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Preparation and Study of Structural, Optical and Electrical Properties of Composite Film [Pva-Peo-Mncl$_2$.4h$_2$o]

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Abstract

The solution casting method was used to make pure polymeric blend film [Polyvinyl Alcohol-Polyethylene Oxide] [PVA-PEO] and polymeric blend films reinforced with $MnCl_2.4H_2O$ salt in various the weight (10, 20, 30, 40, and 50) % wt in the current study. The effects of weight ratio of salt on structural properties for all reinforced polymeric blend films were studied. FTIR spectra were used to establish the interaction between the polymer (PVA) and the polymer (PEO) reinforced by $MnCl_2.4H_2O$ salt, which causes some changes in the vibration modes and the position of the bonds. The effects of weight ratio of salt on optical properties for all reinforced polymeric blend films were studied, as the transmittance and absorbance spectra were recorded within the range of wavelengths (190-1100) nm, and it was found that the energy gap value decreases with an increase of the added salt's weight ratio. Effects of salt's weight ratio on electrical (dielectric) properties for all reinforced polymeric blend films were studied, and the practical results showed a decrease in the dielectric constant (ε') with an increase in frequency for all polymeric blend films, while the practical results also showed an increase in the alternating electrical conductivity ($\sigma_{a.c}$) with increasing frequency for all polymeric blend films, as well as an increase in both the dielectric constant and alternating electrical conductivity with an increase in the added salt's weight ratio at same frequency.

Keywords: PVA-PEO, $MnCl_2.4H_2O$ salt, Blend, Composite films

تحضير ودراسة الخصائص التركيبية والبصرية والكهربائية للأغشية المركبة

.$[PVA\text{-}PEO\text{-}MnCl_2.4H_2O]$

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الخلاصة

تم استخدام طريقة الصب بالمحلول لصنع غشاء الخليط البوليمري النقي [PVA-PEO] وأغشية الخلائط البوليمرية مدعمة بملح $MnCl_2.4H_2O$ بنسب وزنية مختلفة (10, 20, 30, 40, and 50 % wt%) في الدراسة الحالية . وتم استخدام مطياف FTIR لتحديد التفاعل بين البوليمر (PVA) والبوليمر (PEO) المدعم بملح $MnCl_2.4H_2O$، والذي يسبب بعض التغييرات في أنماط الاهتزاز وموقع. تمت دراسة تأثير النسبة الوزنية للملح على الخصائص البصرية لأغشية الخلائط البوليمرية المدعمة كافة، اذ سجل طيفا النفاذية والامتصاصية ضمن مدى الأطوال الموجية nm (190-1100) ، ووجد بأن قيمة فجوة الطاقة تقل بزيادة النسبة الوزنية للملح المضاف. تم دراسة تأثير النسبة الوزنية للملح على الخصائص الكهربائية (العزلية) لأغشية الخلائط البوليمرية المدعمة كافة، وأظهرت النتائج العملية تناقص ثابت العزل (ε') بزيادة التردد لأغشية الخلائط البوليمرية كافة، بينما أظهرت النتائج العملية أيضا زيادة في التوصيلية الكهربائية المتناوبة ($\sigma_{a.c}$) مع زيادة التردد ولأغشية الخلائط البوليمرية كافة، وكذلك زيادة كل من ثابت العزل والتوصيلية الكهربائية المتناوبة مع زيادة النسبة الوزنية للملح المضاف عند التردد نفسه.

Introduction

Discovery of conductive polymers have given a new dimension to the present era. Polymers are known so far as a class of heat sensitive, flexible, electrically insulating and amorphous materials. Electrically Conducting Polymers appear to be ideal candidates for various applications, as many of their properties circumvent problems prevalent with traditional materials, including corrosion, weight, matrix incompatibility, and environmental integrity [1]. In addition to being corrosion resistant and light weight, many critical properties of conducting polymers may be tailored for various applications. The strength to weight, possibility, resistance to corrosion, has given conducting polymers advantage over metals [2]. Carbon and hydrogen, with nitrogen or Sulphur heteroatoms, make up conducting polymers that contain π-conjugation along their polymer backbone. Polymeric materials have been receiving great research attention due to their advantages, such as light-weight, low-cost, high flexibility. These properties make them ideal materials for a broad range of applications in optical, biomedical, and electronic devices The use of polymers has also emerged in the manufacture of solar cells and chemical cells [3].

