

STUDY OF THERMAL AND DIELECTRIC PROPERTIES OF (PVA-MnCl₂·4H₂O) COMPOSITE

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ABSTRACT

The pure film of polymer (PVA) and films filled with Manganese Chloride (MnCl₂·4H₂O) salt with different weight ratios ((1,3,5,7,9,11,13,15) wt%) have been prepared by using casting method. The thermal and dielectric properties of (PVA-Manganese Chloride) composites films have been studied. The results of the thermal tests show that the behavior of the thermal conductivity coefficient for composites films was unsystematic after filling with different weight ratios of the added Manganese Chloride salt, the differential scanning calorimetric (DSC) test shows that in both the glass transition and crystalline melting point began an unsystematic increase by increasing the weight ratio of the added Manganese Chloride salt. The results of the dielectric measurements for composites films show that in both the dielectric constant and dielectric loss a decreases with increased the frequency, and the (A.C) electrical conductivity increases with increased the frequency, and increases the dielectric constant, dielectric loss and (A.C) electrical conductivity with the increase of the weight ratio of the added Manganese Chloride salt.

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INTRODUCTION

The development of new polymers, blends, composites and advanced materials becomes necessity for modification of mechanical, electrical, optical and thermal properties to fulfill the required characteristics (Sperling, 2006). The development runs parallel with intense series of studies aiming to enlighten the structure-property relationship of the modified materials. The optical, electrical and thermal characterization of new polymeric films is an essential for the development of such films (Alterovitz *et al.*, 1989). 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 (Hassan, 1998). (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 (Guirguis and Moselhey, 2012). Moreover, (PVA) is also nontoxic, potential material having high dielectric strength, good charge storage capacity and dopant dependent electrical and optical properties (Hemalatha *et al.*, 2015).

EXPERIMENTAL DETAILS

Materials and samples preparation

In the preparation of composites films we are used polymer Polyvinyl alcohol (PVA), which is product by Central House (P) Ltd of India with molecular weight (13000-23000) g / mol, and Manganese Chloride (MnCl₂·4H₂O) salt which is product by (Central Drug House (P), Ltd. New Delhi-110002(INDIA) company with molecular weight (197.9 g/mol). The polymer (PVA) and (MnCl₂·4H₂O) salt with different weight ratios ((1,3,5,7,9,11,13,15)wt%) were dissolved in distilled water by stirred for (1hr.) by using magnetic stirrer at (80°C) for completely dissolved. The solutions poured on to a glass plates and left to dry for (24 hr.) to remove any residual solvent. Films thickness were (40-140) μm for thermal testing and (1450-1455) μm for dielectric testing by using digital micrometer.

For the purpose of thermal tests:

- **Thermal Conductivity Test:** Using the Lee's Disc method the device manufactured at the company (Griffen and George) English.
- **Glass Transition Temperature (T_g) and Crystalline Melting Temperature (T_m) Test:** Using a Differential

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Scanning Colorimeter (DSC) (Shimadzu) of origin (Linseis Company Japan).

And for the purpose of dielectric measurements, the (LCR Meter) from (Agilent Impedance Analyz 4294A) company of the origin (Taiwan) was used, and the frequency range of (50Hz-5MHz) in the room temperature.

