



Preparation and Study of Some Optical, Thermal and Electrical Properties of polymeric blend Films [PVA: PVP] Reinforced by $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Salt

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Abstract

In this study, films of pure [PVA: PVP] polymeric blends and reinforced with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt were prepared with different weight ratios (10,20,30,40,50 wt. %) by using the solution casting method. However, the optical, thermal, and electrical (insulating) properties of all polymeric blend's films were studied. The transmittance and absorbance spectra were recorded within the wavelength range (190-1100 nm). The impact of salt weight ratio on the energy gap of reinforced polymeric blends films was investigated, and it was discovered that as the weight ratio is increased, the energy gap decreases. Thus, the results showed that indirect electronic transition are allowed. Generally, the practical results of studying the effectiveness of the weight ratio of salt on the thermal properties of reinforced polymeric blends films revealed that as the weight ratio of salt is increased, the thermal conductivity coefficient of reinforced polymeric blends films increases, while the thermal conductivity coefficient of all polymeric blends films remains small. Therefore, these polymeric blends can be used at all weight ratios as heat-insulating shields. It was also discovered that as the weight ratio of salt increases, the glass transition temperature and crystal line melting temperature of reinforced polymeric blends films change. The impact of salt weight ratio on the electrical (dielectric) properties of reinforced polymeric mix films was investigated. The dielectric constant of all polymeric blended films decreased with increasing frequency, according to the experimental data. It also demonstrated that as the frequency of all polymeric blend's films increased, so did the AC electrical conductivity and dielectric constant, as well as a rise in the A.C electrical conductivity and dielectric constant with an increase in the weight ratio of salt at the same frequency.

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Key Words: Polymer blend [PVA-PVP], Calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) salt, differential thermal calorimeter, electrical isolation.

DOI Number: 10.14704/nq.2022.20.5. NQ2256

NeuroQuantology 2022; 20(5):2029-2042

Introduction

Polymers are important materials in the field of modern industries due to their characteristics that made them superior to the traditional materials used. In addition to the low cost of its preparation, it is non-rust and corrosion, it is light in weight, and it has good mechanical properties. Polymerization

and polymers have received the attention of the scientific and industrial community, and a number of researchers have identified polymers and how to study their properties and manufacture, which led to their improvement and expand their uses in various aspects of life. A number of polymers

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Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Received: 24 May 2022 **Accepted:** 30 May 2022



have been classified as insulators, as they have been used in the field of electronic industries to produce useful materials such as electronic circuit boards, materials for electrical insulation, and coatings for electrical wires and electrical connections. Finally, due to the high-temperature characteristics and effort characteristics of a number of polymers, it has become an alternative to many traditional building metals. While the use of reinforced polymers has emerged in prefabricated construction and for good thermal and sound insulation and resistance to weather conditions (Work, Horie, Hess, Stepoto, & chemistry, 2004).

Materials used

1. Base material

1-Polyvinyl alcohol (PVA): it is in the form of granules of white color and it is dissolved faster in distilled water. It is a product of the Indian company HIMEDIA, and its molecular weight averages g/mol (13000-23000).

2-Polyvinylpyrrolidone (PVP): It is in the form of a white, slightly yellowish powder that dissolves faster in distilled water. It is a product of the Indian company HIMEDIA, and its average molecular weight is (40000 g/mol). Figure 1 shows the structural formula of the two polymers above (S. M. K. Kamath, 2015).



Figure 1. The structural formula of the polymers.
a) Polyvinyl alcohol (PVA) b) Polyvinylpyrrolidone polymer (PVP)

2. Reinforcement material

1- Calcium chloride dehydrate

A substance with white crystals soluble in water at a degree (30 oC) bears the chemical formula (CaCl₂.2H₂O). Its most prominent properties are: its molar mass (110.98 g/mol), its density (2.15 g/cm³), and its melting point (772 oC). Figure 2 shows a picture of calcium chloride dihydrate.



Figure 2. Picture of calcium chloride dehydrate (CaCl₂.2H₂O).

Composites Preparation

The casting process was utilized to make the [PVA: PVP] polymeric blend at a certain weight ratio of polymer (PVA) mixed with a specific weight ratio of polymer (PVP). To achieve a homogenous solution, distilled water (15ml) was added to them and stirred for one hour at 60°C using a magnetic stirrer. The solution is then poured into a specific glass mold set on a level surface and let too dry until the solvent evaporates and the sample is ready.

