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

Ahmad A. Hasan, Muna B. Jasim

Department of Physics, College of Science, University of Baghdad, Iraq

E-mail: Ahmadabhasan27@yahoo.com

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 (25x10^3 - 5x10^6 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 exponents $s$ 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.

Article info.

Received: Jan. 2016
Accepted: Mar. 2016
Published: Sep. 2016

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
nанохимикатытен в их особых сиінш и высокой относительной длиной [1]. В последнем столетии, многие исследователи были заинтересованы в полимер/CNT композитах и поэтому интенсивные исследования необходимы, чтобы улучшить их физические свойства и их применения. Эти исследования показывают, что полимер/CNT композиты лучше, чем композиты на основе металлических частиц, состоящих из электрических и тепловых механизмов, даже при небольшом добавлении CNT в композиты, которые улучшают эти свойства [2]. Поливиниловый спирт (PVA) полимеры особенно были обращены в упор в особенности их отличными химическими сопротивлениями, физическими свойствами, и биодеградируемостью. Связывающие характеристики PVA предлагают отличную адгезию к пористым и водопоглощающим поверхностям. Чтобы улучшить электрические свойства PVA, многие исследователи отчетливо улучшили синтез PVA/CNT нанокомпозитов [3]. Полиэтиленоксида (PEO) полимер имеет широкий спектр применения, включая использование в фармацевтических рецептивах, пищевых добавках, пластикаторах. Однако, еще больше прогресса было сделано в электрическом проводимости в полиэтилене (PEO). Предыдущие исследования были сфокусированы на улучшении его ионной проводимости с целью развития материала с обещающим электрическим применением [4]. Предназначенная работа сфокусирована на изучении электрических и диэлектрических свойств для (PVA-PEO) / MWCNTs смеси нанокомпозитов, для показа эффекта концентрации MWCNTs на этих свойствах.

**Экспериментальная часть**

Полиэтиленоксида (PEO) полимеры были получен из Sigma-Aldrich USA, Поливиниловый спирт (PVA) с обычной молекулярной массой (160,000) получен из HIMEDIA, India и MWCNTs от Sigma-Aldrich USA с диаметром 5-15 нм. Все полимерные смеси и смеси композитные пленки были приготовлены с помощью метода casting. Поливиниловый спирт (PVA) и Полиэтиленоксида (PEO) были растворены в дистиллированной воде с помощью магнитного мешалки и нагревались в процессе мешалки, чтобы получить однородное растворение. Чтобы приготовить смеси, массовые проценты MWCNTs (1, 3) % были добавлены к раствору смеси и перемешивали в течение 30 минут с помощью ультразвуковой импульсатор, чтобы получить более однородное растворение, а затем растворы несмешанных смесей были переведены в чистый стеклянный Petri диск диаметром (10 см) в виде пластины. Сухой слой затем был легко удален при помощи клещей. Пробы использовались для электрических измерений и были формированы как плены толщиной приблизительно (0.17 мм). Электрические свойства (AC диэлектрическая и AC проводимость) (PVA/PEO)/MWCNTs в диапазоне частот (25x10^3-5x10^6) Гц были исследованы с помощью Hewlett Packard модели (HP4274A & HP4275A). Пробы (PVA/PEO)/MWCNTs нанокомпозитов были помещены в держатель. AC диэлектрическая и AC проводимость были рассчитаны как функция частоты. AC проводимость \( \sigma_{ac} \), диэлектрическая постоянная \( \varepsilon_r \) и диэлектрическая потеря \( \varepsilon_i \) для приготовленных (PVA/PEO)/MWCNT композитов рассчитывались по следующим уравнениям [5].

