

A.C conductivity and dielectric properties of (PVA/ PEO) blends doped with MWCNTs

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Abstract

A.C electrical conductivity and dielectric properties for poly (vinyl alcohol) (PVA) /poly (ethylene oxide) (PEO) blends undoped and doped with multi-walled carbon nanotube (MWCNTs) with different concentrations (1, and 3 wt %) in the frequency range (25×10^3 - 5×10^6 Hz) were investigated. Samples of (PVA/PEO) blends undoped and doped with MWCNTs were prepared using casting technique. The electrical conductivity measurements showed that $\sigma_{A.C}$ is frequency dependent and obey the relation $\sigma_{A.C} = A\omega^s$ for undoped and doped blends with 1% MWCNTs, while it is frequency independent with increases of MWCNTs content to 3%. The exponent s showed proceeding increase with the increase of PEO ratio ($\geq 50\%$) for undoped blends samples, while s value for doped blends exhibits to change in different manner, i.e. s increases and reach maximum value at 50/50 PVA/PEO, then decreases for residual doped blends samples with 1% MWCNTs on the other hand the exponent s decrease and reach minimum value at 50/50 PVA/PEO for samples doped with 3% MWCNTs, then return to increase. The results explained in different terms.

Key words

Carbon nanotubes, Poly (vinyl alcohol), poly (ethylene oxide), (PVA/PEO) blends, Nanocomposites, Electrical properties.

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التوصيلية الكهربائية المتناوبة و الخواص الكهربائية العزلية لخلطات بولي فينيل الكحول/

بولي اثيلين اوكسايد المطعمة بأنابيب الكربون النانوية

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الخلاصة

درست التوصيلية الكهربائية و الخواص الكهربائية العزلية المتناوبة لخلطات بولي فينيل الكحول بولي اثيلين اوكسايد غير المطعمة و المطعمة بنسب وزنية مختلفة (1% and 3% wt) من انابيب الكربون النانوية ضمن مدى الترددات (25×10^3 - 5×10^6) هرتز. حضرت نماذج خلطات بولي فينيل الكحول /بولي اثيلين اوكسايد غير المطعمة و المطعمة بأنابيب الكربون النانوية باستخدام تقنية الصب. اظهرت قياسات التوصيلية الكهربائية للخلطات غير المطعمة و المطعمة بنسبة (1%) انها تعتمد على التردد حسب العلاقة: $\sigma_{A.C} = A\omega^s$. بينما لا تعتمد على التردد عند النسبة 3%. اظهرت قيم العامل الاسي (s) زيادة ملحوظة مع زيادة تركيز البولي اثيلين اوكسايد ($\leq 50\%$) في الخلطات الغير المطعمة. بينما اظهرت قيم (s) للخلطات المطعمة بنسبة (1%) سلوكاً مغايراً، حيث زادت لتصل اعلى قيم عند تركيز 50/50 PVA/PEO ثم تناقصت لبقية نسب الخلط، من جانب اخر فان قيم العامل الاسي (s) للخلطات المطعمة بنسب (3%) اظهرت تناقصاً ليصل اقل قيمة عند نسبة خلط 50/50 PVA/PEO ثم تعود للزيادة لبقية نسب الخلط. فسرت النتائج بدلالة رموز مختلفة.

Introduction

Carbon nanotubes (CNTs) are the excellent material for the high technology applications where

electrical properties are sought, due to their excellent electrical conductivity. CNTs were applied generally as reinforcing fillers for various

nanocomposites due to their exceptional strength and high aspect ratio [1]. In the last decade, many researchers were interested in polymer/CNT composites and so continuous studies are needed to improve their physical properties and their applications. These studies show that the polymer/CNT composites are better than composites filled with metallic particles consisting electrical and thermal transfer mechanisms, even a small amount of CNT added to the composites will enhance these properties [2]. Polyvinyl alcohol (PVA) polymers have especially been given a great deal of attention. These polymers are useful in broad applications due to their excellent chemical resistance, physical properties, and biodegradability. The binding characteristics of PVA offer excellent adhesion to porous and water-absorbent surfaces. To further improve the electrical properties of PVA, many researchers have reported the synthesis of PVA/CNT nanocomposites [3]. The PEO polymer has a wide range of application including the use as pharmaceutical recipients, food additives and plasticizers. However, much progress was made in the electrical conduction in polyethylene (PEO). Previous studies were centered on the enhancement of its ionic conductivity with the aim of developing the material to have the promising electrical application [4]. The present work is focused on the study of the electrical conductivity and dielectric properties for (PVA-PEO) /MWCNTs blends nanocomposites, to show the effect of MWCNTs concentrations on these properties.