A- Polyvinyl alcohol (PVA): It's a polymer that comes in the form of an odorless, non-toxic white powder that dissolves rapidly in distilled water. The molecular weight range is (13000–23000g/mol), and it was developed by an Indian business called Central House (P) Ltd. [4,5].

B- Polyethylene Oxide (PEO): Developed by Cheng Du Micxy Chemical Co Ltd, the polymer known as polyethylene oxide is made through the polymerization of ethylene oxide, resulting in a varying molecular weight range from (150,000 to 10 million). With its versatile nature, PEO finds purpose in a multitude of industrial applications. The polymer's structural formula can be observed in Figure (1). [4,5].

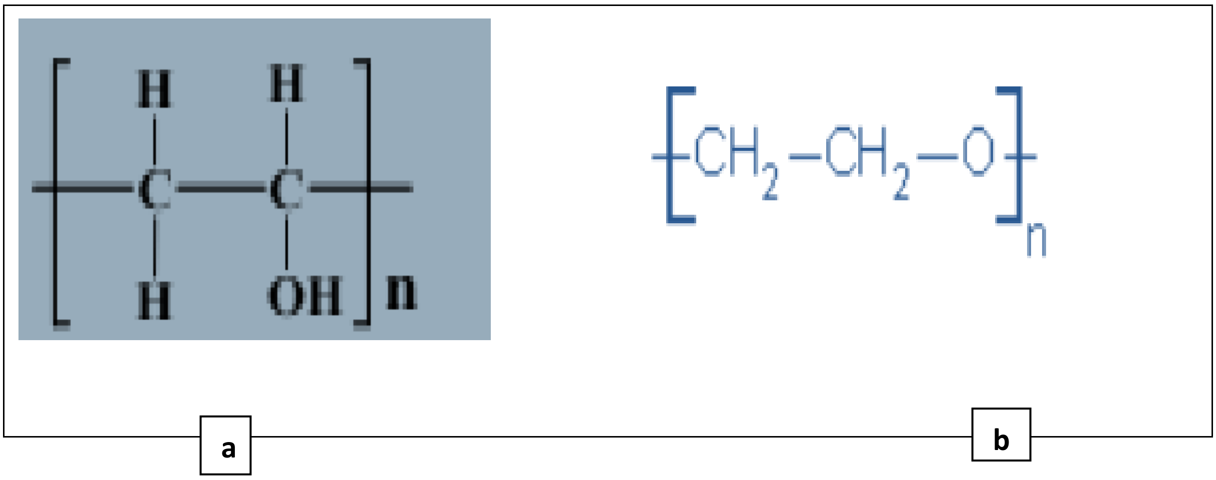


Figure 1: The structural formula of the polymer:

a) Polyvinyl Alcohol Polymer (PVA). b) Polyethylene Oxide Polymer [4,5].

A- Manganese Chloride: The chemical formula of anhydrous manganese chloride or anhydrous manganese chloride is $MnCl_2 \cdot 4H_2O$. The compound also exists in another form, as pink crystals with a molecular weight of (197.9 g/mol) bound to four water molecules. Central Pharmacy (P) Ltd., New Delhi, 110002, India, provided the chemical samples used in this experiment. It is easily soluble in ethanol and water.

Using the casting method, a homogeneous solution was obtained for the pure [PVA-PEO] polymeric blend film by mixing certain weight percentages of (PVA) polymer and (PEO) polymer, and adding (35ml) of distilled water. The mixture was stirred using a magnetic stirrer for (3h) at (70 ^{o}C) before being poured into a special glass mold, where it was left to evaporate into the required sample film. To prepare the composite (PVA-PEO-$MnCl_2$), weight percentages of (PVA) polymer, (PEO) polymer, and $MnCl_2$ salt were mixed, and distilled water was added in the same manner as before. The solutions were stirred using a magnetic stirrer for (3h) at (70 ^{o}C) until they were homogeneous, before being poured into special glass molds and left to evaporate into the required sample films.

