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Investigation of the dielectric properties of Sn – doped PMMA/PVA blends

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Abstract

Blends of Polymethyl methacrylate (PMMA)/polyvinyl alcohol (PVA) doped with 2% weight percentage of Sn were prepared with different blend ratios using casting technique. The measurements of A.C conductivity $\sigma_{a.c}$ within the frequency range (25kHz – 5MHz) of undoped and Sn doped PMMA/PVA blends obeyed the relationship $\sigma = Aw^s$ were the value of s within the range $0 < s < 1$. The results showed that $\sigma_{a.c}$ increases with the increase of frequency. The exponent s showed preceding increase with the increase of PVA content for PMMA/PVA blends doped with Sn. The dielectric constant, dielectric loss, A.C electrical conductivity are varied with the concentration of PVA in the blend and frequency of applied electrical field.

Key words

PMMA/PVA blends,
Doping with Sn,
A.C electrical conductivity.

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دراسة الخصائص العزلية لخلطات بولي مثيل ميثا اكريلايت / بولي فنيل الكحول المطعمة بالقصدير

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الخلاصة

حضرت خلطات من بولي مثيل ميثا اكريلايت/ بولي فينيل الكحول المطعمة بنسبة وزنية 2% من القصدير وبنسب خلط مختلفة باستخدام تقنية الصب. أظهرت قياسات التوصيلية الكهربائية المتناوبة ضمن مدى التردد (25كيلو هرتز- 5 مليون هرتز) للخلطات المطعمة وغير المطعمة بالقصدير انها تخضع للعلاقة $\sigma = Aw^s$ حيث إن قيم s ضمن المدى $0 < s < 1$. النتائج اظهرت زيادة التوصيلية الكهربائية مع زيادة التردد. قيم الاس s تزداد مع ازدياد نسبة بولي فينيل الكحول في خلطات بولي مثيل ميثا اكريلايت/ بولي فينيل الكحول المطعمة بالقصدير. ثابت العزل الحقيقي، ثابت العزل الخيالي، التوصيلية الكهربائية تتغير مع تركيز بولي فينيل الكحول في الخلطة ومع تردد المجال الكهربائي المسلط.

Introduction

Polymer blends have become very important subject for scientific investigation in recent years because of their growing commercial acceptance, and they can possess unusual combinations of properties [1,2]. Blending polymers is an economic method to develop new polymeric materials. Commonly, the final properties of the blend depend on the properties of its polymeric components [3]. Polymer composites filled with metal are of interest for many fields of engineering. This interest arises from the fact that the electrical characteristics of such composites are close to the properties of metals, whereas the mechanical properties and processing methods are typical for plastics [4]. Polymer materials have been widely used in various fields such as industrial products [5]. Polymethyl methacrylate (PMMA) is a nonbiodegradable polymer with good transparency, mechanical strength, less weight, chemical resistance, colorlessness, resistance to weathering corrosion and good insulating properties. PMMA is the most commonly used polymer among the methacrylate family and has found tremendous applications in automotive and home appliances [6]. Polyvinyl alcohol (PVA) has fascinating properties and a wide variety of applications due to it has high dielectric strength, good charge storage capacity, high elasticity[7]. Polyvinyl alcohol (PVA) is a good insulating material with low conductivity and hence is of importance to microelectronic industry. It electrical conductivity depends on the thermally generated carriers and also on the addition of suitable dopants[8]. The present work describes the results of our investigations on dielectric properties of blends PMMA/ PVA blends doped with tin, over a wide range of frequency at room temperature.

Theoretical part

In an alternating (AC) field, the dielectric constant is a complex quantity (ϵ^o), which consist of two combinations, the real part which is known as the dielectric constant (ϵ_r) and imaginary part called the dielectric loss or dissipation factor (ϵ_i).

The electrical conductivity σ defined by[9]:

$$\sigma_{a.c} = \frac{d}{R_s A} \qquad (1)$$

Where :

A = guard electrode effective area.

R_s = polymer resistance (Ohm).

d = average thickness of sample (cm).

In this model the electrodes have circular area.

$A = \pi r^2$ where r = 0.5 cm.

The dielectric properties of Sn doped PMMA/PVA blends were measured using (Agilent impedance analyzer 4294A).

In the frequency(f) range (25×10^3 - 5×10^6) Hz at room temperature 23 ˚C.