Experimental part

Polyethylene oxide (PEO) of molecular weight (8×10^6) were purchased from (Sigma-Aldrich USA),

Polyvinyl alcohol (PVA) with an average molecular weight of (160,000) supplied by (HIMEDIA, India) and MWCNTs from (Sigma-Aldrich USA) with diameter between 5-15 nm. All polymer blends and blends composite films were prepared using casting technique. The polyvinyl alcohol (PVA) and Polyethylene oxide (PEO) was dissolved in deionize water using magnetic stirrer and heating throughout mixing process to get homogeneous solution. To prepare doped blends, weight percentages of MWCNTs are (1, and 3) wt.% were added to the blends solutions and mixed for 30 minute using ultrasonic homogenizer to get more homogenous solution, then the solutions of undoped blends was transferred to clean glass Petri dish of (10 cm) in diameter placed on plate form. The dried film was then removed easily using tweezers clamp. Samples used for electrical measurements were shaped as films with thicknesses values approximately (0.17mm). The electrical properties (AC dielectric and AC conductivity) of (PVA/PEO) + MWCNTs in the frequency range (25×10^3 - 5×10^6) Hz were investigated using Hewlett Packard model (HP4274A & HP4275A). The samples of (PVA/PEO)/ MWCNTs nanocomposites were placed in the holder. AC dielectric and AC conductivity were calculated as a function of frequency. The AC conductivity $\sigma_{ac}(\omega)$, dielectric constant (ϵ_r) and dielectric loss (ϵ_i) of the prepared (PVA/PEO)/MWCNT composites were calculated from the following relations [5].

$$\sigma = \frac{t}{R.A} \quad (1)$$

$$\epsilon_r = \frac{c.t}{\epsilon_0 A} \quad (2)$$

$$\epsilon_i = \tan(\delta)\epsilon_r \quad (3)$$

where ϵ_0 : is the permittivity of free space = 8.85×10^{-14} F/cm, t , A thickness and surface area of the sample respectively. R : resistance of the composite, ϵ_r : dielectric constant. A.C electrical conductivity $\sigma_{a.c}(\omega)$ is measured by the following equation [5]

$$\sigma_{a.c} = \sigma_{tot}(\omega) - \sigma_{d.c}(T) \quad (4)$$

where ω is the angular frequency ($=2\pi f$), $\sigma_{tot}(\omega)$ is the measured total electrical conductivity, $\sigma_{d.c}(\omega)$ is the DC conductivity which depends strongly on temperature, it dominates at low frequencies and high temperatures, Whereas the $\sigma_{a.c}(\omega)$, which has a weaker temperature dependence than $\sigma_{d.c}$ and dominates at high frequency and low temperature. The relation for the frequency dependence AC conductivity is given by:

$$\sigma_{a.c} = A\omega^s \quad (5)$$

A is a constant, and (s) is a function of temperature which is determined from the slope of a plot $\ln \sigma_{d.c}(\omega)$ versus $\ln(\omega)$ [5], then the value of s can be calculated from;

$$s = \frac{d[\ln \sigma_{a.c}(\omega)]}{d[\ln(\omega)]} \quad (6)$$

Results and discussions

1. A.C electrical conductivity

AC electrical conductivity of undoped and doped (PVA-PEO) nanocomposites samples with different concentration were studied as a function of frequency, as shown in Fig. 1. The increase of AC with frequency referred that is obey the relation (5). The increase of a.c conductivity with frequency indicate that charge carriers are transported by hopping through defect sites along the chains [6]. The 1% and 3%wt MWCNT nanocomposites show a slight increase in the conductivity compared to that of the pure sample, but still the samples at this wt% remains an