In this research we will study the structural properties (FTIR) of the polymeric compound (PVA-PEO) using a device made by Shimadzu, a Japanese manufacturer, the infrared spectrum of a pure polymeric blend film of PVA and PEO, as well as polymeric blend films reinforced by $MnCl_2.4H_2O$ salt, was recorded for the wavenumber range of (400-4000 cm^{-1}) with an (IR Affinty-1CE (FTIR) spectrophotometer).

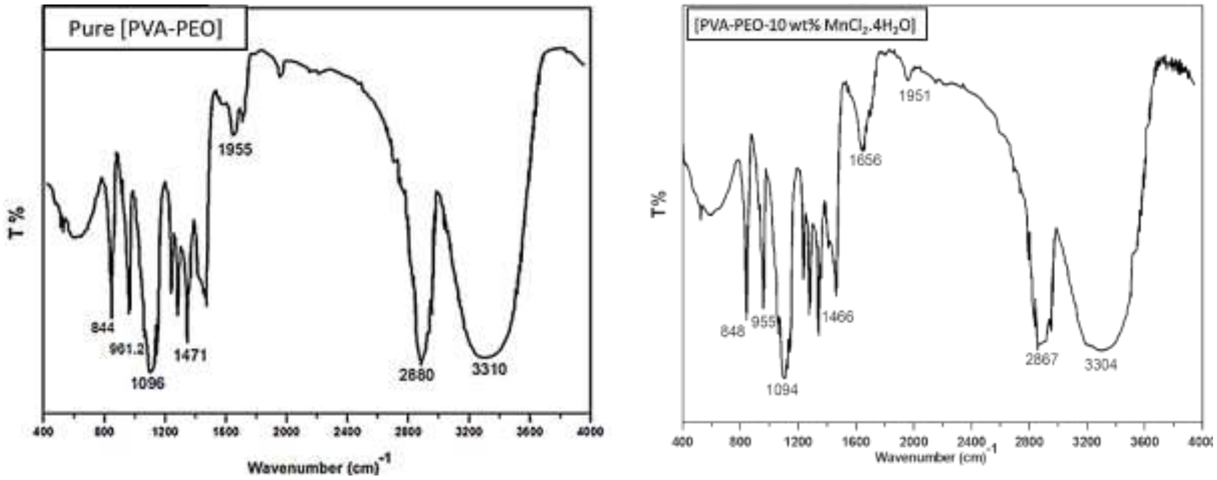
The transmission and absorption spectra of pure polymer blend films [PVA-PEO] were recorded at room temperature using a (UV-Vis 1800 dual-beam spectrophotometer), covering the wavelength range of (1100-190 nm). $MnCl_2 \cdot 4H_2O$ salts are also used to strengthen polymer blend films. The procedure is performed at Shimadzu's facilities in Japan.

Using an Agile Impedance Analyze 4294A (Tawan origin) LCR Metter, the electrical (dielectric) tests, represented by the dielectric constant (ε') and the alternating electrical conductivity ($\sigma_{a.c}$), were conducted as a frequency function for both pure polymeric blend films [PVA-PEO] and the polymeric blend films reinforced by $MnCl_2.4H_2O$ salt.

Results and Discussion

The interaction of PVA and PEO was analyzed in this study using FTIR spectra, with the aid of $MnCl_2.4H_2O$ salt reinforcement. This caused some noticeable changes in bond position and vibrational modes. Several polymeric blend films were analyzed, including the pure blend film [PVA-PEO], and those with different weight ratios of $MnCl_2.4H_2O$ salt. Figure (2) provides an overview of the FTIR spectra, which showed a reduction in relative intensities for certain characteristic vibrational bonds in the MnCl2.4H2O salt-reinforced films.