A frequency dependence on A.C conductivity $\sigma_{a.c}$ (ω) has been observed in many amorphous semiconductors and insulators both inorganic and polymeric material, has the form [10]:

$$\sigma_{a.c}(\omega) = A\omega^s \qquad (2)$$

where, s is the exponent in the range 1 >s> 0 and A is the proportional factor. The total measured conductivity σ_t (ω) at a given frequency (ω) is separable into d.c and a.c components, namely[10]:

$$\sigma_t(\omega) = \sigma_{a.c}(\omega) + \sigma_{d.c} \qquad (3)$$

where $\sigma_{d.c}$ is the d.c component at low frequency, while $\sigma_{a.c}$ (ω) is due to relaxation processes .The measured capacitance, Cp was used to calculate the dielectric constant, ϵ_r using the following expression [9]:

$$\epsilon_r = Cp\, A / \epsilon^o\, d \qquad (4)$$

Where d is sample thickness and A is surface area of the sample. whereas for dielectric loss ϵ_i [9]:

$$\epsilon_i = \epsilon_r \times \tan\delta \qquad (5)$$

Where tan δ is dissipation factor.

Experimental Description

PMMA with an average molecular weight of (15,000) (HIMEDIA, India) and PVA with an average molecular weight of (160,000)(HIMEDIA, India) and Filler Tin(Sn)as a micro powder with grain size (50μm) is used in this work. N-N, Dimethyl Formamide (DMF)(CHEM Limited, India) was used as a solvent for PMMA and PVA.

Appropriate weights of PMMA and PVA with the different weight blend ratios (100 PMMA, 75 PMMA + 25 PVA, 50 PMMA +50 PVA, 25 PMMA + 75 PVA,100 PVA) were dissolved separately in DMF. The two mixtures were stirred and heated up to 80 °C for two hours until PMMA and PVA solutions took a homogeneous viscous liquid appearance, then PVA solution was added to PMMA solution and mixture solution was left to cool down to laboratory temperature while the stirring of the mixture was carried out to ensure a homogenous composition.

The resulting solution was then poured into a casting glass plate with diameter 5cm and the DMF was allowed to evaporate in air at room temperature 23˚C. This procedure provided mechanically stable, free standing and flexible films. The films were further dried in oven at 50℃ for 48 hour to remove any trace of DMF.

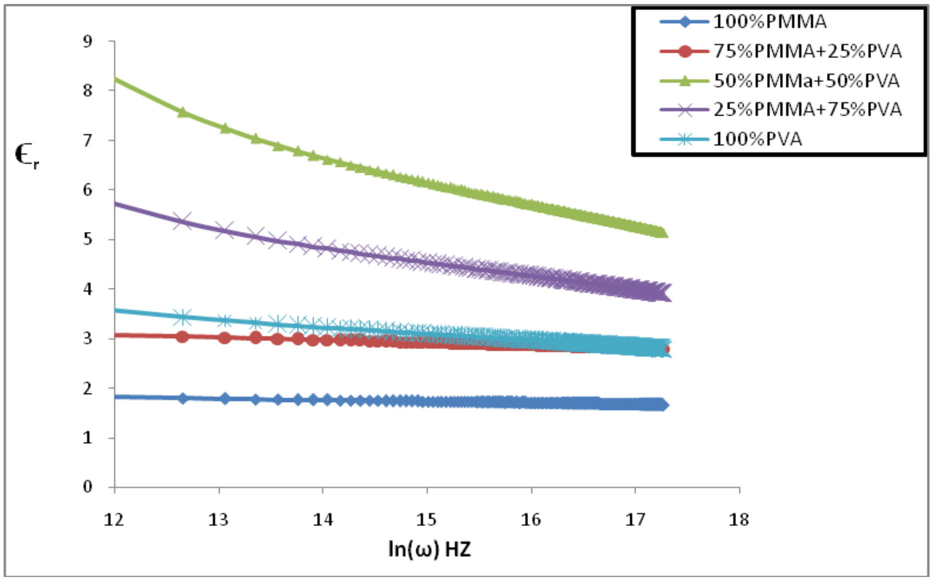
To prepare the doped blends with 2% weight percentage (wt.%) of Sn was added to the blend mixture solutions (as prepared above) with the different blend ratios and stirred for 30 minutes and the same procedure above was repeated to get a blend films doped with 2% of Sn with thickness range for undoped and doped samples (0.27- 0.3) mm.