insulator. The reason of such behavior can be attributed to the tunneling conduction mechanisms (TCM). This behavior may be explained as: at the surface of MWCNTs the carboxylic groups decrease the tunneling current making the tunneling difficult occurs leading to a slightly increasing of the conductivity. Also it can be noticed that at high content of MWCNT i.e. 3% the nanocomposites become independent of frequency which indicates the electron type of the charge transport. So it can be seen that the change in the electrical conductivity depends on the amount of MWCNT in the nanocomposites. At small amount, the conductivity of the nanocomposites increases with increasing frequency while at higher amount the conductivity shows a direct current and a non-dielectric behavior. This agrees with the result mentioned by other workers [7, 8]. On the other hand it is evident that addition of PEO to PVA increases the conductivity of the latter i.e. increases the charge carriers The exponential factor (s) were obtained from the plotting of $\ln(\sigma(w))$ versus $\ln(w)$, the values of (s) were listed in Tables 1-3. It is clear that (s) values exceeded unity for undoped blends samples which indicate that the conductivity is pure A.C. The results showed that s value decreases i.e. less than unity with addition of nano filler to blends samples which confirmed the hopping mechanism. It is obvious that s value increases with the increase of PEO ratio in undoped samples. To explain our results we suggests small polaron (SP) model while s value increases with the increase of PEO ratio and reach maximum value then decreases for residual doped blends samples at 1%MWCNT, thus the convenient models are small polaron (SP) and Correlated Barrier Hopping (CBH). The results declared that at 3% MWCNT doped blends samples s value decrease and reach minimum value but then return

to increase for other blends samples, the suitable models are small polaron (SP) and Correlated Barrier Hopping (CBH). Small Polaron (SP) is the most suitable when the exponent s get to rise, this occurs when addition of charge carrier to the covalent solid causes a large degree of local lattice distortion, which form

small polaron. The second model is called correlated barrier hopping (CBH) when the electrons hop over the potential barrier between two sites, the a.c conductivity is due to hopping between defect states or dangling bonds ($D^+ D^-$) [9].