While, for the purpose of preparing the [PVA: PVP] polymeric blend reinforced by CaCl₂.2H₂O salt, certain (PVA) polymer weight ratios were blended with specific weight ratios of (PVP) polymer as well as CaCl₂.2H₂O salt (10,20,30,40,50 wt%) and distilled water was added to them at an amount of (15ml) by using a magnetic stirrer for one hour at (60 oC) to obtain a homogeneous solution. The solutions are then poured into a specific glass mold set on a level surface and permitted to dry until the solvent evaporates and the needed samples are obtained.

The Equipment Used

1. UV-Visible Spectrophotometer

The transmittance and absorption spectra of pure [PVA:PVP] polymeric blends and films of polymeric blends reinforced with CaCl₂.2H₂O salt were recorded within the wavelength range (1100-190 nm) at room temperature, using an apparatus (UV-Visible 1800 double beam spectrophotometer) the factory in the company (Shimadzu, Japanese).

2. Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) and crystalline melting temperature (T_m) were calculated for the pure [PVA:PVP] polymeric blends and films of polymeric blends reinforced with CaCl₂.2H₂O salt using a differential thermal calorimeter (Differential Scanning Colorimeter (DSC) of the type (evo 131) of origin (Setaram French).

3. LCR Metter

The electrical (dielectric) tests represented by the dielectric constant (ε') and the alternating electrical conductivity (σ_{a.c}) for the pure [PVA:PVP] polymeric blends were carried out as a frequency function and films of polymeric blends reinforced with CaCl₂.2H₂O salt using a (LCR Metter) of the type (Agilent Impedance Analyze 4294A) of (Tawan origin).

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Results and Discussion
Optical properties

The optical properties of the film of pure [PVA:PVP] polymeric blends and films of polymeric blends reinforced with CaCl₂.2H₂O salt at different weight ratios were studied, and the transmittance and absorption spectra were recorded at room temperature, as well as the calculation of the energy gap value.

The energy gap for the allowed indirect transition was determined, and figure (3) illustrates the relationship between $(\alpha h\nu)^{1/2}$ and the photon energy (hv) for the film of pure [PVA:PVP] polymeric blend and the films of the polymeric blends reinforced with CaCl₂.2H₂O salt at different weight. The intersection of the (x-axis) of the photon's energy at point $(h\nu/2 = 0)$ is the extension of the best straight line along which most points pass after the absorption edge. The energy gap value of the allowable indirect transition is represented by this point. The energy gaps of all polymeric blend films are shown in Table 1. However, it may be noted from the table that the energy gap value of the film of the pure [PVA: PVP] polymeric blend is (5.169 eV), but when reinforced with CaCl₂.2H₂O salt at various weight ratios, the energy gap value decreases marginally. The decrease in the value of the energy gap by increasing the weight ratio of the added salt can be attributed to the fact that the initial arrangement of the charge carriers and their re-installation as a result of the change in the field size and levels (Ahmed, 2014) .

Table 1. Energy gap value of the allowed indirect transition of [PVA: PVP]-CaCl₂ composite films with the weight ratio of the CaCl₂.2H₂O salt.

Weight Ratio (wt%) of Salt	PVA- PVP- CaCl ₂ .2H ₂ O Eg (eV)
Pure [PVA: PVP] Blend	5.169
10	5.158
20	5.136
30	5.111
40	5.093
50	5.071

Thermal properties
Thermal conductivity

The thermal conductivity coefficient (k) was calculated using (Lee's Disc Method) for the pure [PVA:PVP] polymeric blend film and those films reinforced with CaCl₂.2H₂O salt at different weight ratios. Thus, figure (4) showed that the value of the thermal conductivity coefficient of the pure [PVA:PVP] polymeric blend film is (0.032037 (W/mK)) and when reinforced with CaCl₂.2H₂O salt at different weight ratios, the value of thermal conductivity coefficient increased slightly with increasing the weight ratio of CaCl₂.2H₂O add salt as shown in table (2). The reason for this is that when it is added to the salt, the density of crosslinking increases, which has a significant impact on the molecular chains because the presence of spaces between the polymeric chains decreases as crosslinking increases, making heat transfer from one end to the other through the composite material easier. On the other hand, the thermal conductivity coefficient depends on the ionic diameter and the atomic mass of calcium (Ca⁺) as the electrolyte solution in the polymer. Also, the addition of salt leads to the modification of the hydroxyl groups on the surface of the composite layer and will greatly improve the phonon scattering in polymeric composites. (H.W. AbdAllah, 2016)

