Some electrical properties of PVA:PEG/$MnCl_2$ thin film composites

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Abstract

PVA:PEG/$MnCl_2$ composites have been prepared by adding ($MnCl_2$) to the mixture of the poly vinyl alcohol (PVA) and poly ethylene glycol (PEG) with different weight percentages (0, 2, 4, 6, 8 and 10) wt.% by using casting method. The type of charge carriers, concentration (n_H) and Hall mobility (μ_H) have been estimated from Hall measurements and show that the films of all concentration have a negative Hall coefficient. In D.C measurement increase temperature leads to decrease the electrical resistance. The D.C conductivity of the composites increases with the increasing of the concentration of additive particles and temperature. The activation energy decreases for all composites with increasing the concentration of the additive particles. The A.C conductivity increases with increasing of the frequency and the concentration of $MnCl_2$ particles. The A.C electrical properties show that the dielectric constant and dielectric loss of the composites decrease with increasing of the frequency.

Key words
Electrical properties, PEG matrix, $MnCl_2$ filler, Composite, Dielectric constant, AC-Conductivity, Polarization.

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بعض الخواص الكهربائية للاغشية لخليط بولي فنيل الكحول (PVA) وبولي اثيلين كلايكول (PEG) مع اوكسيد المنغنيز

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الخلاصة

أظهرت نتائج دراسة تأثير إضافة ثنائي أوكسيد المنغنيز ($MnCl_2$) لخليط بولي فنيل الكحول (PVA) وبولي اثيلين كلايكول (PEG) بتراكيز وزنية مختلفة (0, 2, 4, 6, 8 and 10) wt.% باستخدام طريقة الصب. تم قياس نوع حاملات الشحنة والتركيز ومعامل هول من قياسات هول وتبين ان الأغشية المحضرة لكل النسب هي من نوع معامل هول السالب. من قياسات الكهربائية المستمرة تبين بزيادة درجة الحرارة تزداد المقاومة الكهربائية. التوصيلية المستمرة تزداد للمتراكب بزيادة تراكيز المادة المضافة ودرجه الحرارة. طاقة التنشيط تقل لجميع المتراكبات مع زيادة تركيز كلوريد المنغنيز ودرجة الحرارة. التوصيلية المتناوبة تزداد بزيادة التردد وتركيز اوكسيد المنغنيز. الخواص الكهربائية المتناوبة بينت ان ثابت العزل وثابت الفقد للمتراكب تقل مع زيادة التردد.

Introduction

Polymeric materials were given a great interest, such as the ease of fabrication, low cost, light weight, ease of chemical modification and excellent insulation or good conduction properties, in many industrial application owing to their desirable characteristics and properties which made them favorable compared to other commercial materials [1,2]. Considerable efforts focused on an applied research in the field of polymer composites to turn these materials into useful products for electronic industry. This is mainly because they possess interesting properties which can be utilized to develop a lot of related potentials. Recently, many reports have appeared in literature dealing with the effects of the filler concentration, frequency of the applied field and temperature on the physical properties of the conductive polymer composite such as impedance, dielectric behavior and electrical conduction [3-5].

Many studies showed that physical properties of polymers clearly depended on many factors concerning their preparation methods and chemical structure [6]. The thermal stabilities of crystalline PEG-$MnCl_2$ system depend on the salt molar ratio, the PEG molecular weight, the choice of the solvent and the concentration and the thermal history. The melting temperatures also, depend on the nature of the complexion salts [7].

The poly vinyl alcohol (PVA) is a polymer with exceptional properties such as water solubility, biodegradability, biocompatibility, non-toxicity, and non-carcinogenetic that possesses the capability to form hydrogels by chemical or physical methods [8]. PVA has high enough tensile strength and satisfactory flexibility. The PEG polymer has a wide range of application including the use as pharmaceutical recipients, food additives and plasticizers [9]. Studies were centered on the enhancement of its ionic conductivity with the aim of developing the material to have the promising electrical application [9,10]. In the present study, the electrical properties of PVA:PEG/$MnCl_2$ composites is investigated as a function of applied frequency and concentration to use this polymeric materials in many industrial applications owing to their desirable characteristics and properties which made them favorable compared to other commercial materials.