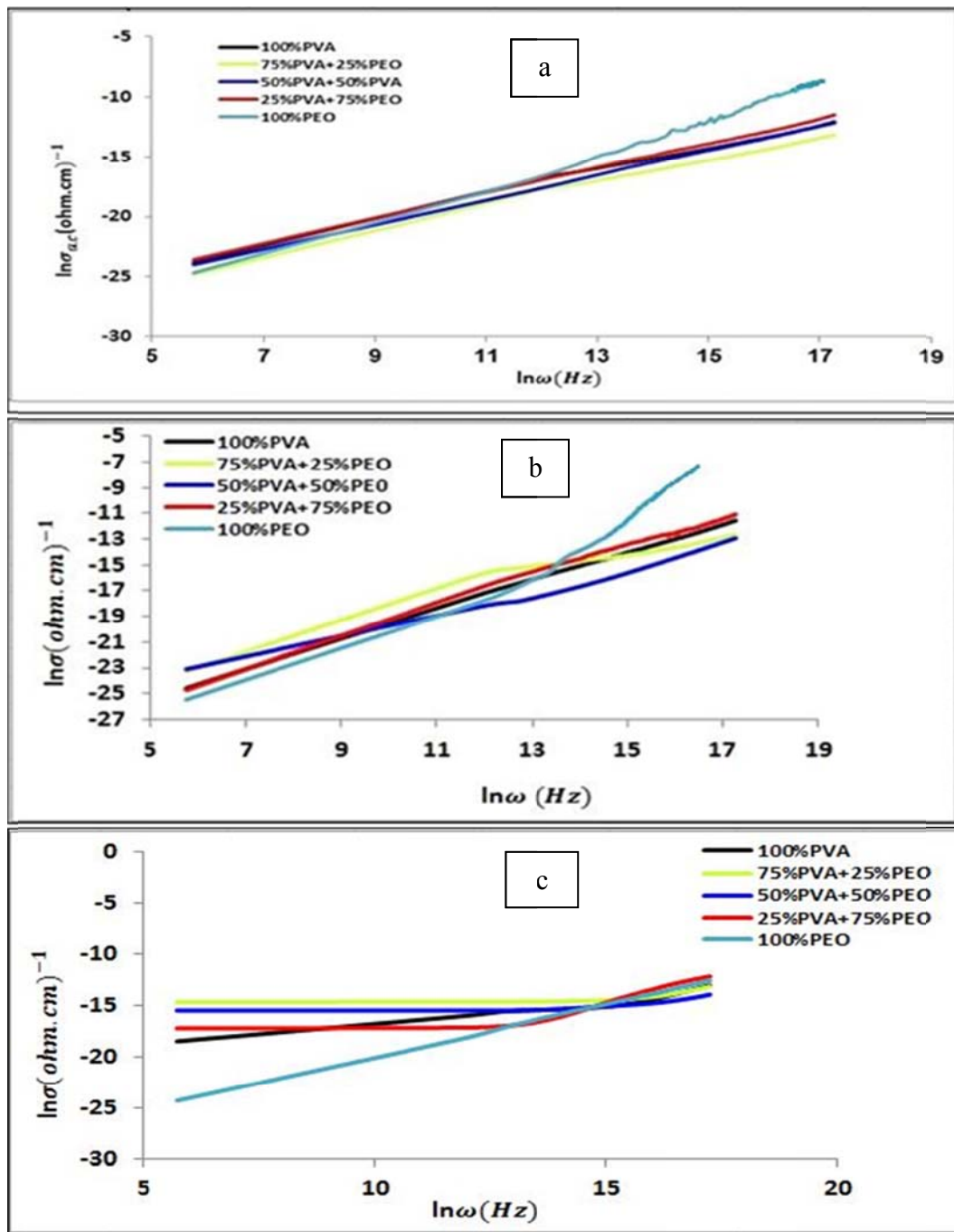


Fig.1: Variation of $\ln\sigma$ (a.c) (ω) with $\ln(\omega)$ for (a) undoped (PVA-PEO) blend (b) doped with 1% MWCNT (c) doped with 3% MWCNT.

Table 1: s values of PVA / PEO blends.	
Blend Ratios	S
100%PVA	0.9526
75%PVA+25%PEO	0.9526
50%PVA+50%PEO	1.0351
25%PVA+75%PEO	1.0329
100%PEO	1.4737

Table 2: s values of PVA/ PEO blends doped with 1% MWCNT.	
Blend Ratios	S
100%PVA	0.7738
75%PVA+25%PEO	0.8183
50%PVA+50%PEO	0.8606
25%PVA+75%PEO	0.7446
100%PEO	0.7232

Table 3: s values of PVA/ PEO blends doped with 3% MWCNT.	
Blend Ratios	S
100%PVA	0.6097
75%PVA+25%PEO	0.2934
50%PVA+50%PEO	0.2796
25%PVA+75%PEO	0.8555
100%PEO	0.829

2.The dielectric constants

The dielectric constant components were evaluated by measuring equivalent parallel capacitance C_p and dissipation factor or equivalent parallel resistance R_p of the sample. Fig. 2 shows the variation of real dielectric constant ϵ_r as a function of frequency ω for undoped (PVA-PEO) blends, doped (PVA-PEO) blends while Fig. 3 illustrates the variation of imaginary part of dielectric constant ϵ_i as a function of frequency ω for undoped (PVA-PEO) blends and doped (PVA-PEO) blends. The results show that the values of ϵ_r tends to decrease with the

increase of PEO weight fraction but then return to increase with further addition of PEO, although the value of ϵ_r of pure samples are exceeded those of blend one, while it decreases with increasing frequency to reach a lower values at high frequency which represent the onset frequency. This result can be explained by the fact that the electrode blocking layers is dominated mechanism at low frequency region [10]. Thus the dielectric behavior is affected by electrode polarization. At high frequency the dielectric signal is not affected by electrode polarization .The

trends of ϵ_r behavior vary for doped blends, i.e. ϵ_r value declare maximum value for 50/50 PVA/PEO while 100% PVA declare maximum value for blends doped with 1 and 3% MWCNT

respectively. The interesting result is the proceeding increase of ϵ_r with increase of weight fraction of filler which reflect the increase of capacitance.