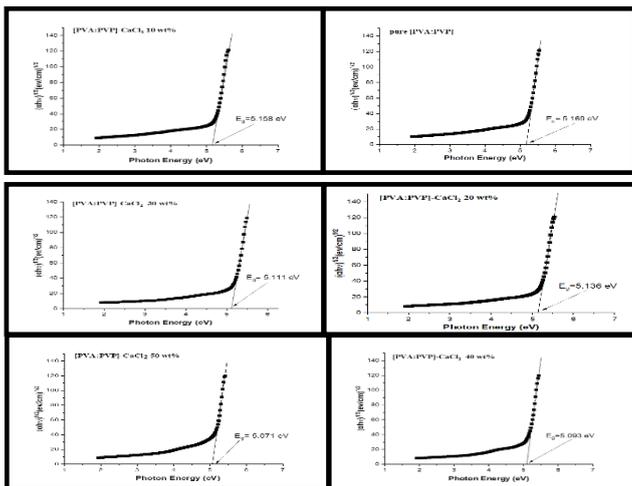


Figure 3. Energy gap of the allowed indirect transition of [PVA: PVP]-CaCl₂ composite films with the different weight ratios of the CaCl₂.2H₂O salt.



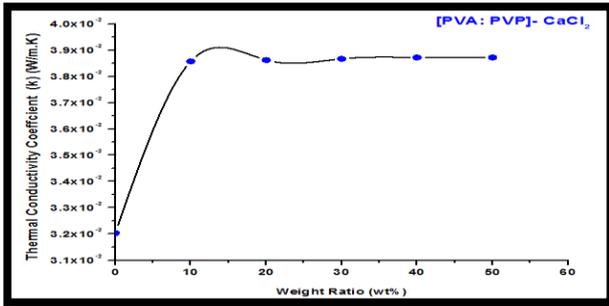


Figure 4. Thermal conductivity coefficient of [PVA:PVP]-CaCl₂ composites films as a function of the weight ratio of the CaCl₂.2H₂O salt.

Table 2. The value of the thermal conductivity coefficient of [PVA:PVP]-CaCl₂ composites films with the weight ratio of the CaCl₂.2H₂O salt.

Weight Ratio (wt%) of Salt	(PVA-PVP-CaCl ₂ .2H ₂ O) k(W/m.K)
Pure [PVA:PVP] Blend	0.032037
10	0.038571
20	0.038621
30	0.038671
40	0.038720
50	0.038721

Glass Transition Temperature

Glass transition temperature (T_g) was calculated, for the film of the pure [PVA:PVP] polymer blend and the films of polymeric blends reinforced with CaCl₂.H₂O salt, at different weight ratios using a differential thermal calorimeter (DSC). Figure (5) shows the values of the glass transition

Table 3. The value of the glass transition temperature of [PVA:PVP]-CaCl₂ composite films with the weight ratio of the CaCl₂.2H₂O salt.

Weight Ratio (wt%) of Salt	[PVA:PVP]-CaCl ₂ .2H ₂ O T _g (°C)
Pure [PVA:PVP] Blend	96.8
10	139
20	130.9
30	122.5
40	110
50	101.8

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temperature of the films of all polymeric blends, as shown in table (3). It may be noted that the value of the glass transition temperature in the polymeric blend film [PVA:PVP] is (96°C) and after reinforcement with CaCl₂.H₂O salt in different weight ratios, we notice that the glass transition temperature increase at the weight ratio (10 wt%) of the reinforcement to reach (139 °C), then it starts decreasing with increasing the weight ratio of CaCl₂.H₂O add salt. This irregular change in the glass transition temperature is caused by the formation of nano-crystal regions of various dimensions and the appearance of varying thicknesses in the crystal fields as a result of the interaction of salt crystals and the matrix material ([PVA:PVP] (polymer [PVA:PVP] blend) (H. M. Zidan). As well as to the decrease in the movement of the chains of the [PVA:PVP] polymeric blend reinforced by salt. When the concentration of salt atoms is increased, the degree of glass transition decreases (Elashmawi, Abdelrazek, Yassin, & Technology, 2014) which is due to agglomeration of salt atoms. It also notice the appearance of an upward peak before the glass transition temperature at the weight ratio (10 wt%) of the reinforcement, which is symbolized by the symbol (T_w), its value (34.8°C). This value indicates the presence of a small amount of moisture in the prepared sample (Es-Saheb & Elzatahry, 2014).



