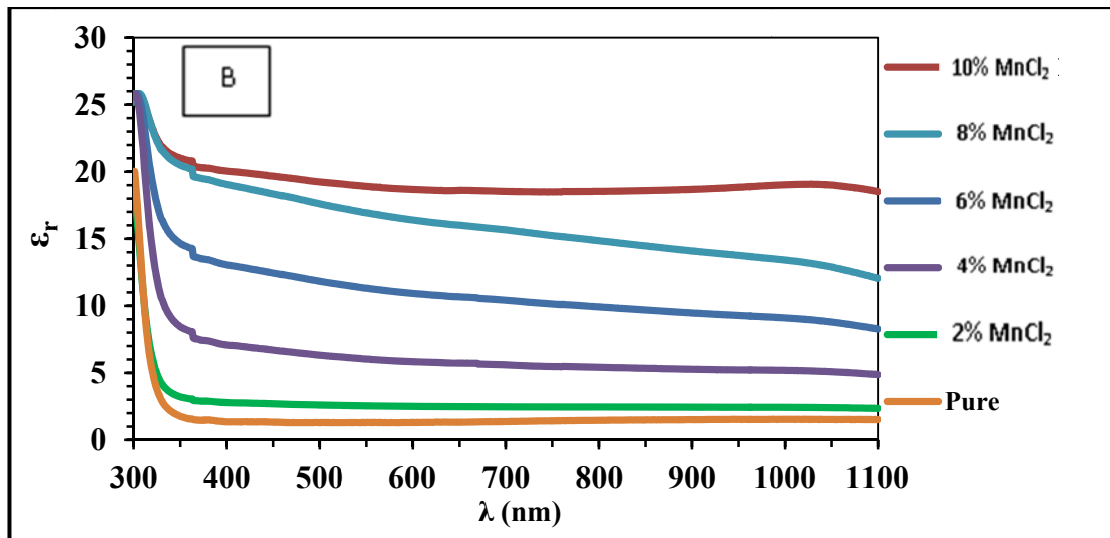*Fig. 8A: Real part of dielectric constant of PVA, PEG, and PEG:PVA composites.*

Fig.8B: Real part of dielectric constant of PVA and PEG:PVA/MnCl₂ with different concentration of (MnCl₂).

It can be seen that ε_r considerably depends on (n^2) due to low value of (k^2). Generally from figure, we can note that the real dielectric constant increases with the increase of the concentrations of (MnCl₂) because of increasing of absorption coefficient (α). In imaginary part of dielectric constant, the Figs. 9A and 9B shows the change of ε_i as a function of wavelength for both (PVA, PEG, and PEG:PVA) and (PEG:PVA and PVA:PEG with adding different concentration of MnCl₂) composites respectively.
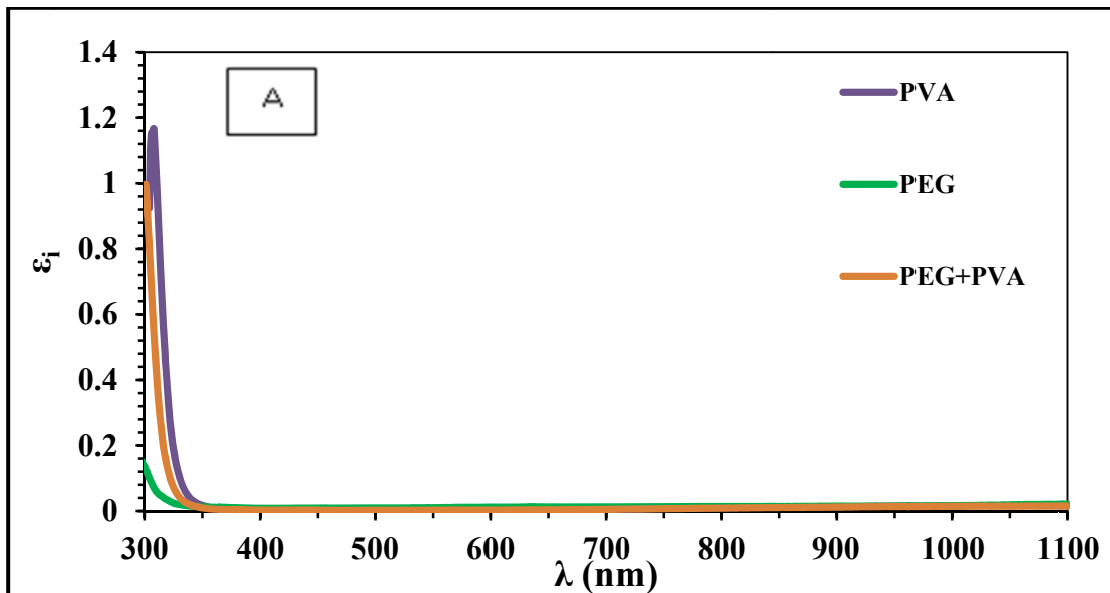