RESULTS AND DISCUSSION

Thermal Properties

Thermal Conductivity (k): The thermal conductivity coefficient (k) was calculated using Lee's Disc Method. Figure (1) shows the thermal conductivity coefficient values of pure (PVA) polymer film and films filled with (MnCl₂) salt with different weight ratios ((1,3,5,7,9,11,13,15) wt%), we observe through the figure that the thermal conductivity coefficient value of pure (PVA) polymer film is (0.028126W/m.K) and when it is filled with (MnCl₂) salt with different weight ratios, the value of the thermal conductivity coefficient changes. We observe through the figure that the thermal conductivity coefficient value increases with increase in the weight ratio of the added (MnCl₂) salt from (1wt%) to (3wt%) and when increasing the weight ratio of the added (MnCl₂) salt to (5wt%) the value of the thermal conductivity coefficient will become unsystematic, in general, the process of filled with (MnCl₂) salt at most weight ratios increased the thermal conductivity coefficient value of a pure (PVA) polymer film. That the unsystematic of the value of the thermal conductivity coefficient may be because the not homogeneous between the base material (polymer (PVA)) and (MnCl₂) salt because to large surface area for (MnCl₂) salt (Kovacevic *et al.*, 2002). The Table (1) shows the thermal conductivity coefficient values for (PVA-MnCl₂) composites films.

Table 1. Thermal conductivity values for (PVA-MnCl₂) composites films with the weight ratio of (MnCl₂) salt

Concentration (wt%) of Salt	(PVA-MnCl ₂) k (W/m.K)
Pure (PVA)	0.028126
1	0.04815
3	0.445466
5	0.036325
7	0.058088
9	0.186024
11	0.067885
13	0.020475
15	0.093227

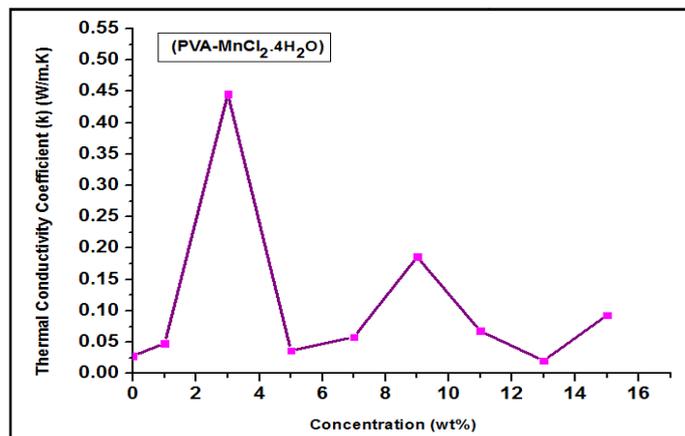


Figure 1. Thermal conductivity for (PVA-MnCl₂.4H₂O) composites films as a function of the weight ratio of (MnCl₂.4H₂O) salt

Glass Transition Temperature (T_g)

The glass transition temperature (T_g) was calculated of pure (PVA) polymer film and films filled with (MnCl₂) salt with different weight ratios ((1,3,5,7,9,11,13,15)wt%), by using Differential Scanning Colorimeter (DSC), figures from (2) to (10) show the values of the glass transition temperature (T_g) of pure (PVA) polymer film and (PVA-MnCl₂.4H₂O) composites films and as shown in the table (2), we observe in the pure (PVA) polymer film and (PVA-MnCl₂.4H₂O) composites films the appearances of the peak towards the top (exothermic) and which is symbolized by the symbol (T_w) and it's located before the glass transition temperature at (25.58 °C) for a pure (PVA) polymer film and within the temperature range (28.12-39.1)°C of (PVA-MnCl₂.4H₂O) composites films, the reason for the appearance of this peak is the presence of a small amount of moisture in the prepared samples (Elashamwi *et al.*, 2014). We also observe that the glass transition temperature value of pure (PVA) polymer film is (110.28 °C). When filled with (MnCl₂) salt we observe that the glass transition temperature value begins to increase unsystematic to reach the highest value is (216.90 °C) at the weight ratio (1wt%), this the unsystematic increase in the glass transition temperature value results from the interaction between the molecules (the Hydrogen atoms) that occurs between the pure (PVA) polymer and (MnCl₂) salt (Mudigoudra *et al.*, 2012).