Results and discussion

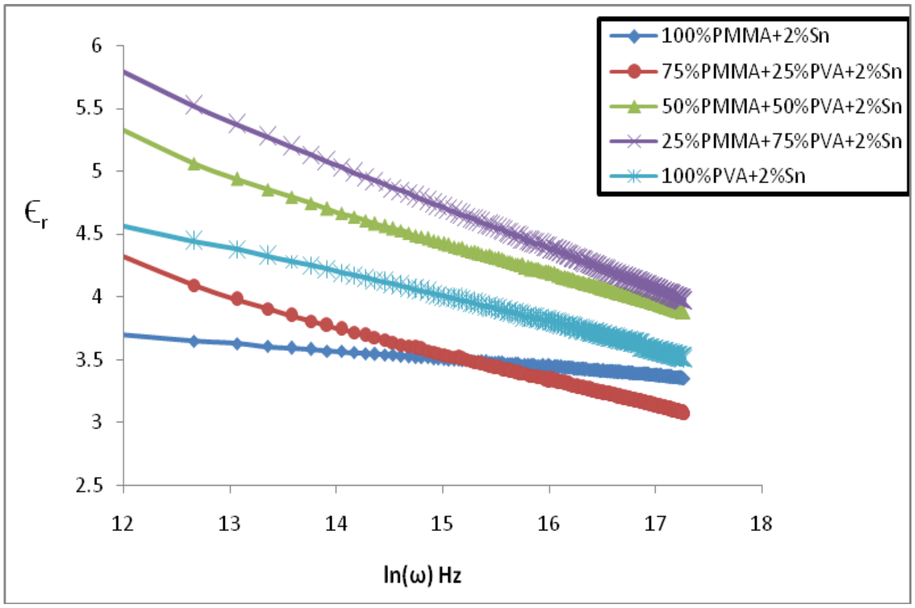
1- Frequency dependence of dielectric constant

Figs. 1(a) and (b) show the variation of real dielectric constant (ϵ_r) as a function of frequency (ω) for PMMA/PVA blends undoped and doped with 2% of Sn. The results show that the values of (ϵ_r) tends to increase with increasing PVA content up to 50% and then decreases but with doped 2% of Sn the values of (ϵ_r) tends to increase with increasing PVA content up to 75% and then decreases, while it decreases with increasing frequency reach a lower values at high frequency which represent the onset frequency. The decrease of (ϵ_r) with frequency can be explained, at low frequencies (ϵ_r) for polar materials are due to the contribution of multi-component of polarizeability deformational polarization (electronic, ionic, orientation, and interfacial). This behavior was attributed to the polar nature of the PVA [11]. When the frequency is increased the dipole will no longer be able to rotate sufficiently rapidly, so their oscillations being to be lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation stopped [11]. The variation of dielectric constant for blend with additives as function of frequency at low frequency region in addition to polarization, the space charge polarization plays a major role in increasing dielectric.

Figs. 2 (a) and (b) illustrate the variation of imaginary part of dielectric constant (ϵ_i) as a function of frequency (ω) for (PMMA/PVA) blends undoped and doped with 2% of Sn. Imaginary part of dielectric constant (ϵ_i) represents the loss through the dielectric material. The dielectric loss is due to the loss of energy (friction) due to micro-Brownian motions of dipoles and as a result depends on the internal viscosity of the system. It is obvious that ϵ_i for (100% PMMA, 75% PMMA+25%PVA) decreases monotonically with increasing the frequency and show the reduction for (50% PMMA+50%PVA, 25% PMMA+75%PVA and 100%PVA) in three stages i.e., at low, medium and high frequencies. The increase in ϵ_i with frequency is higher at low frequencies, shows a plateau for medium range and very low for high frequency values. The higher values of ϵ_i at low frequencies can be attributed to the accumulation of charge carriers near the electrodes. However, at higher frequencies, the dipoles or polar molecules are unable to orient themselves in the direction of the applied field. Hence, ϵ_i appears to be steady with increasing the applied frequency [7]. The PVA itself exhibits flexible side groups with polar bond as the bond rotating having an intense dielectric a-transition. Thus, there is a chemical composition change of the polymer repeated unit due to the formation of hydrogen bonds with hydroxyl groups through the polymerization process, which in turn makes the polymer chain flexible and hence enhances the electrical conductivity [12].