Experimental part

The materials used in the present work were poly-vinyl alcohol (PVA) and Poly-ethylene glycol (PEG) with addition of different concentrations from ($MnCl_2$). All the polymer composite films were prepared by casting from solution. Equal weights (one gram of PVA and PEG) with ratio (50:50) wt.% was first dissolved in the common solvent (30 ml of distilled water) and then both polymers were homogeneously mixed using a magnetic stirrer at the constant temperature 325K for 12 hours. Complete homogeneous solution was casted on teflon petri-dishes and left until the evaporation of the solvent. The resulting PVA:PEG films were dried up to four 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 and 10) wt.%. mixed using a magnetic stirrer at the constant temperature at 373 K for 12 hours until a homogenous solution is obtained. The resulting solution was then cast to glass slides and leave over it for about 72 hr. After drying, the films were kept in vacuum desiccators until use. The thicknesses of films were in ranging from 0.15 to 0.2 μm using micrometer. The type of charge carriers, concentration (n_H) and Hall mobility (μ_H), have been estimated from Hall measurements.

Results and discussion

1- Hall effect

The films of all concentration have a negative Hall coefficient (n–type charge carriers). Table 1 illustrates electrical parameters for (PVA:PEG/$MnCl_2$) films at different concentration of $MnCl_2$ (2, 4, 6, 8 and 10) wt.%.

Table 1: Electrical parameters for PVA:PEG/$MnCl_2$ thin films.

Sample	σ_{RT} *10^{-6} (Ω^{-1}.cm^{-1})	R_H*10^5	n (cm^{-3})*10^{13}	type	μ_H (cm^2/V.sec)
PVA	7.73	140	0.045	p	108.22
PEG	5.74	-225	0.028	n	129.16
PVA:PEG	4.46	-30.5	0.205	n	13.62
PVA:PEG With $MnCl_2$					
2%	5.43	-20.5	0.305	n	11.14
4%	6.94	-3.80	1.643	n	2.64
6%	8.80	-0.924	6.764	n	0.81
8%	12.3	-0.323	19.344	n	0.40
10%	17.3	-0.083	75.211	n	0.14

It is note from Table 1 that the carriers' concentration (n_H) increases while Hall mobility (μ_H) decreases with the increase of the $MnCl_2$ particles concentration.

2- D.C conductivity

The variation of D.C electrical conductivity of PVA:PEG as a function of ($MnCl_2$) particles concentrations is shown in Fig. 1 From this figure, the electrical conductivity increases with the increase of the concentration of ($MnCl_2$) particles. The increase in D.C electrical conductivity of composite is a result to the rearrangement of $MnCl_2$ particles throughout the polymer matrix [11]. The electrical conductivity could be increased as a result of increasing of electronic charge carriers which can be increased due to increasing filler content [12].