Crystalline Melting temperature

The crystalline melting temperature (T_m) was calculated for the film of the pure [PVA: PVP] polymer blend and the films of polymeric blends reinforced with $CaCl_2 \cdot 2H_2O$ salt at different weight ratios using a differential thermal calorimeter (DSC), where the crystalline melting temperature is used to determine the nature of the material and its purity (Es-Saheb & Elzatahry, 2014). Figure (5) shows the crystalline melting temperature values for the films of all polymeric blends. as shown in table (4), we note that the crystalline melting temperature value of the film of the pure [PVA:PVP] polymeric blend is (215 °C). Following the addition of $CaCl_2 \cdot 2H_2O$ salt in various weight ratios, we note that the crystalline melting temperature begins to rise erratically as the weight ratio of the $CaCl_2 \cdot 2H_2O$ add salt increases. The creation of polymeric molecules that interact with each other is the result of this uneven increase in the crystalline melting temperature. Because the [PVA: PVP] polymeric blend is reinforced by salt, this reaction will affect the crystalline melting temperature of the [PVA: PVP] polymeric blend, as well as a decrease in the bonding strength between salt particles and the tiny size of their crystals (Baraker, Lobo, & Calorimetry, 2018). In general, adding salt $CaCl_2 \cdot 2H_2O$ to the procedure increased the crystalline melting temperature of the pure [PVA: PVP] polymeric blend film. We also notice the appearance of a peak towards the top after the crystalline melting temperature in the pure [PVA: PVP] polymeric blend sample which represents the degree of dissolution (dissociation) and is symbolized by (T_d) and its value (285 oC) (El-Khodary, 2009).

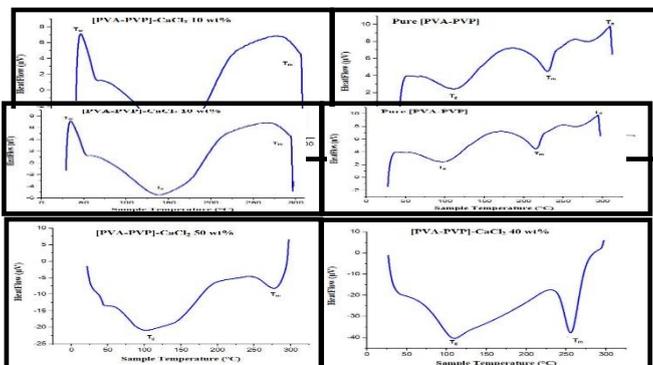


Figure 5. Thermo gravimetric (DSC) plot of the [PVA:PVP]- $CaCl_2$ composite films with the weight ratio of the $CaCl_2 \cdot 2H_2O$ salt.

Table 4. The value of the crystalline melting temperature of [PVA:PVP]- $CaCl_2$ composite films with the weight ratio of the $CaCl_2 \cdot 2H_2O$ salt.

Weight Ratio (wt%) of Salt	[PVA:PVP]- $CaCl_2 \cdot 2H_2O$ T_m (°C)
Pure [PVA:PVP] Blend	215
10	294
20	282
30	262.3
40	255.7
50	276.8

Electrical Properties (Insulating) Dielectric Constant

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At room temperature and throughout the frequency range, the dielectric constant (ϵ') was computed for films made of pure [PVA:PVP] polymer blends and films made of polymeric blends reinforced with $CaCl_2 \cdot 2H_2O$ salt at various weight ratios (50Hz-5MHz). The dielectric constant of all polymeric mixes films falls as the frequency increases, as seen in Figure . We also noticed that all polymeric blend films had high dielectric constant values at low frequencies, but that as the frequency increased, the dielectric constant values decreased. This can be explained by the fact that in the low frequency zone, the time period is long enough for the dipoles to arrange and align the molecules along the direction of the electric current flowing between the two poles. In the case of high frequencies, the time period is short, and it is shorter than the time required by molecules to align themselves with the external electric field's direction. (Rabee & Hashim, 2011). The difference in phases of the matrix material, the reinforced material resulting in inter-polarization, and the polarity of the electrodes are also reasons for high dielectric constant values at low frequencies. The generation of the sample charge between the two electrodes is closely related to the polarization originating from the electrodes. This is determined by the composition of the sample, the distances, and impurities present in the sample. As seen in the figure, with an increase in the weight ratio



of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ added salt, the dielectric constant at the same frequency rises. The rise in the dielectric constant is generally related to an increase in

period due to the high energy barrier (Prakash, Manjunath, & Somashekar, 2013).