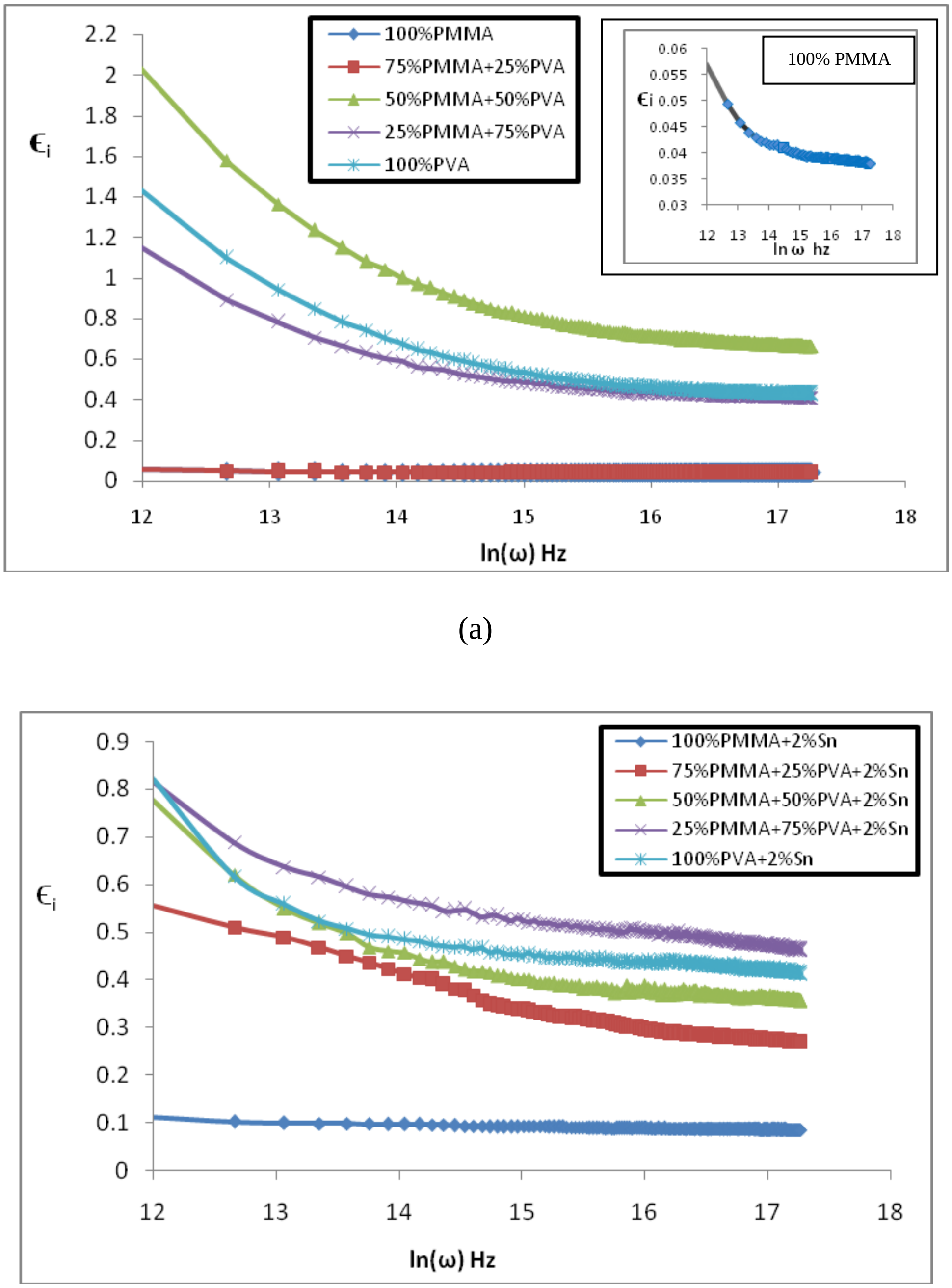


(a)



(b)

Fig.1: Variation of ϵ_r with ln (ω) for PMMA / PVA blends
(a) Undoped (b) Doped with 2% Sn.