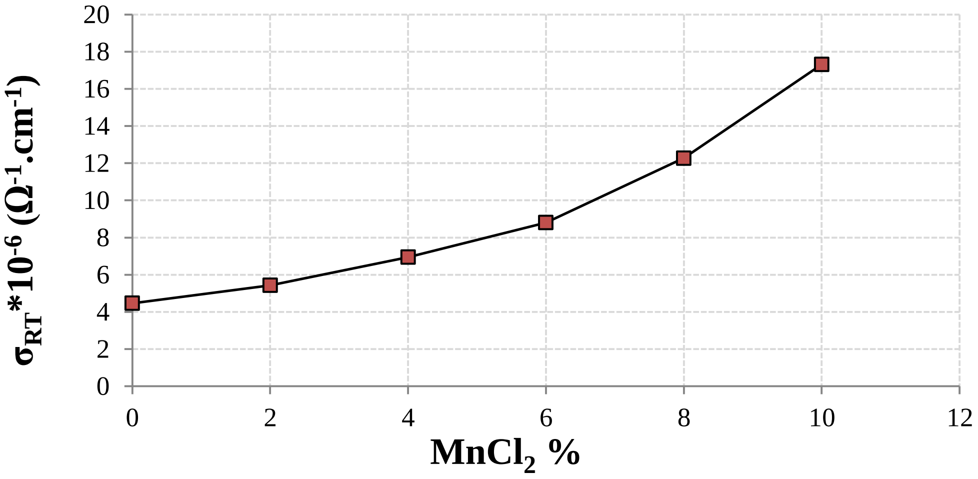

Fig.1: D.C conductivity with different concentration of $MnCl_2$ particles.

3- The activation energy of PVA:PEG/$MnCl_2$ composites

The relation between ln(σ) and the inverse absolute temperature for (PVA:PEG/$MnCl_2$) composites shown in Fig. 2 (A and B).

The activation energy was calculated by using equation [13]:

$$\sigma = \sigma_O \exp\left(-E_{act} / K_B T\right)$$

where:

σ: is electrical conductivity at temperature T.

σ_0: is electrical conductivity at absolute zero temperature.

K_B: is Boltzmann constant.

E_{act}: is Activation Energy.

The high values existence for activation energy in state pure polymer.

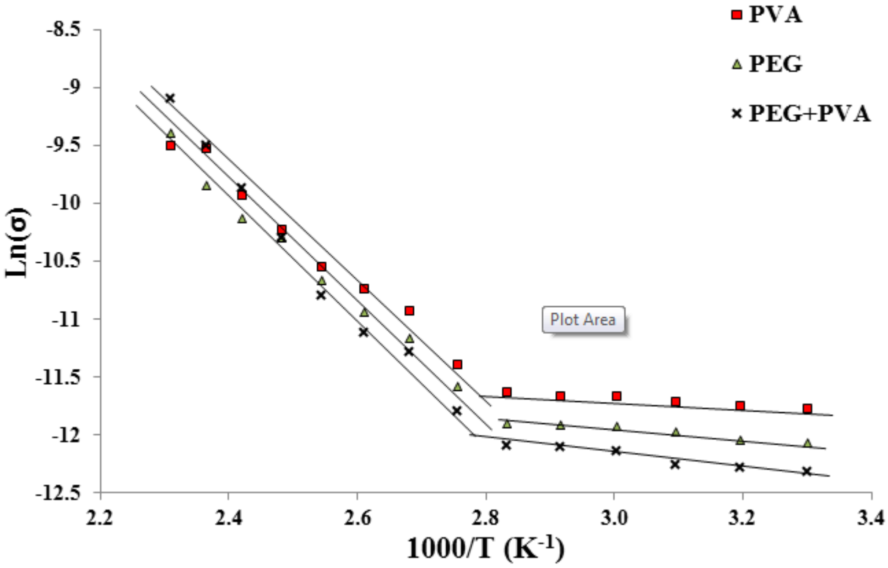

Fig. 2(A): The relation between ln(σ) and the inverse absolute temperature for (PVA, PEG and PVA:PEG) composites.