The polymer matrix separate it broad bonds at approximately (3310) cm^{-1} due to the asymmetric vibration of O-H group in each sample examined [6]. Meanwhile, the appearance of peaks around (2880) cm^{-1} can be linked to the presence of the C-H stretching vibration group, whereas the bonds at (1955) cm^{-1} displayed the C=C stretching vibration. The films reinforced with Polyvinyl Alcohol - Polyethylene Oxide blend demonstrated a peak at (1096) cm^{-1}, which experts attribute to C-O-C stretching [7]. Adding to the mix, an out-of-plane rings C-H bending vibration shift from 961.2 to 955 cm^{-1} occurred [8]. Ultimately, these observations hint at the chemical interactions between $MnCl_2.4H_2O$ salt and polymeric blend [PVA-PEO]. Around the (1471 cm-1 and 844 cm^{-1}) marks, two firm connections were detected and are attributed to the bending and stretching vibrations of the CH_2 cluster, accordingly [6]. $MnCl_2.4H_2O$ salt addition resulted in a change in the spectral intensities of the PVA-PEO polymeric blend by causing certain bonds to shift [9]. In Table (1), a more in-depth look at the wave number values of the absorption bands for every polymeric blend film is provided.



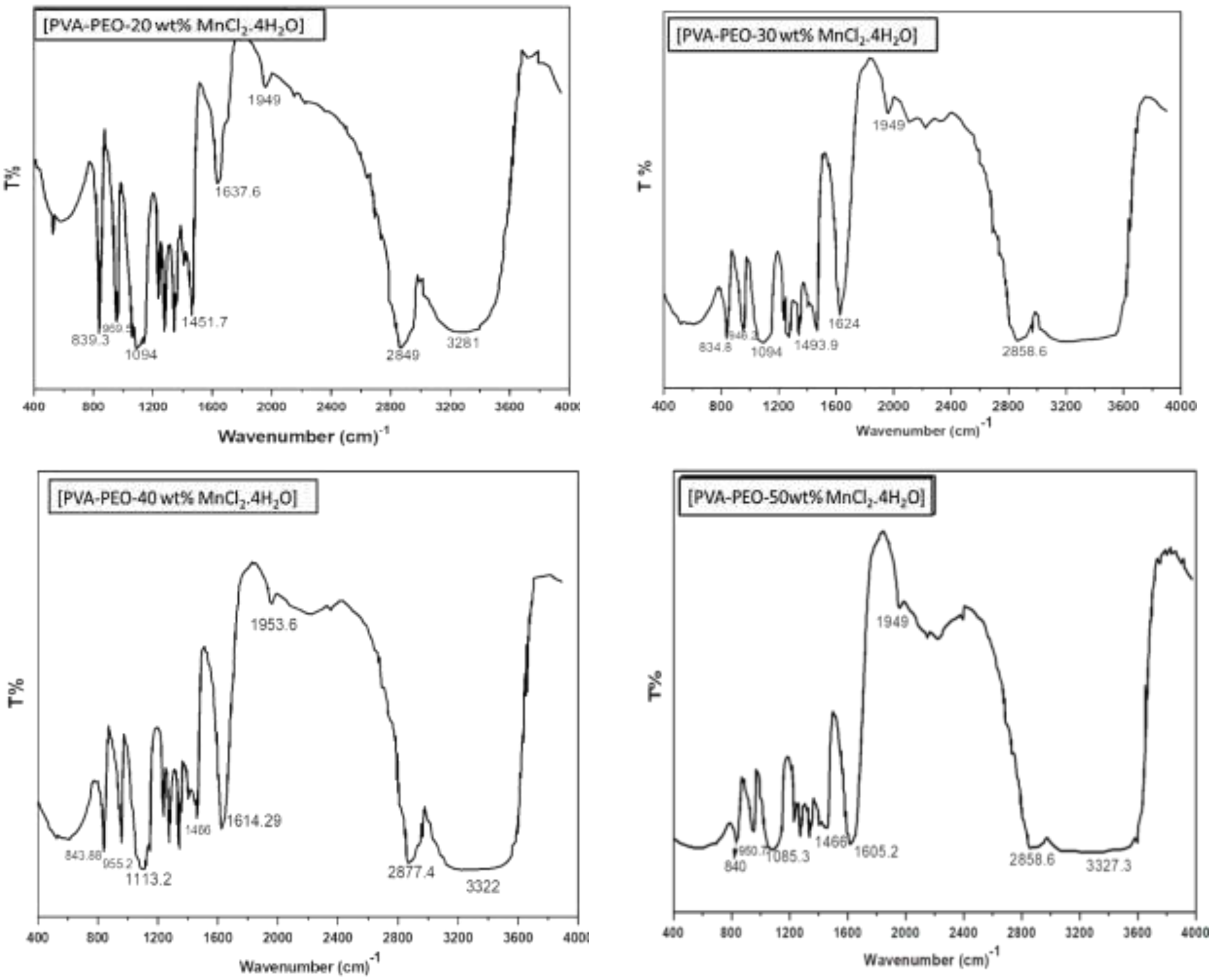


Figure 2: FTIR spectra of pure polymer blend membrane [PVA-PEO] and polymer blend membrane reinforced with different weight ratios of $MnCl_2.4H_2O$ salts.

Table 1: Absorption band wave value of composite film [PVA-PEO-$MnCl_2.4H_2O$] and $MnCl_2.4H_2O$ salt weight ratio.

Bond	**Wavenumbers (cm) $^{-1}$ [PVA-PEO-$MnCl_2.4H_2O$]**					
	Weight Ratio of Additive $MnCl_2.4H_2O$ salt (wt%)					
	Pure Polymeric Blend [PVA-PEO]	**10 (wt%)**	**20 wt%)(**	**30 wt%)(**	**40 (wt%)**	**50 wt%)(**