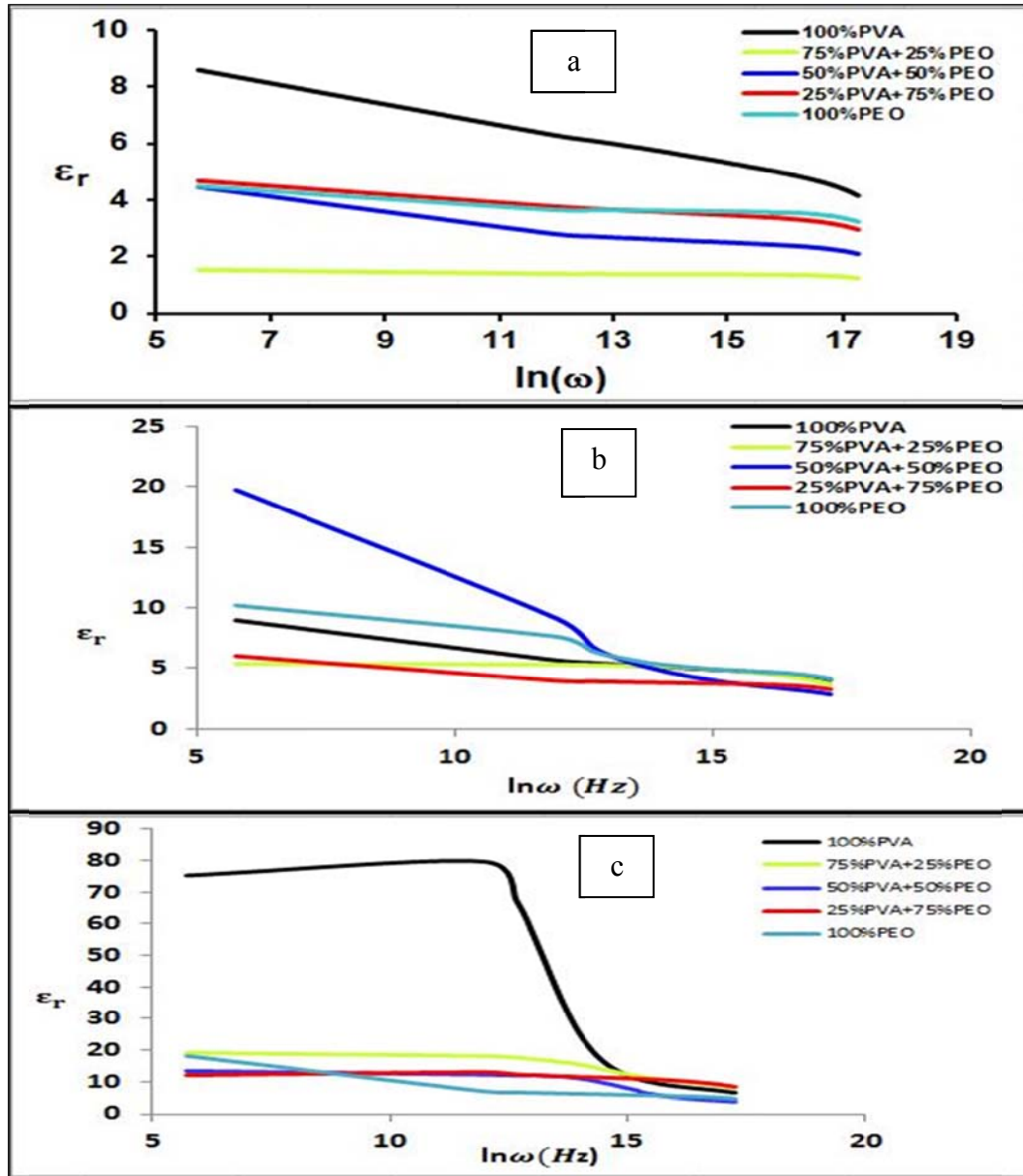


Fig. 2: Variation of ϵ_r with $\ln(\omega)$ for (PVA-PEO) blends (a) undoped (b) doped with 1% MWCNT (c) doped with 3% MWCNT.