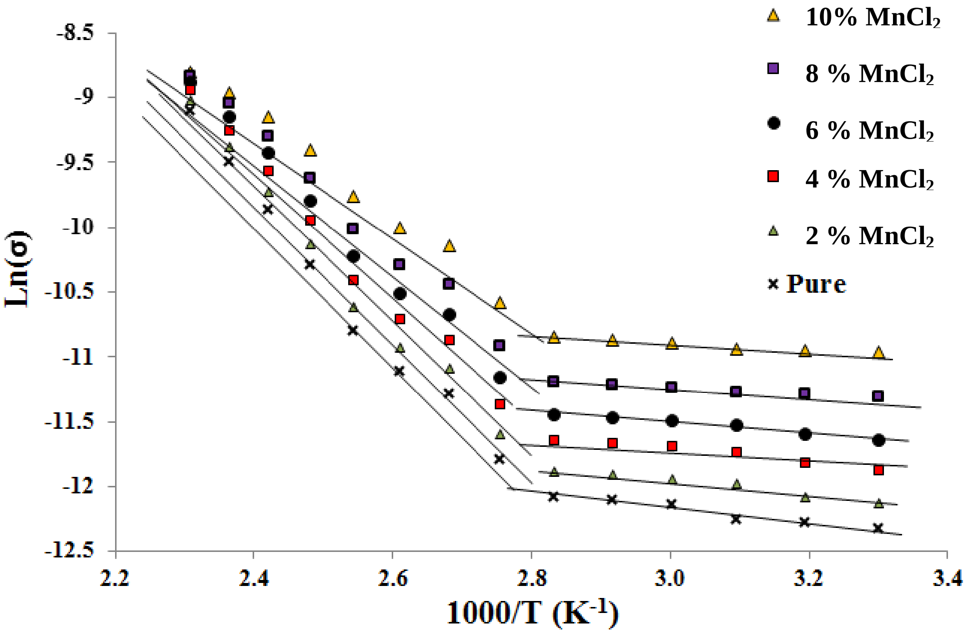

Fig. 2(B): The relation between ln(σ) and the inverse absolute temperature for (PVA:PEG/$MnCl_2$) composites.

When adding $MnCl_2$ particles, the values of the activation energy decreases for all (PVA:PEG/$MnCl_2$) composites as a result of the impact of space charge. The addition of $MnCl_2$ creates local energy levels in the forbidden energy gap which act as traps for charge carriers, which move by hopping among these levels [4]. When increasing $MnCl_2$ particles concentrations, the activation energy decreases as a result of the increase of local centers, as shown in Table 2.

Table 2: Activation energy for (PVA:PEG/$MnCl_2$) composites.

Sample	E_{a1} (eV)	Range (K)	E_{a2} (eV)	Range (K)	σ_{RT} x10^{-6} ($\Omega^{-1}.cm^{-1}$)
PVA	0.026	303-353	0.367	353-433	7.73
PEG	0.034	303-353	0.395	353-433	5.74
PEG:PVA(0%)	0.047	303-353	0.492	353-433	4.46
2 %	0.045	303-353	0.474	353-433	5.43
4 %	0.044	303-353	0.450	353-433	6.94
6 %	0.037	303-353	0.428	353-433	8.80
8 %	0.022	303-353	0.396	353-433	0.123
10 %	0.022	303-353	0.345	353-433	0.173

4- The A.C electrical properties of the Composite

Fig. 3A shows the variation of the dielectric constant of (PVA, PEG and PVA:PEG) composites with frequency.

Fig. 3B shows the variation of the dielectric constant of (PVA:PEG-$MnCl_2$%) composites with frequency.