O-H Asymmetric Vibration	3310	3304	3281	3858.6	3322	3327.3

C-H Stretching Vibration	2880	2867	2849	2858.6	2877.4	2858.6
C=C Stretching Vibration	1955	1951	1949	1949	1953.6	1949
C=C Acetyle group	1660	1656	1637.6	1624	1614.29	1605.2
Bending of CH_2 Vibration	1471	1466	1451.7	1493.9	1466	1466
C-O-C Stretching	1096	1094	1094	1094	1113.2	1085.3
C-H Bending Vibration	961.2	955	969.5	946.2	955.2	950.7
Stretching of CH_2 Vibration	844	848	839.3	834.8	843.8	840

We've managed to calculate the energy gap (E_g) for an allowed indirect transition, using a good old value of (r=2). Check out Figure (3)- it presents how tightly interrelated $(\alpha h\upsilon)^{1/2}$ and photon energy ($h\upsilon$) are for both non-strengthened polymeric blend films [PVA-PEO] as well as those reinforced with $MnCl_2.4H_2O$ salt at different weights. The best straight-line fit passing through most of the points after the absorption edge intersects the photon energy axis (x-axis) at the point where $(\alpha h\upsilon)^{1/2} = 0$, representing the value of the energy gap for the allowed indirect transition. Table (2) shows the values of the energy gap for all the polymeric blend films. we notice from the table that the value of the energy gap for the pure polymeric blend film [PVA-PEO] is (5.6 eV), but after reinforcement by $MnCl_2.4H_2O$ salt with different weight ratios, the value of the energy gap slightly decreases with an increase in the weight ratio of added $MnCl_2.4H_2O$ salt. The decrease in the value of the energy gap with an increase in the weight ratio of the added $MnCl_2.4H_2O$ salt can be attributed to the fact of the initial arrangement of charge carriers and their reconfiguration due to the change in the size of the field and levels [10].