Crystalline Melting Temperature (T_m)

The crystalline melting temperature (T_m) was calculated of pure (PVA) polymer film and films filled with (MnCl₂) salt with different weight ratios ((1,3,5,7,9,11,13,15)wt%), by using Differential Scanning Colorimeter (DSC), the crystalline melting temperature is used to determine the nature of the substance and it's purity (4). Figures from (2) to (10) show the values of the crystalline melting temperature (T_m) of pure (PVA) polymer film and (PVA-MnCl₂.4H₂O) composites films and as shown in the Table (2), we observe that the crystalline melting temperature value of pure (PVA) polymer film is (220.25 °C). When filled with (MnCl₂) salt we observe that the crystalline melting temperature value begins to increase unsystematic to reach the highest value is (283 °C) at the weight ratio (7wt%), this the unsystematic increase in the crystalline melting temperature value it is due to an increase in (PVA) polymer crystalline phase because filled of (MnCl₂) salt (El-Khodary, 2009).

Table 2. Glass transition temperature (T_g) and crystalline melting temperature (T_m) for (PVA-MnCl₂) composites films with the weight ratio of (MnCl₂) salt

Concentration (wt%) of Salt	(PVA-MnCl ₂) T _g (°C)	(PVA-MnCl ₂) T _m (°C)
Pure (PVA)	110.28	220.25
1	216.90	278.2
3	214.21	255.39
5	212.23	280.5
7	210.53	283
9	212.31	280
11	207.30	279.08
13	207.93	275
15	205.32	274.71

Dielectric Properties

Dielectric Constant: The dielectric constant (ε') of pure (PVA) polymer film and films filled with (MnCl₂) salt with different weight ratios ((3,7,11,15)wt%) at room temperature and frequency range (50-1000000)Hz as shown in Figure (11),