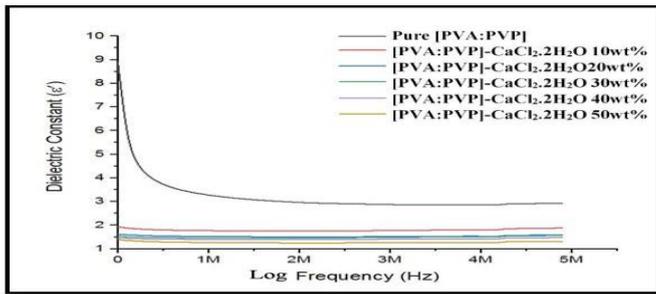


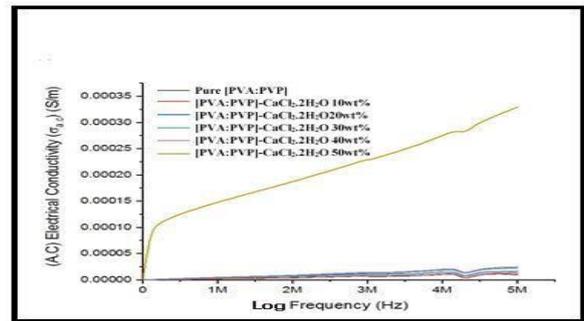
figure 6. The dielectric constant as a function of the frequency of [PVA:PVP]- CaCl_2 composites films with the different weight ratios of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt.

AC Electrical Conductivity

A.C electrical conductivity ($\sigma_{a.c}$) is a function of frequency. The AC electrical conductivity for the film of the pure [PVA:PVP] polymer blend and the films of polymeric blends reinforced with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt was calculated with different weight ratios at room temperature and within the frequency range (50Hz-5MHz). Figure (7) shows that the AC electrical conductivity of all polymeric blends films improves exponentially with increasing frequency due to the electric field oscillation, which causes an increase in polarization in the sample, which results in an increase in A.C electrical conductivity. The rapid transfer between sites of various types, such as electrons or dipoles, causes alternating electrical conductivity (Ramesan, Athira, Jayakrishnan, & Gopinathan, 2016).

It is worth noting that the quantity of power lost when an A.C electric field is applied is the A.C electrical conductivity in the insulator. When the dipoles rotate in their places, heat is generated, and the vibration of the charges is caused by changing the alternating electric field, which is frequency dependent (Popielarz, Chiang, Nozaki, & Obrzut, 2001). Figure (7) shows that raising the weight ratios of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ added salt enhances the A.C electrical conductivity at the same frequency, and that this increase is highly influenced by several aspects, including material purity and dispersion. This increase in A.C electrical conductivity is attributable to decreased insulator resistance due to the increased number of conductive molecules in the polymeric mix film [14], as well as the increased number of charge carriers with a long relaxation

figure 7. A.C electrical conductivity as a function of the frequency [PVA: PVP]- CaCl_2 composites films with the different weight ratios of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt.



Conclusions

After conducting the study and research on the films of pure [PVA: PVP] polymeric blends and reinforced with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt with different weight ratios ((10, 20, 30, 40, 50) wt

%), it was found that the transmittance and absorbance spectrum of the films of all polymeric blends have an absorption coefficient less than (104 cm^{-1}) this, the indirect electronic transitions are allowed indirect within the range of wavelengths (1100-190) nm, and the energy difference narrowed as the weight ratio of additional salt increased. The study showed an conductivity coefficient of the film of the pure [PVA:PVP] polymeric blend after the process of reinforced with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt. The glass transition temperature and crystalline melting temperature of pure [PVA:PVP] polymeric blends reinforced with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt with different weight ratios start to increase irregularly with the increase in the weight ratio of the added salt for all weight ratios, according to differential thermal calorimetry (DSC). When the weight ratio of the reinforcement material is increased at the same frequency within the frequency range, the value of the dielectric constant and the A.C electrical conductivity increases (50 Hz-5 MHz).

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