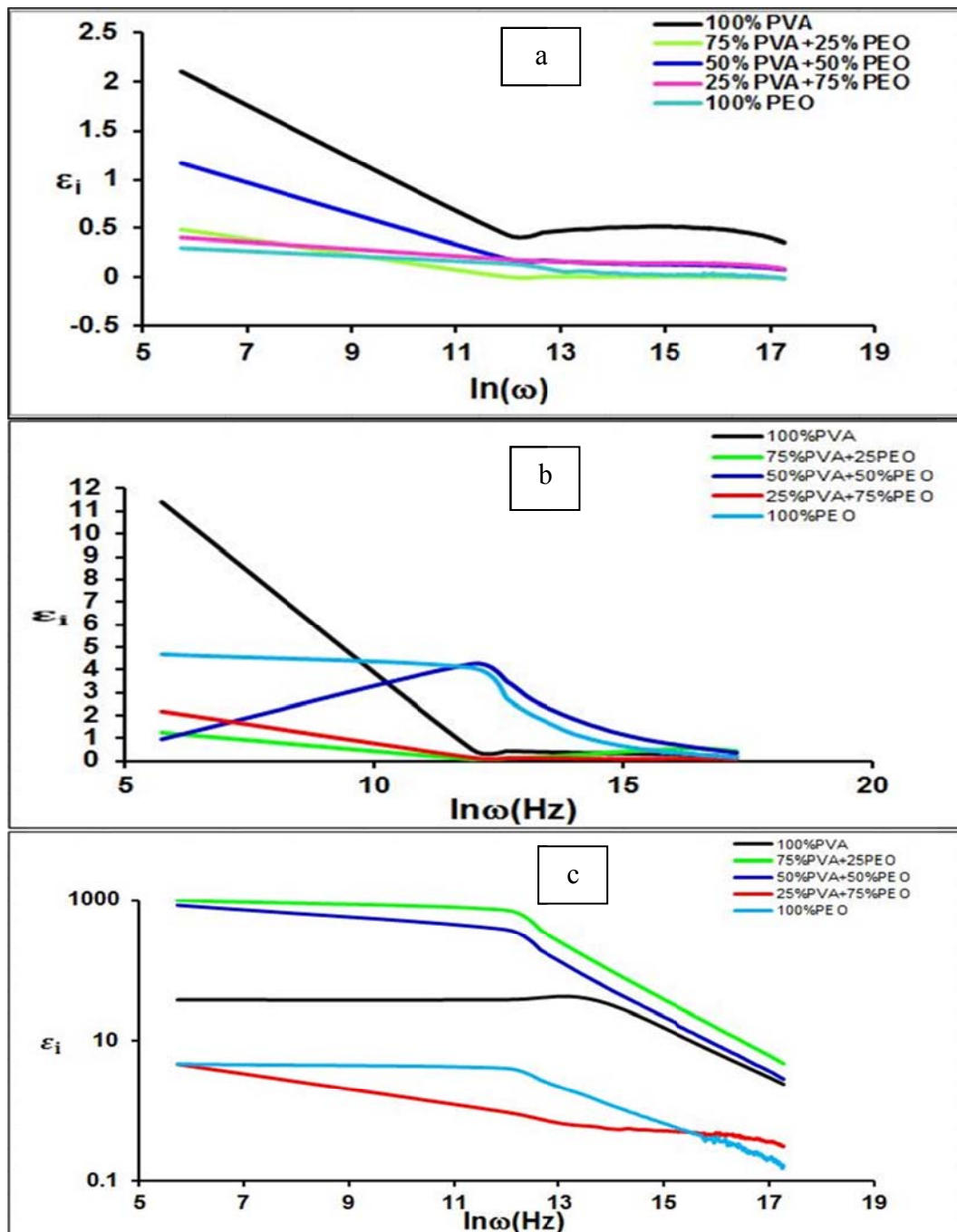


Fig. 3: Variation of ϵ_i with $\ln(\omega)$ for (PVA-PEO) blends (a) undoped (b) doped with 1% MWCNT (c) doped with 3% MWCNT.

Imaginary part of dielectric constant ϵ_i represents the loss through the dielectric material. The results showed that ϵ_i firstly decreased with the increase of frequency up to 10^3 Hz but then the values of ϵ_i in all blends are grown up to create a small peak which is called the loss peak. The peak exists at a constant position for each blend. At high frequencies the values of ϵ_i are

decreased rapidly with the frequency. This behavior is reported by Mijovic[11], and Valentini et al. [12]. The dielectric constant decreases with increasing the frequency. The same behavior was noticed for the higher concentration of MWCNT (3% wt.). This is because the MWCNT form large clusters. Such behavior of the dielectric constant can be understood

by the interfacial polarization effect[2]. When the MWCNT distributed in the polymer matrix to form nanocomposites, it creates a lot of interfaces a large dominate of nomadic electron could provide with large π -orbital of the MWCNT. The interface polarization can take place when electrons oriented under electric field[2]. Further increase of CNT concentration will increase the number of interfaces but increase above a certain value will lead to the contact between the MWCNT leading to the decrease of interfaces (percolation threshold), which will resulting in the decrease of the dielectric constant. Also it can be noticed from Fig. 3 that ϵ_r showed proceeding increase of with increase of weight fraction of filler which reflect the increase of conductivity. Maximum value of ϵ_i obtained for doped blends, for 50/50 PVA/PEO while 75/25 PVA/PEO declare maximum value for blends doped with 1 and 3% MWCNT respectively. Fig. 4 shows the variation of capacitance (C) as a function of frequency (ω) for (PVA/PEO) blends, at Fig. 4(a) The results show that the values of C tends to decrease with the increase of PEO content and reach minimum value for 100%PEO, also the capacitance decreases with the increase of the frequency reach a lower values at high frequency. Maximum value of capacitance obtained at 100% PVA for all doped and undoped samples. It is