(a)

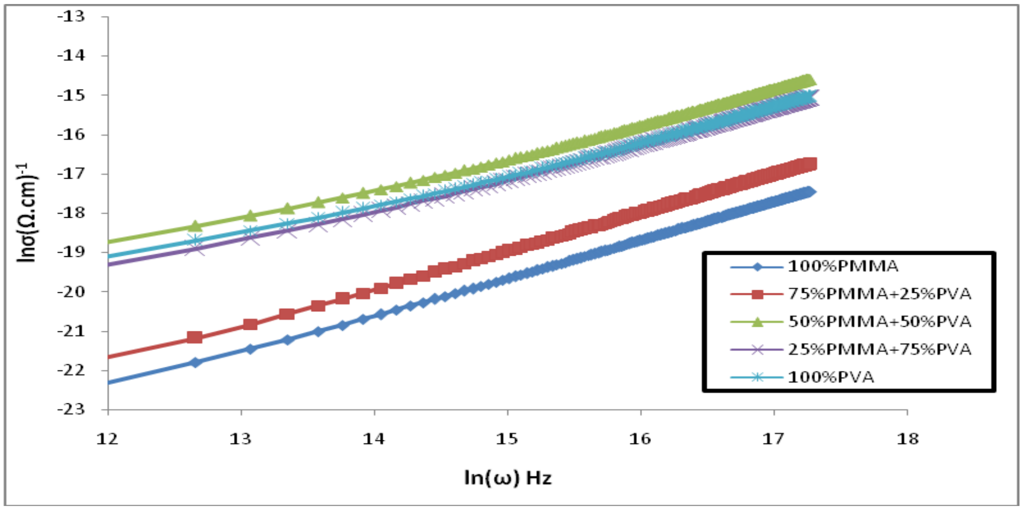
(b)

Fig. 2: Variation of ϵ_i with ln (ω) for PMMA/ PVA blends (a)Undoped (b) Doped with 2% Sn.

2- Frequency dependence of $\sigma_{a.c}$ (ω)

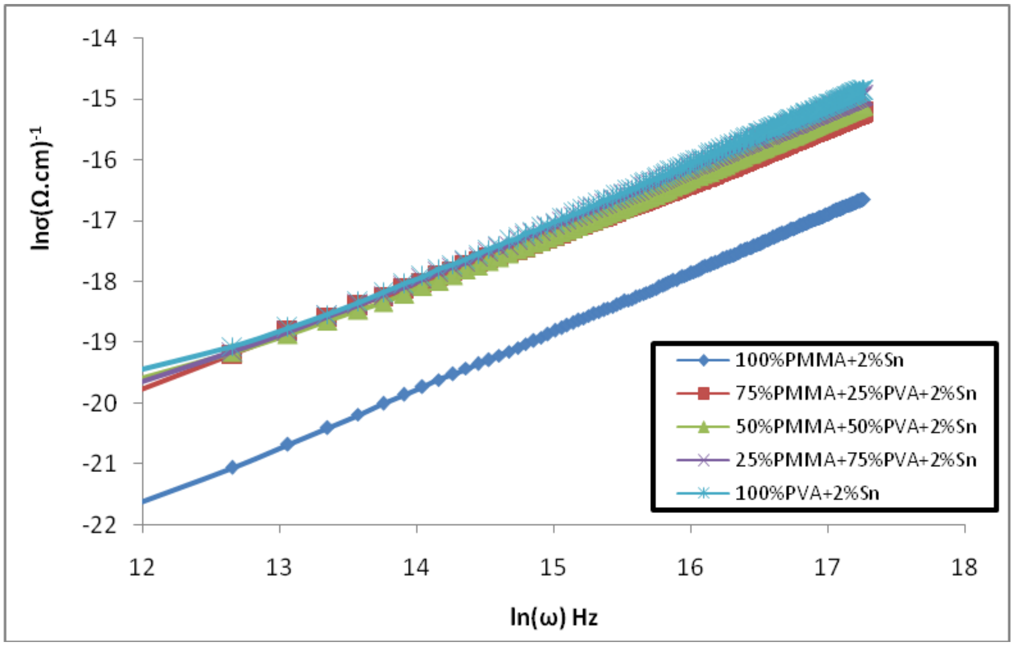
Fig. 3 (a) and (b) show the behavior of $\sigma_{a.c}$(ω) with the frequency for PMMA/PVA blends undoped and with doped 2% of Sn. Hence, it is proposed that two factors influence $\sigma_{a.c}$ (ω), which are ions motions and polymer backbone (main chain) motion. Furthermore ions motion is contributed at high frequencies and temperatures only, the increase of A.C. conductivity with frequency and a weak temperature dependence indicate that charge carriers are transported by hopping through defect sites along the chains [13]. The increasing of $\sigma_{a.c}$ (ω) in the high frequency range $>10^3$ Hz referred to the electronic polarization effect, and the conductivity is a.c conductivity in this region, i.e at higher frequencies molecules of blends start to vibrate with large amplitude within the polymeric chains hence the effect of increase in conductivity of blends [14]. Therefore, the $\sigma_{a.c}(\omega)$ at high frequencies is proportional to the angular frequency (ω) according to equation 2. The results showed that $\sigma_{a.c}(\omega)$ increase with the increase of frequency for all blends due to ions motion and the transport near or at the interstitial surface between blend and additives. The results also showed the higher value of conductivity for PVA sample doped with 2% of Sn in comparison with PMMA sample or with blends samples. The frequency dependent conductivity is caused by the hopping of the charge carriers in the localized state and also due to the excitation of charge carriers to upper states in the conduction band[15]. The interesting result was the $\sigma_{a.c}(\omega)$ values exceeded those values of (PMMA/PVA) blends. $\sigma_t(\omega)$ increases rapidly in the higher frequency range which referred to the electronic polarization and the conductivity is pure A.C. For the present case, these are shown in Fig. 3.