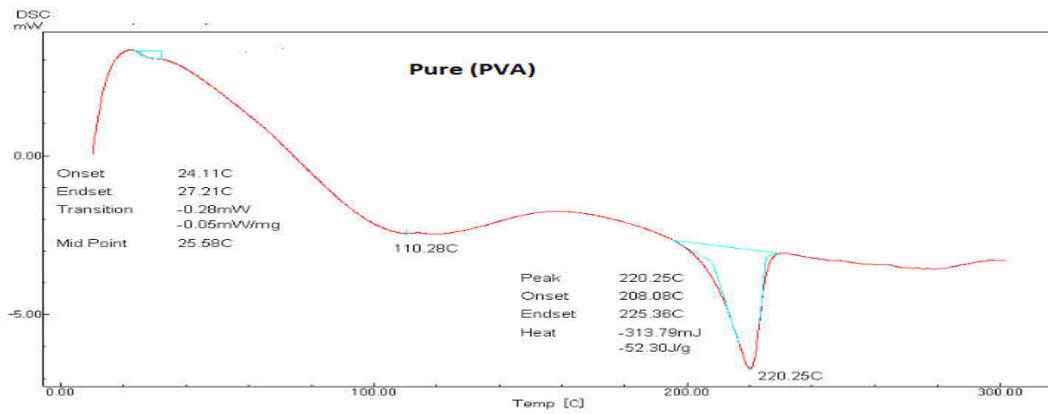


Figure 2. Diagram of weight thermal (DSC) of pure (PVA) polymer film

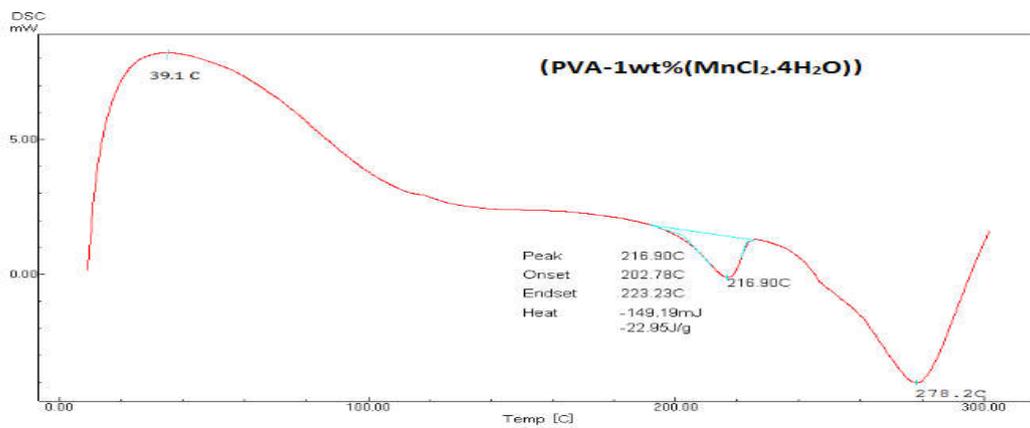


Figure 3. Diagram of weight thermal (DSC) for (PVA-MnCl₂.4H₂O) composite film at the weight ratio (1wt%) of (MnCl₂.4H₂O) salt

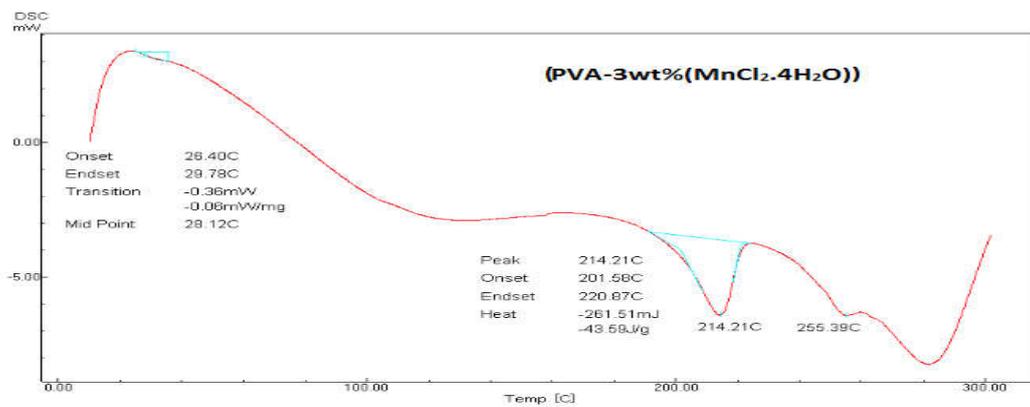


Figure 4. Diagram of weight thermal (DSC) for (PVA-MnCl₂.4H₂O) composite film at the weight ratio (3wt%) of (MnCl₂.4H₂O) salt

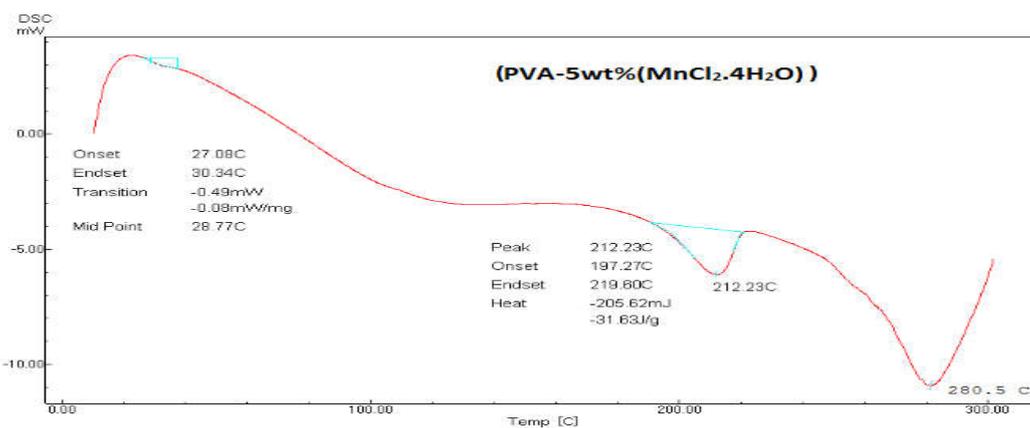


Figure 5. Diagram of weight thermal (DSC) for (PVA-MnCl₂.4H₂O) composite film at the weight ratio (5wt%) of (MnCl₂.4H₂O) salt