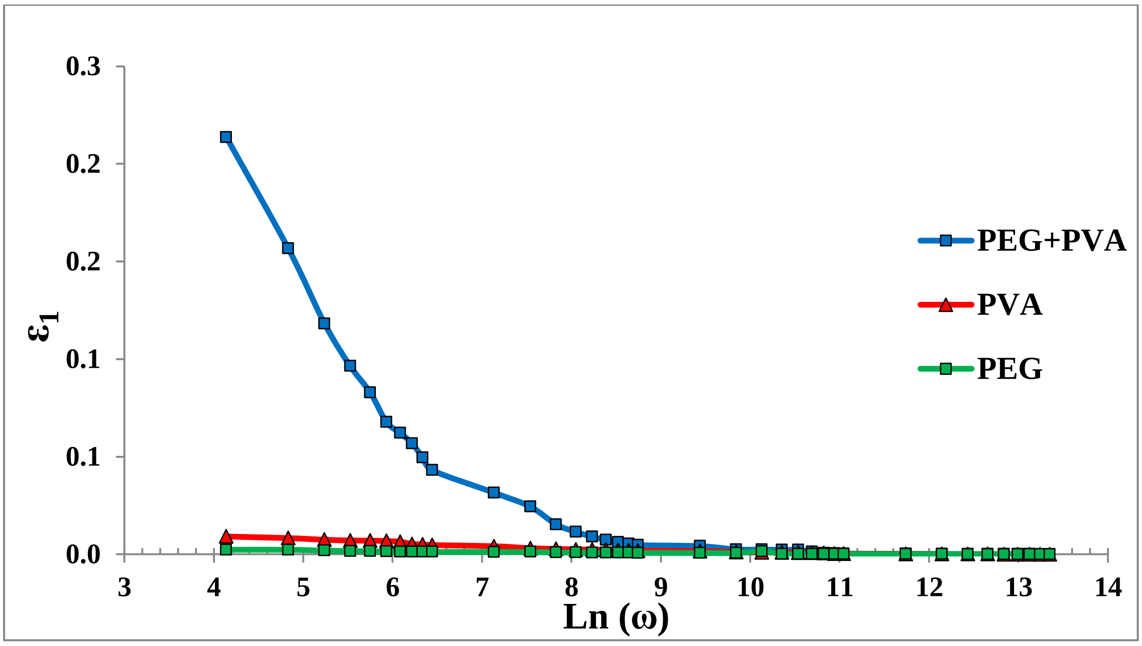

Fig. 3A: The variation of the dielectric constant with frequency for PVA, PEG and PVA+PEG composites.

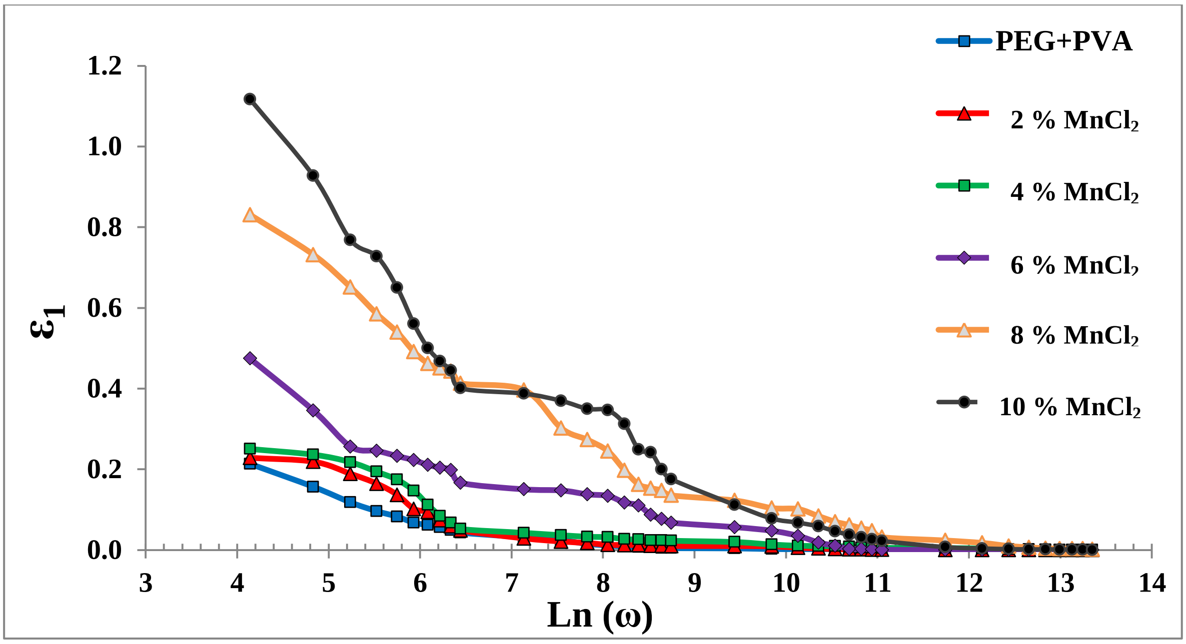

Fig. 3B: The variation of the dielectric constant of (PVA:PEG- ($MnCl_2$%) with frequency.