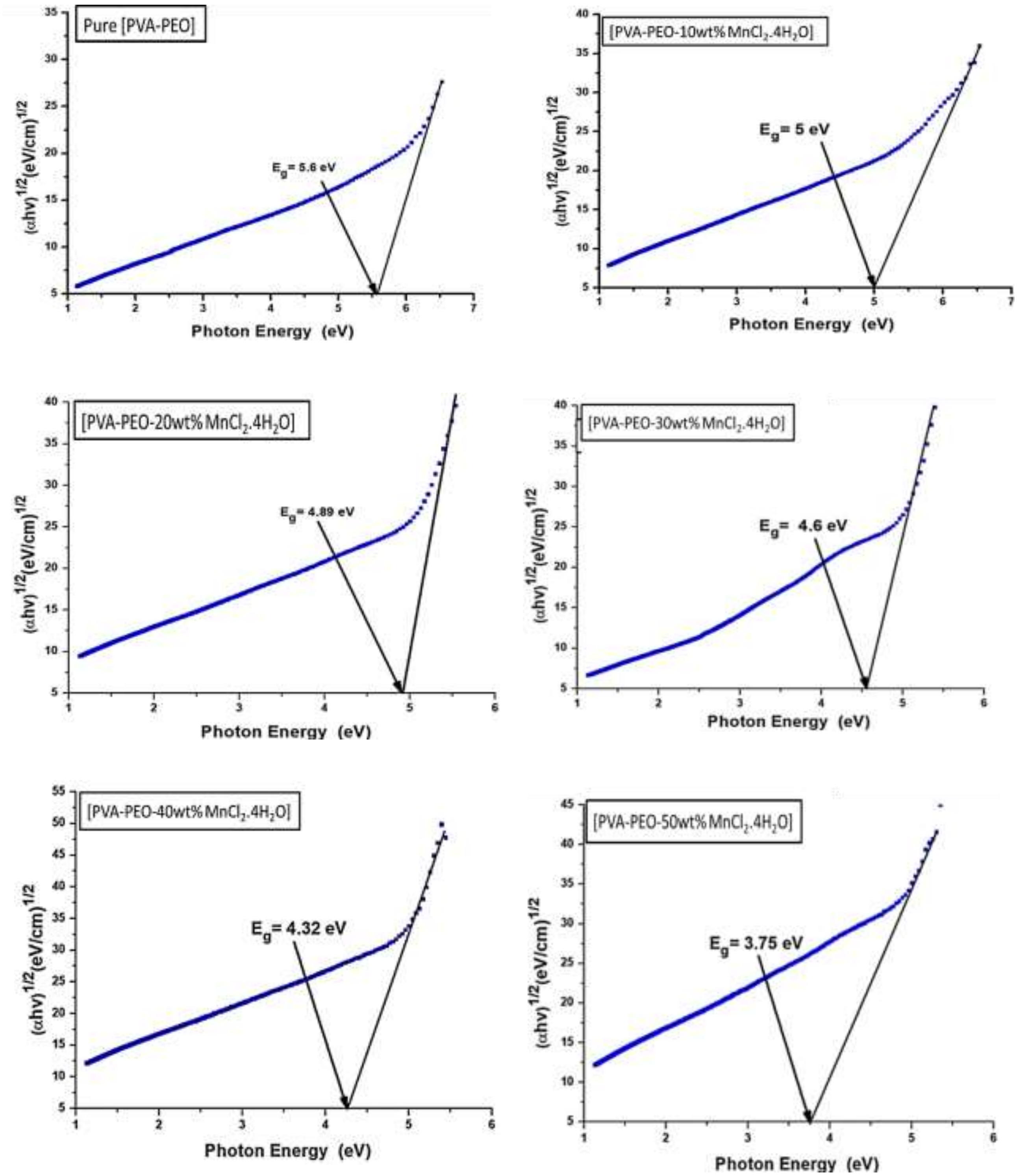


Figure 3: The energy gap of pure polymer blend film [PVA-PEO] and different weight ratios of $MnCl_2.4H_2O$ salt-enhanced polymer blend films allowing indirect transitions.

Table 2: Allowable indirect transition energy gap value of composite film [PVA-PEO-$MnCl_2.4H_2O$] and $MnCl_2.4H_2O$ salt weight ratio.