Fig. 9A: Imaginary part of dielectric constant of PVA, PEG and PEG:PVA composites.
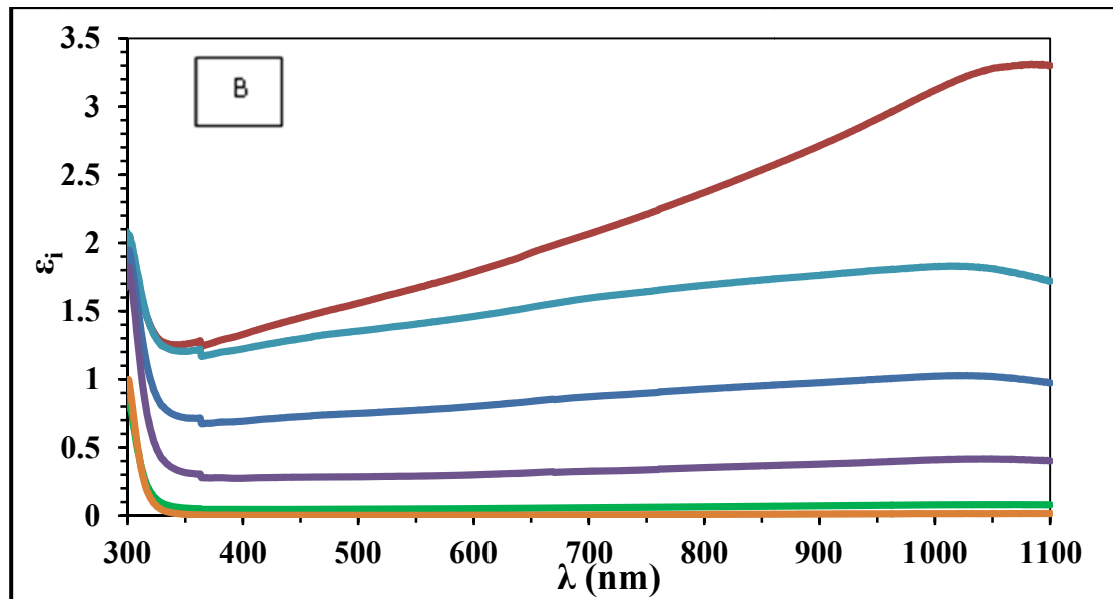
Fig. 9B: Imaginary part of dielectric constant of PEG:PVA, and PVA:PEG/MnCl₂ with different concentration of (MnCl₂).

It can be seen that ε_i is dependent on (k) values that change with the change of the absorption coefficient due to the relation between (α) and (k) [31].

From figure, we can see that the imaginary part of dielectric constant increases with increasing the weight percentages of the concentration of nanoparticles for (MnCl₂) in the polymer composites [32]. It is clear from Eq. (5,6), that the variation of ε_r follows the same trend as refractive index (n) on photon energy hν, whereas the variation of ε_i mainly follows the behavior of the extinction coefficient k and the absorption coefficient (α) is the same.

Conclusions

Good quality, highly transparent of PVA:PEG/MnCl₂ were grown by solution growth technique. Pure PVA:PEG films and 2% concentrations adding from (MnCl₂) show amorphous structures and become polycrystalline with increase the MnCl₂ more than 2%. FTIR spectra were measured and the functional groups were assigned. The calculated optical constants (refractive index (n), extinction coefficient (k), the real and imaginary parts of the dielectric constant) and the optical band gap E_g (was deduced from the data of the absorption coefficient (α) and the type of transition was allowed direct and indirect) were clearly depend on the increasing of concentration of MnCl₂ in the composite. This makes the material more prominent for device applications of various optoelectronics and photonic devices.

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