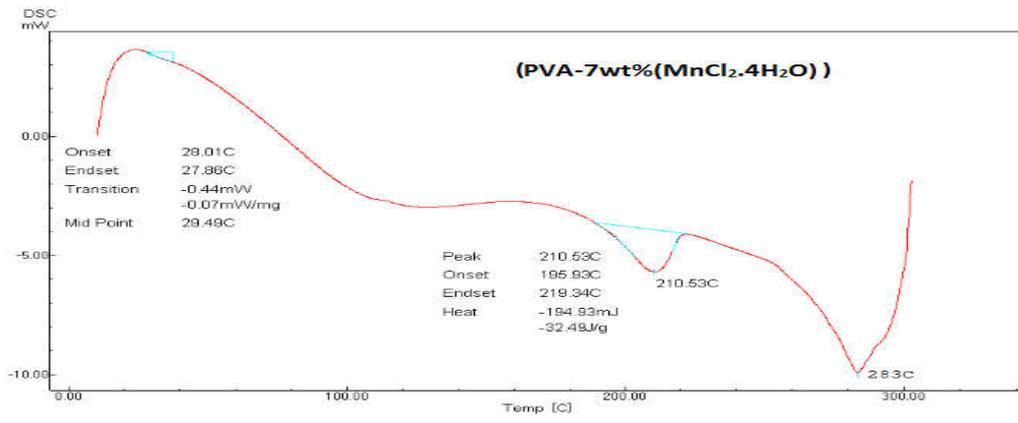


Figure 6. Diagram of weight thermal (DSC) for (PVA-MnCl₂·4H₂O) composite film at the weight ratio (7wt%) of (MnCl₂·4H₂O) salt

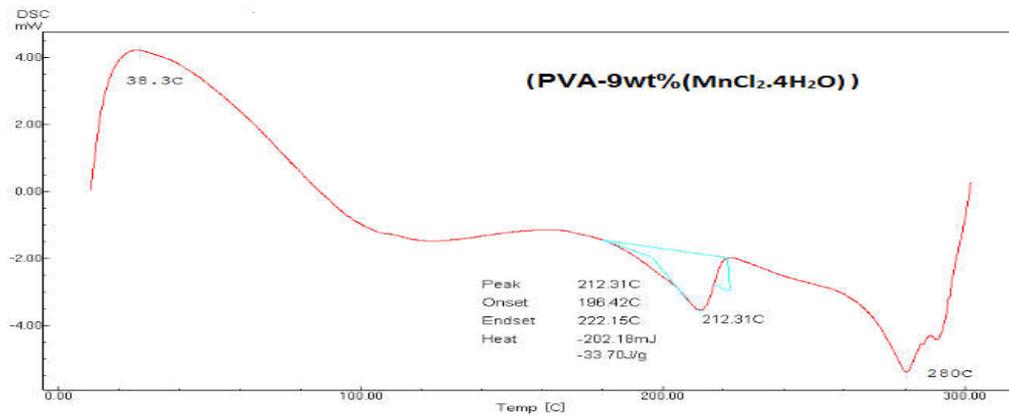


Figure 7. Diagram of weight thermal (DSC) for (PVA-MnCl₂·4H₂O) composite film at the weight ratio (9wt%) of (MnCl₂·4H₂O) salt