This figure shows that the dielectric constant of PVA:PEG/$MnCl_2$% decreases when increasing the frequency. This is attributed to decrease of space charge polarization with respect to the total polarization. The space charge polarization becomes more contributing type of polarization at low frequencies, and less contributing with the increase of frequency [14]. The other types of polarizations appear at subsequent frequencies. The ionic polarization reacts slightly to the variation in the field frequencies compared with electronic polarization; this is because the mass of ion is greater than that of the electron. The electrons respond even to the high frequencies of the field vibrations. The low mass of electron makes the electronic polarization was the only type of polarization at higher frequencies, this makes the dielectric constant approximately constant for all samples at high frequencies [15].

Fig. 4A show the dielectric loss of PVA, PEG and PVA:PEG as a function of frequency.

The effect of adding $MnCl_2$ particles on the dielectric loss at room temperature (30^0C) is shown in Fig.4B.

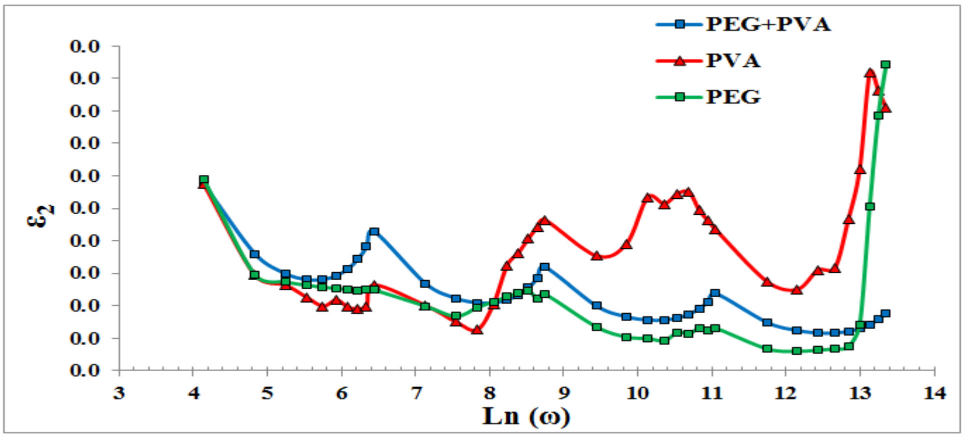

Fig. 4A: Variation of the dielectric loss with frequency for PVA, PEG and PVA:PEG composites.