The linear positive slope indicates that the Schottky Richardson mechanism is applicable to the conduction process in PMMA/PVA blend [16]. Tables 1 and 2 reveal that the value of conductivity and exponential factor (s), the values of exponent s were estimated by similar way discussed in previous section. Table 2 reveals that s values declare proceeding increase with the increase of PVA content thus small poloran (SP) is the suitable model which can be adopted to explain this result. The result of Table 1 showed the addition of Sn to (PMMA/PVA) blends has significant effect, i.e doping with Sn enhanced the conductivity values of doped blends, were exceeded those for any undoped blends except 50%PMMA/50%PVA sample. This result attributed to reduction of intermolecular interaction accompanied the addition of Sn to (PMMA/PVA) blends which comes from high atomic number of Sn (Z=50), thus doping with Sn increase the volume required for ionic carriers to drift in the polymer matrix.



(a)

Fig. 3: Variation of ln(σ) with ln (ω) for PMMA/PVA blends (a) Undoped.



(b)

Fig. 3: Variation of ln(σ) with ln (ω) for PMMA/PVA blends (b) Doped with 2% Sn.

Table 1: Values of electrical conductivity at frequency 5 MHz for PMMA / PVA blends undoped and doped with 2% Sn.

Ratios blend	Electrical conductivity($\sigma_{a.c}$) $(\Omega.cm)^{-1}$ for undoped samples	Electrical conductivity($\sigma_{a.c}$) $(\Omega.cm)^{-1}$ for Sn - doped samples
100 PMMA	2.63E - 8	5.8E - 8
75 PMMA + 25 PVA	5.28E - 8	2.43E -7
50 PMMA + 50 PVA	4.6E - 7	2.73E -7
25 PMMA + 75 PVA	2.83E - 7	3.22E -7
100 PVA	2.97E -7	3.55E -7

Table 2: s values of PMMA / PVA blends undoped and doped with 2% Sn.

Blend Ratios	s for samples undoped	s for samples doped with 2% Sn
100%PMMA	0.874	0.879
75%PMMA+25% PVA	0.889	0.93
50%PMMA + 50% PVA	0.935	0.945
25% PMMA + 75% PVA	0.917	0.956
100% PVA	0.924	0.962

Conclusions

1- Generally the exponent s values increase with the increase of PVA content in the blends.

2- The results indicates that the dielectric permittivity and dielectric loss was found to be decrease with increasing frequency. This behavior was attributed to the polar nature of the PVA.

3- The electrical conductivity $\sigma_{a.c}$ for PMMA/PVA blends undoped and doped with 2wt.% Sn was increases with the increase of frequency.

4-High value for electrical conductivity was found equal to $4.6\mathrm{x}10^{-7}(\Omega.\mathrm{cm})^{-1}$ for 50/50 undoped sample blend and equal to $3.5\ \mathrm{x}10^{-7}\ (\Omega.\mathrm{cm})^{-1}$for 100%PVA doped with 2 wt.% Sn.

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