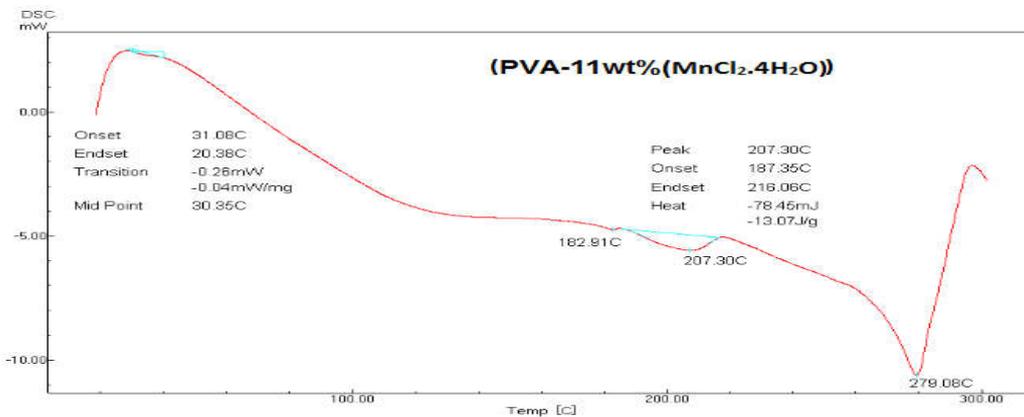


Figure 8. Diagram of weight thermal (DSC) for (PVA-MnCl₂·4H₂O) composite film at the weight ratio (11wt%) of (MnCl₂·4H₂O) salt

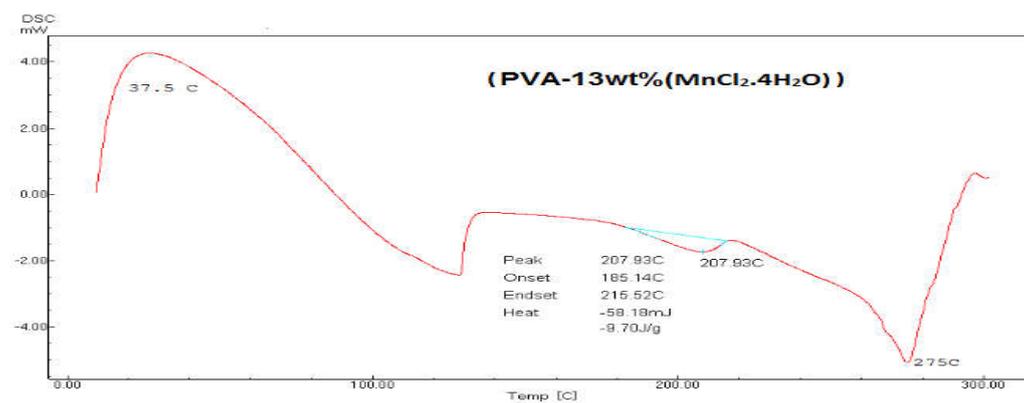


Figure 9. Diagram of weight thermal (DSC) for (PVA-MnCl₂·4H₂O) composite film at the weight ratio (13wt%) of (MnCl₂·4H₂O) salt

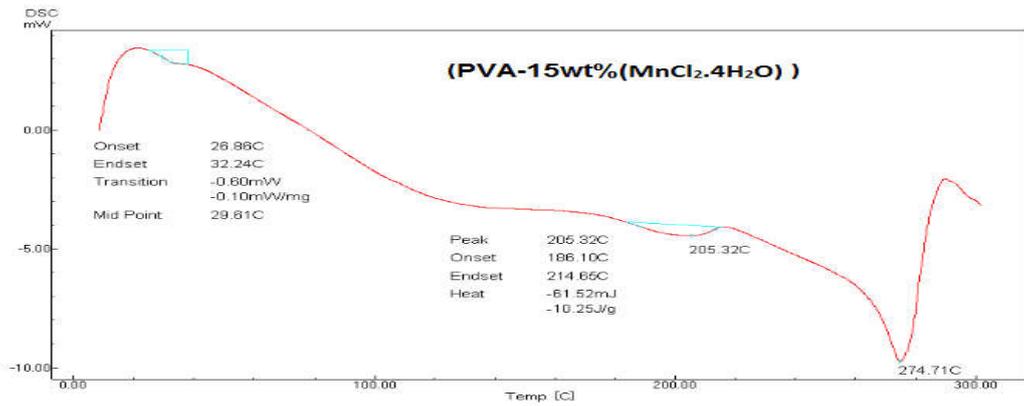


Figure 10. Diagram of weight thermal (DSC) for (PVA-MnCl₂.4H₂O) composite film at the weight ratio (15wt%) of (MnCl₂.4H₂O) salt