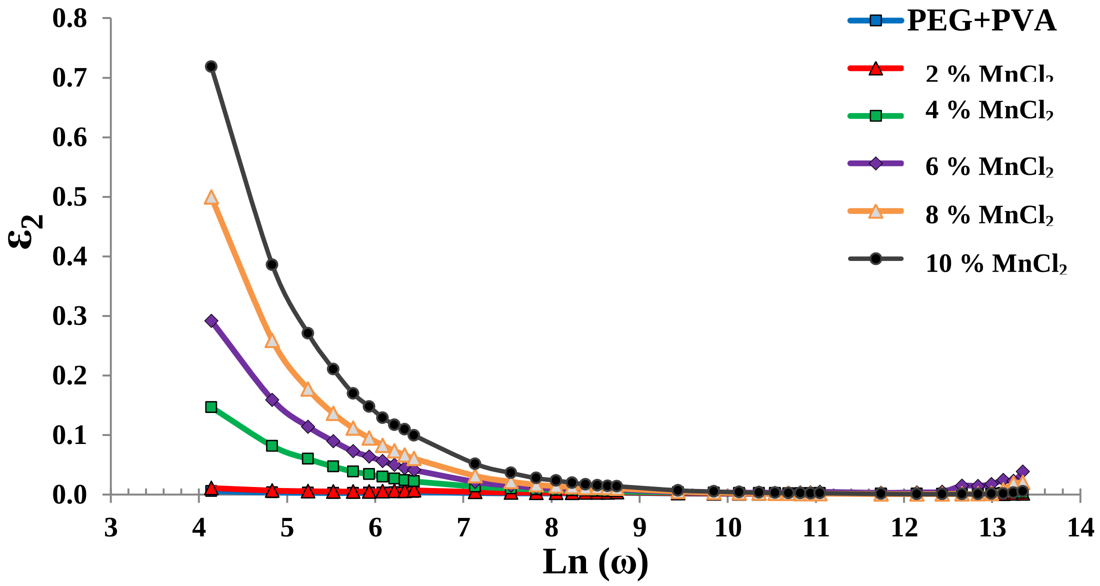

Fig. 4B: Variation of the dielectric loss with frequency for PVA:PEG-$MnCl_2$ composites.

It is clear from the figures that dielectric loss decreases with frequency. The larger value of dielectric loss at low frequency could be due to the mobile charges within the polymer backbone. This is attributed to the decrease of the space charge polarization contribution when increasing the frequency [16].

From the behavior of the dielectric constant (ε_1) and the dielectric loss (ε_2), one can observe a strong frequency dependence especially at low frequencies, which reflects the behavior of the polar materials. It is clearly seen that both ε_1 and ε_2, increase with salt concentration and decrease with the frequency of the electric field. They have a high value at low frequencies and a low value at high frequencies. These results suggest that polar entities of the composite are effectively operating under the electric field. This behavior can be understood as follows: at low frequencies, the time interval required for the molecular dipoles of the polymer to response to the applied electric field is sufficient. This enables these dipoles to follow the oscillating field, i.e., the orientation polarization is high, which leads to enhance the dielectric constant values. While at high frequencies, the time interval needed for the dipoles to response to the applied electric field is insufficient. Hence, the dipoles are unable to follow the rapid alternation of the oscillating field, i.e., the orientation polarization drops down greatly and lead to very small value of ε_1 and ε_2 at high frequencies [17] which is similar to the behaviour for polar polymer and materials. This dielectric behaviour explains the increasing in the AC conductivity at high concentration [18].

The variation of the conductivity for PVA, PEG and PVA:PEG composites with frequency is shown in Fig. 5A.

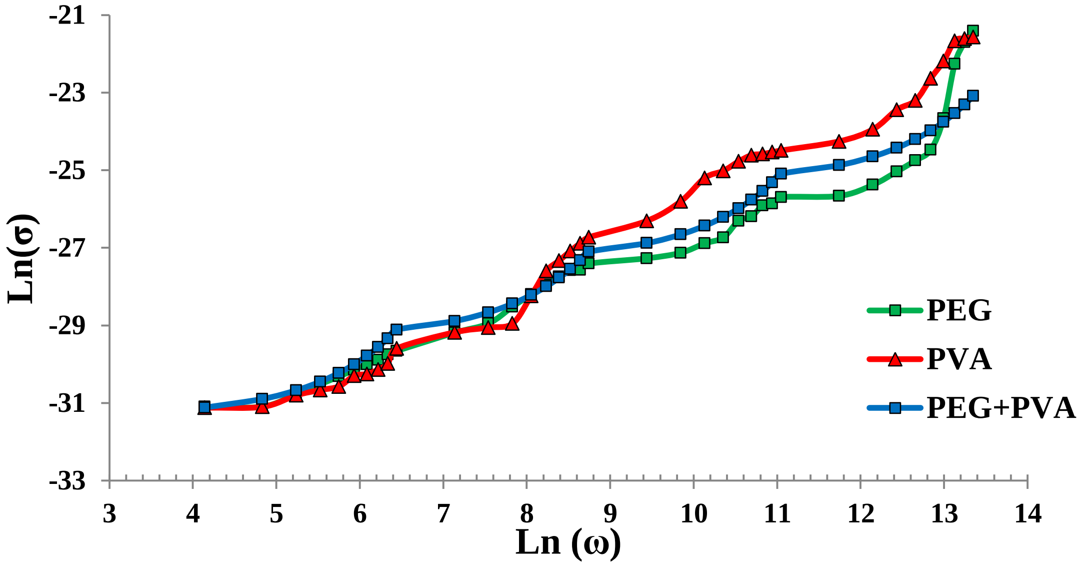

Fig. 5A: The variation of the conductivity for PVA-PEG-PVA:PEG composites with frequency.