WEIGHT RATIO OF ADDITIVE $MNCL_2.4H_2O$ SALT (WT %)	[PVA-PEO-$MNCL_2.4H_2O$] E_G (EV)
Pure Polymeric Blend [PVA-PEO]	**5.6**
10	**5**
20	**4.89**
30	**4.6**
40	**4.32**
50	**3.75**

The curious case of pure polymeric blend film, which we know as [PVA-PEO], reveals that its dielectric constant (ε′) could be measured at room temperature. $MnCl_2.4H_2O$ salt was added in varying weight proportions to bolster these films and the impact was gauged within a frequency bracket of (50Hz-5MHz) all this is vividly illustrated in figure (4). For any polymeric blend film, it is noticed that the dielectric constant falls with increasing frequency. It is also evident that all of the polymeric mix films have high dielectric constant values at lower frequencies. The dielectric constant values for all polymeric blend films, however, decrease with increasing frequency. This can be explained by the fact that at low frequencies, there is enough time for the electrical dipoles to arrange and align molecules with the direction of the electric current flowing between the poles. However, at higher frequency regions, the time period becomes short and less than the time period for the molecules to orient themselves with the direction of the external electric field [11]. Also, the reason why the values of the dielectric constant are high at low frequencies is due to the difference in the phases of the matrix material and the reinforced material, which results in the creation of interfacial polarization. In addition, the generation of the sample charge between the poles, which is dependent on the sample's composition, distance, and impurities, is directly tied to the polarity of the electrical dipoles and the polarization created by the electrodes. As shown in the figure, it is also observed that the dielectric constant at the same frequency increases with an increase in the weight ratio of added $MnCl_2.4H_2O$ salt. In general, this increase in the value of the dielectric constant can be attributed to an increase in the polarizability [12].

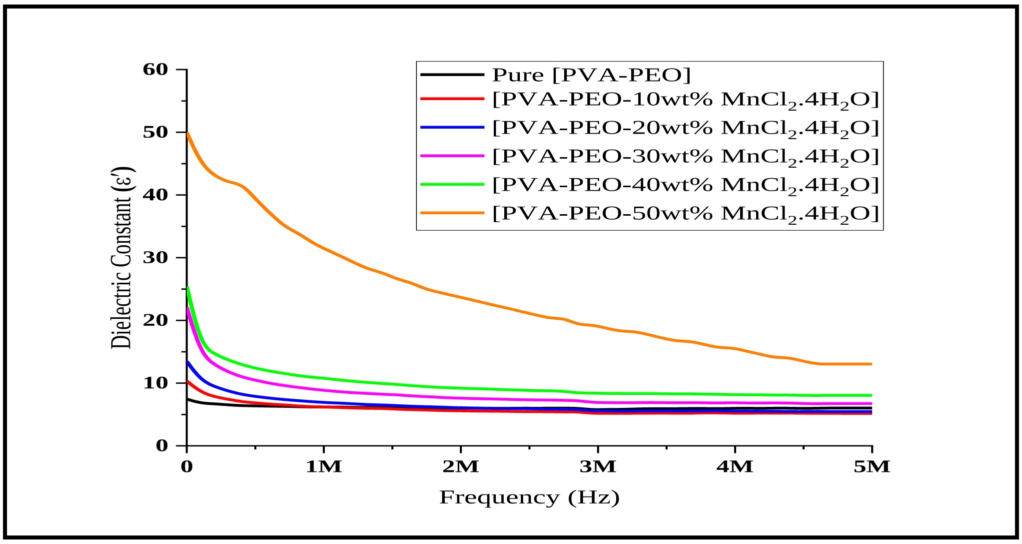


Figure 4: The dielectric constant of the composite film [PVA-PEO-$MnCl_2.4H_2O$] as a function of frequency under different weight ratios of $MnCl_2.4H_2O$ salts.