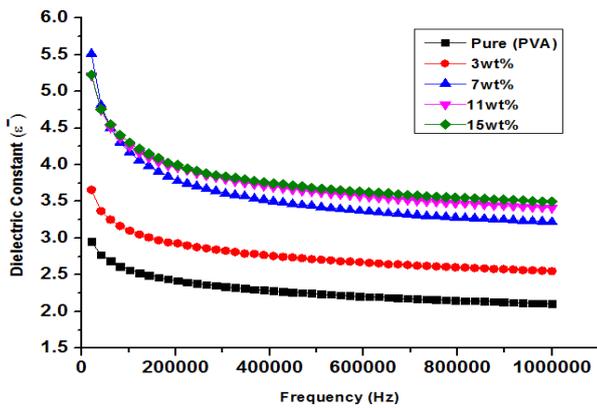


Figure 11. Dielectric constant as a function of frequency for (PVA-MnCl₂.4H₂O) composites films with different weight ratios of (MnCl₂.4H₂O) salt

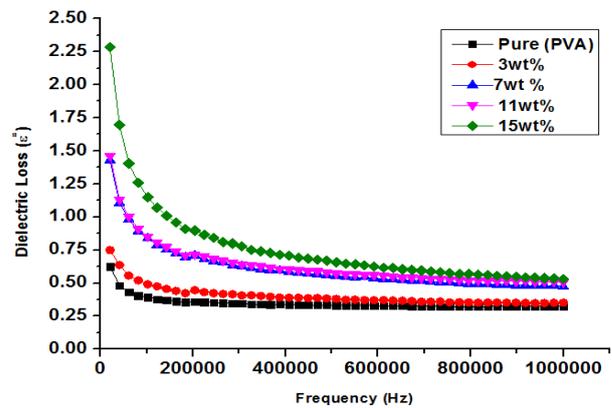


Figure 12. Dielectric loss as a function of frequency for (PVA-MnCl₂.4H₂O) composites films with different weight ratios of (MnCl₂.4H₂O) salt

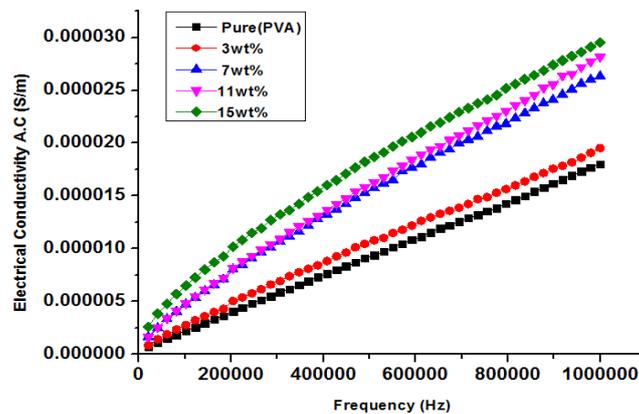


Figure 13. Electrical conductivity (A.C) as a function of frequency for (PVA-MnCl₂.4H₂O) composites films with different weight ratios of (MnCl₂.4H₂O) salt

we observe through the figure that the dielectric constant decreases with increasing frequency for all composites films. We also observe that at low frequencies all composites films have high values of the dielectric constant and when increasing the frequency the values of dielectric constant is decreasing, this can be explained that at the region of the low frequency the time period is enough for the dipoles to arrange the particles and toss them with the direction of the electric current which walking between the poles, but at high frequencies the time period is short and less than the time period which molecules need it to be able to arrange themselves with the direction of the external electric field (Rabee and Hashim, 2011).