And the variation of the conductivity for PVA:PEG-$MnCl_2$ composites with frequency shown in Fig. 5B.

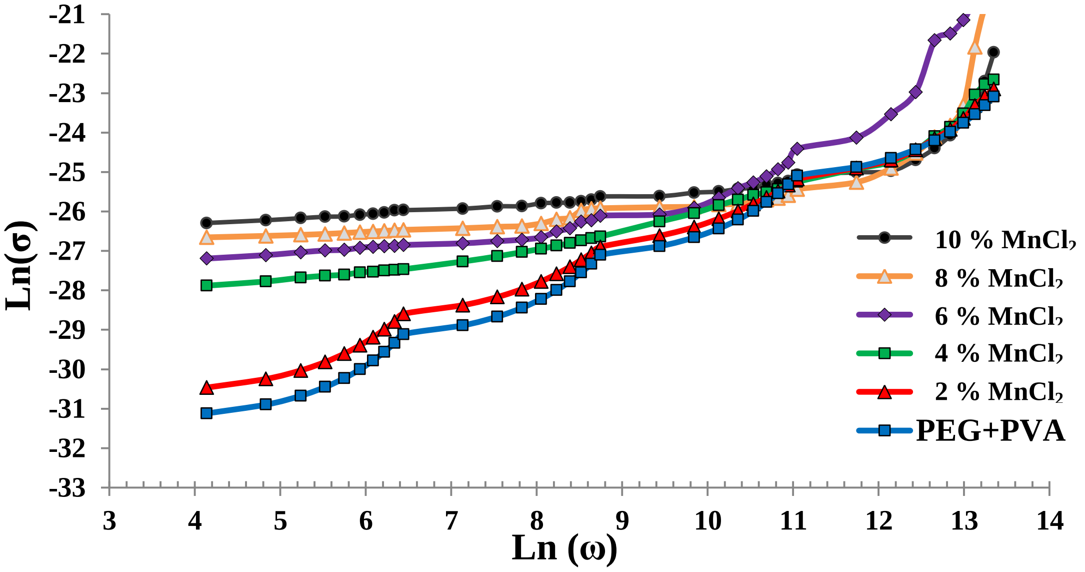

Fig. 5B: The variation of the conductivity for (PVA-PEG-PVA:PEG) composites with frequency.

The conductivity is increasing when increasing the frequency for all different concentration of $MnCl_2$ nanoparticles for PVA:PEG/$MnCl_2$ composites.

These figures show that A.C electrical conductivity increases with the increase of frequency. This is attributed to the space charge polarization that occurs at low frequencies, and also to the motion of charge carriers by hopping process. The increasing of the conductivity is small at high frequencies; this is attributed to the electronic polarization and the charge carriers which travel by hopping process [19].

Conclusion

The electrical conductivity, dielectric behavior of PVA:PEG/$MnCl_2$ composite were studied as a function of $MnCl_2$ particles concentration and the applied frequency. Frequency and M nCl_2 concentration affect on the electrical and dialectical behavior of the composite and explained on the basis of the interfacial (space charge) polarization, dipolar polarization and on the decrease of the hindrance of the polymer matrix. Activation energy for all composites decreased with increasing of concentration. Dielectric constant and dielectric loss decrease with increasing of frequency and increase with increasing of concentration, while the A.C electrical conductivity ($\sigma_{a.c}$) increased with increasing of frequency and $MnCl_2$ concentration due to enhancement of ionic conduction in the membrane bulk for all samples.

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