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

\[
\varepsilon_r = \frac{c_f}{\varepsilon_0.A} \quad (2)
\]

\[
\varepsilon_i = \tan(\delta)\varepsilon_r \quad (3)
\]
where, $\varepsilon_0$: is the permittivity of free space $= 8.85 \times 10^{-14} \text{F/cm}$, $t$, A thickness and surface area of the sample respectively. $R$: resistance of the composite, $\epsilon_r$: dielectric constant. A.C electrical conductivity $\sigma_{a.e}(\omega)$ is measured by the following equation [5]

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

where $\omega$ 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 $\sigma_{a.e}(\omega)$, 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:

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

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;

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

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 $\ln (\sigma(\omega))$ versus $\ln(\omega)$, 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 hope 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) ($\omega$) 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.

<table>
<thead>
<tr>
<th>Blend Ratios</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%PVA</td>
<td>0.9526</td>
</tr>
<tr>
<td>75%PVA + 25%PEO</td>
<td>0.9526</td>
</tr>
<tr>
<td>50%PVA + 50%PEO</td>
<td>1.0351</td>
</tr>
<tr>
<td>25%PVA + 75%PEO</td>
<td>1.0329</td>
</tr>
<tr>
<td>100%PEO</td>
<td>1.4737</td>
</tr>
</tbody>
</table>

Table 2: $s$ values of PVA/PEO blends doped with 1% MWCNT.

<table>
<thead>
<tr>
<th>Blend Ratios</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%PVA</td>
<td>0.7738</td>
</tr>
<tr>
<td>75%PVA + 25%PEO</td>
<td>0.8183</td>
</tr>
<tr>
<td>50%PVA + 50%PEO</td>
<td>0.8606</td>
</tr>
<tr>
<td>25%PVA + 75%PEO</td>
<td>0.7446</td>
</tr>
<tr>
<td>100%PEO</td>
<td>0.7232</td>
</tr>
</tbody>
</table>

Table 3: $s$ values of PVA/PEO blends doped with 3% MWCNT.

<table>
<thead>
<tr>
<th>Blend Ratios</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%PVA</td>
<td>0.6097</td>
</tr>
<tr>
<td>75%PVA + 25%PEO</td>
<td>0.2934</td>
</tr>
<tr>
<td>50%PVA + 50%PEO</td>
<td>0.2796</td>
</tr>
<tr>
<td>25%PVA + 75%PEO</td>
<td>0.8555</td>
</tr>
<tr>
<td>100%PEO</td>
<td>0.829</td>
</tr>
</tbody>
</table>

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 $\varepsilon_r$ as a function of frequency $\omega$ for undoped (PVA-PEO) blends, doped (PVA-PEO) blends while Fig. 3 illustrates the variation of imaginary part of dielectric constant $\varepsilon_i$ as a function of frequency $\omega$ for undoped (PVA-PEO) blends and doped (PVA-PEO) blends. The results show that the values of $\varepsilon_i$ tends to decrease with the increase of PEO weight fraction but then return to increase with further addition of PEO, although the value of $\varepsilon_i$ 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 $\varepsilon_r$ behavior vary for doped blends, i.e. $\varepsilon_r$ 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 $\varepsilon_r$ with increase of weight fraction of filler which reflect the increase of capacitance.

Fig. 2: Variation of $\varepsilon_r$ with ln($\omega$) for (PVA-PEO) blends (a) undoped (b) doped with 1% MWCNT (c) doped with 3% MWCNT.
Imaginary part of dielectric constant $\varepsilon_i$ represents the loss through the dielectric material. The results showed that $\varepsilon_i$ firstly decreased with the increase of frequency up to $10^3$ Hz but then the values of $\varepsilon_i$ in all blend are grown up to create small peak which is called the loss peak. The peak exists at constant position for each blend. At high frequencies the values of $\varepsilon_i$ 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 $\pi$-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 $\varepsilon_r$ showed proceeding increase of with increase of weight fraction of filler which reflect the increase of conductivity. Maximum value of $\varepsilon_i$ 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 ($\omega$) 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 (ω) for (a) undoped (PVA-PEO) blend (b) doped with 1% MWCNT (c) doped with 3% MWCNT.

References