Also, the reason that the values of the dielectric constant be high at low frequencies is the phases difference of the base material and the filler material which results from it the inter polarization as well as the polarization of poles, the resulting polarization, from electrodes has a strong relationship in the composition of sample charge between poles, and this depends on the structural of sample, distances and impurities found within the sample. We also observe by figure (11) that the value of the dielectric constant at the same frequency increases by increasing the weight ratio of the added (MnCl₂) salt, in general, this increases in the value of the dielectric constant is due to increased the polarization (Liang and Tjong, 2008 and Psarras *et al.*, 2007).

Dielectric Loss: Is the part of the energy of the electric field that dissipates as heat through the dielectric. The dielectric loss (ϵ'') of pure (PVA) polymer film and films filled with (MnCl₂) salt with different weight ratios ((3,7,11,15) wt%) at room temperature and frequency range (50-1000000)Hz as shown in figure (12), we observe through the figure that the dielectric loss decreases with increasing frequency for all composites films. And we observe that the value of the dielectric loss be high at the low frequencies for all composites films as a result of the mobility of the dipoles because in order not to keep up the dipoles with the applied electric field and the dielectric loss remains constant at high frequencies (Rabee and Hashim, 2011). We also observe by figure (12) that the value of the dielectric loss at the same frequency increases by increasing the weight ratio of the added (MnCl₂) salt (Barzic and Barzic, 2015), in general, this increases in the value of the dielectric loss is attributable to the increase in ionic charge carriers (Noor and Mehdi, 2015).

Electrical Conductivity (A.C): The electrical conductivity (A.C) is a function of frequency. The electrical conductivity (A.C) of pure (PVA) polymer film and films filled with (MnCl₂) salt with different weight ratios ((3,7,11,15)wt%) at room temperature and frequency range (50-1000000) Hz as shown in figure (13), we observe through the figure that the electrical conductivity (A.C) increase with increasing frequency for all composites films. We also observe by figure (13) that the electrical conductivity (A.C) at the same frequency increases by increasing the weight ratio of the added (MnCl₂) salt, this increase is strongly affected by many factors including purity of matter and dispersion, the reason for increasing the electrical conductivity (A.C) by increase in the weight ratio of the added (MnCl₂) salt to that the electrical conductivity (A.C) for the (MnCl₂) salt can be high compared to the electrical conductivity (A.C) of the base material (polymer (PVA)) and which are few as well as to create network from (MnCl₂) salt on shape conglomerates at increase the weight ratio for (MnCl₂) salt which create is a continuous path conductive inside the composite material whenever increase the weight ratio for the salt (Verma *et al.*, 2014). And the reason for a continuous path conductive lead to increase the electrical conductivity (A.C) and there value is determined by effect of polarization and movement of electrons in the base material (Mohamed and Saadi, 2016).

CONCLUSIONS

The main conclusions of this study were:

- The value of thermal conductivity coefficient increases with increase the weight ratio of the added (MnCl₂) salt from (1wt%) to (3wt%) and when increasing the weight ratio of the added (MnCl₂) salt to (5wt%) the value of the thermal conductivity coefficient will become unsystematic.
- We observe that the glass transition temperature value of pure (PVA) polymer film is (110.28 °C). When filled with (MnCl₂) salt we observe that the glass transition temperature value begins to increase unsystematic to reach the highest value is (216.90 °C) at the weight ratio (1wt%).
- We observe that the crystalline melting temperature value of pure (PVA) polymer film is (220.25 °C). When filled with (MnCl₂) salt we observe that the crystalline melting temperature value begins to increase

unsystematic to reach the highest value is (283 °C) at the weight ratio (7wt%).

- We observe that the dielectric constant, dielectric loss and electrical conductivity (A.C) at the same frequency increases by increasing the weight ratio of the added (MnCl₂) salt.

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