The conductivity of electrical currents ($\sigma_{a.c}$) is influenced by frequency when it oscillates. To compare the electrical conductivity of a pure blend of (PVA) and (PEO) to blends fortified with $MnCl_2.4H_2O$ salt at different weight ratios, the alternate electrical conductivity of the samples was evaluated at room temperature using a frequency range of (5Hz to 50MHz) as exhibited in figure (5). The results demonstrated that the conductivity of all blend types increased proportionally with frequency. This is due to the oscillation of the electric field, which induces increased polarization and conductivity. The increase in polarity is manifested by the rise in electrical conductivity that shifts between distinct features rapidly, including electrons or dipoles [13]. It is important to note that the alternating electrical conductivity of an insulator functions as an indicator of the power lost when an alternating electric field is applied. The loss of this power results in the production of heat via the rotation of dipoles and oscillation of charges during fluctuations in the electric field's oscillation. It is noteworthy that the abrupt change between different species is the origin of the alternating electrical conductivity. The frequency determines the oscillation of the electrical conductivity [14]. Upon observation of the diagram, it is evident that an increase in the weight proportion of $MnCl_2.4H_2O$ salt results in an increase in the electrical conductivity that oscillates at the same frequency [15]. This growth in electrical conductivity is affected by numerous factors, including the material's purity and distribution. Generally, the escalation of conductivity that alternates is due to the decline of insulation resistance caused by the addition of more conductive molecules to the polymeric blend film. Additionally, the surge in electrical conductivity that alternates is influenced by the number of high relaxation time charge carriers due to the high energy barrier [16].

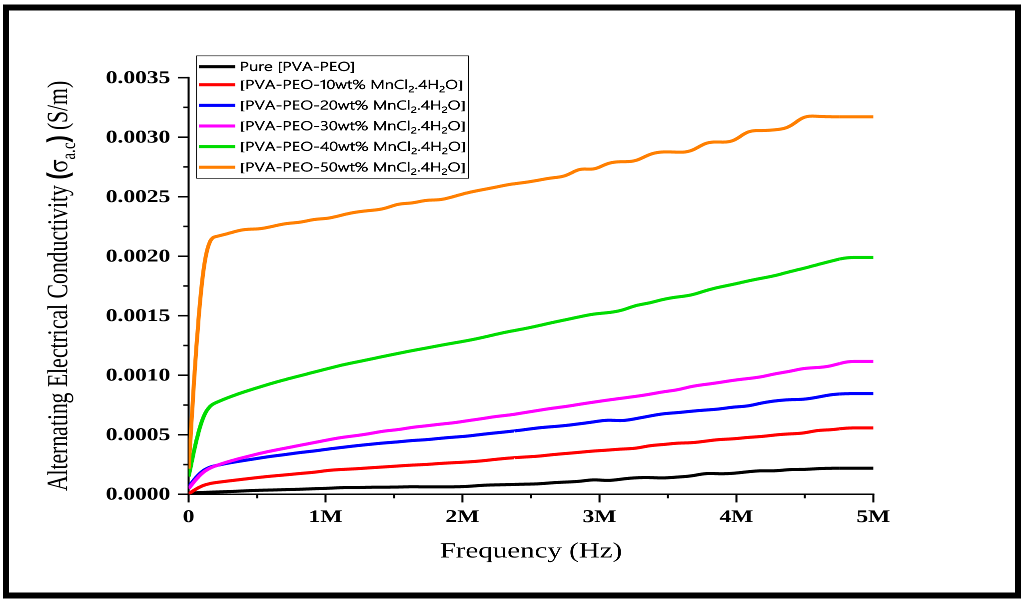


Figure 5: Changes in conductivity of composite films [PVA-PEO-$MnCl_2.4H_2O$] with frequency under different weight ratios of MnCl2.4H2O salts.

Conclusions

During our investigation of pure polymeric blend films that were reinforced by $MnCl_2.4H_2O$ salt, we discovered intriguing outcomes. We experimented with various weight ratios (10, 20, 30, 40, 50) wt% and detected fascinating interactions between the two polymers (PVA) and (PEO) and MnCl2.4H2O salt through the (FTIR) spectral. Our findings demonstrated that an increase in the weight ratio of $MnCl_2.4H_2O$ salt in composite films [PVA-PEO-$MnCl_2.4H_2O$] resulted in a decrease in the energy gap value of the allowed indirect transition of the films. Based on these results, we speculate that these films could potentially serve as an excellent protective covering for solar cells due to their outstanding optical properties. Additionally, as the weight ratio of $MnCl_2.4H_2O$ salt increases in composite films [PVA-PEO-$MnCl_2.4H_2O$], the dielectric constant and alternating electrical conductivity also increase, regardless of frequency, this property makes these polymeric blends perfect for manufacturing electric batteries and capacitors.

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