seen that the capacitance decreases in the low frequency range and attains a constant value in the high frequency range, it is the usual behavior observed in many dielectric films. The decrease of capacitance with increasing frequency is attributed to the increasing inability of the dipoles to orient themselves in a rapidly varying applied field [13].

The observed increase in the dielectric constant as seen from Fig. 3 which is related to the increase in the electrical conductivity is take place as a result of incorporation concentration of MWCNT nano particles especially at high concentration in the PVA/PEO blend matrix was reported as inter phase between particles, polymer matrix, and composite morphology[14].

Conclusion

The following conclusions can be made from this work:

A.C conductivity is frequency dependence for undoped and doped blends with low ratio of MWCNT while it is frequency independence for doped blends with high ration of MWCNT. Increase of MWCNT content in blends leads to increase real and imaginary dielectric constants. The exponent s show maximum value for undoped blends and minimum value for doped blends with high MWCNT concentration.

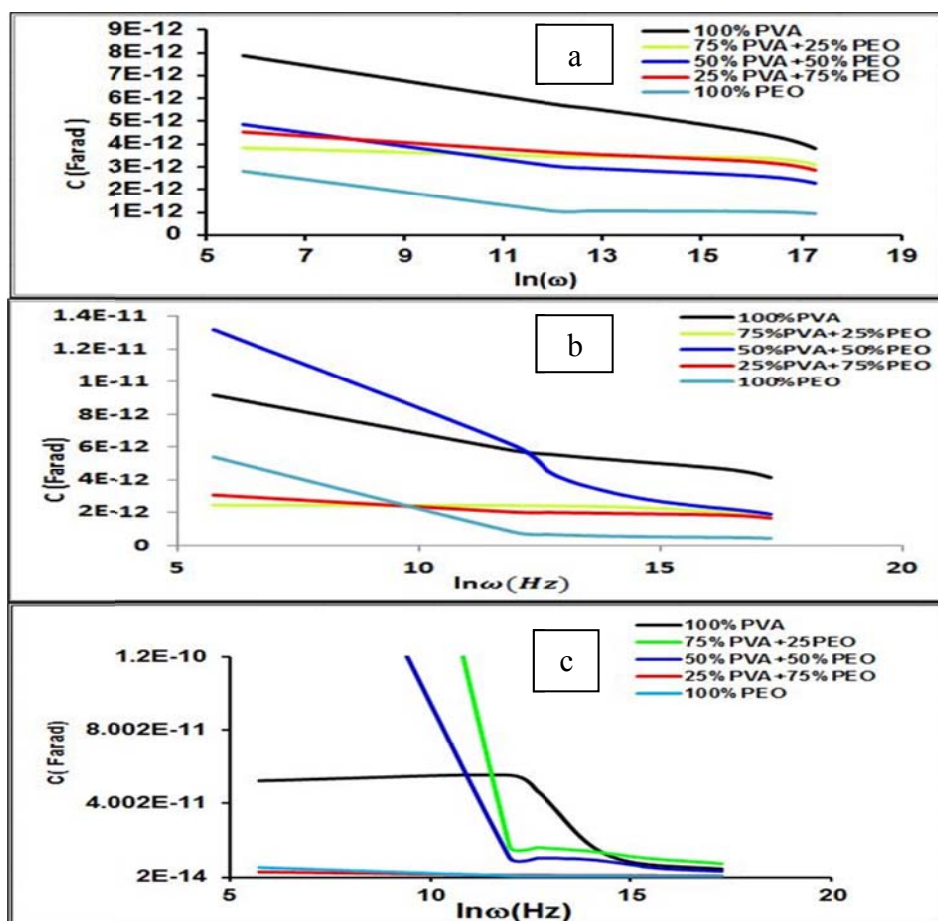


Fig. 4: Variation of capacitance (C) with $\ln(\omega)$ for (a) undoped (PVA-PEO) blend (b) doped with 1% MWCNT (c) doped with 3% MWCNT.

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