

## **Structural and AC Electrical Properties of (LDPE-MWCNTs) Polymer Nanocomposite.**

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### **Abstract**

In this paper, the effect of Multi Walled Carbon Nanotubes (MWCNTs) on AC electrical properties of (LDPE-MWCNTs) nanocomposites bulk has been studied. The (LDPE-MWCNTs) nanocomposites were prepared in different (MWCNTs) volume fraction which were (1%, 2%, 3%, 4%). Ultrasonic dispersion and magnetic stirring techniques were used to prepare the nanocomposites specimens using flash molds at standard conditions. The morphology of samples have been studied using (SEM) technique, which showed grain distribution at surface morphology and grain aggregates with increasing of MWCNTs vol.%. The FTIR spectrum of samples were measured and shown the type of bond for polymer and the addition of MWCNTs did not effect on the chemical structure of LDPE. The experimental results (XRD) showed the samples transmutation from semicrystalline to crystalline because increased ratio particle of MWCNTs. AC electrical properties were measured at room temperature with different frequencies; it is found that the dielectric constant increases with increasing the MWCNTs vol.%, but decreases with increasing frequency attributed to polarization effects of the nanocomposite. Also the dielectric loss of polymers composites has been measured. The results refer that the dielectric loss is reduced with increasing of frequency and the AC conductivity increases with the increasing of volume fraction of MWCNTs because of the increase of the charge carriers and formation of a continuous network of MWCNTs inside the nanocomposites.

**Key words:** dielectric constant, dielectric loss, AC conductivity, nanocomposites, MWCNTs

## الخلاصة

تم في هذا البحث دراسة تأثير الانابيب الكربونية النانوية على الخصائص الكهربائية المتناوبة للمادة المتراكبة النانوية والتي حضرت لتغيرات الكسر الحجمي للأنابيب الكربونية النانوية وبنسب حجمية (١،٢،٣،٤) % من الانابيب الكربونية النانوية . تم استخدام تقنيتي الاهتزازات الفوق الصوتية والخلط المغناطيسي لتحضير المتراكبات النانوية باستخدام القوالب المارقة تحت الظروف القياسية.

تم قياس الخصائص الكهربائية في درجة حرارة الغرفة بتأثير ترددات مختلفة . اظهرت النتائج بأن ثابت العزل الكهربائي يزداد مع زيادة نسبة الانابيب الكربونية النانوية و يقل مع زيادة التردد. و يعزى ذلك يؤدي الى تأثير الاستقطاب على المادة المتراكبة النانوية ، كذلك تم قياس عامل الفقد للمادة المتراكبة و وجد بأن عامل الفقد يقل مع زيادة التردد كما اظهرت النتائج ان التوصيلية المتناوبة تزداد مع زيادة تركيز الانابيب الكربونية النانوية بسبب زيادة حاملات الشحنة وتكوين شبكة مستمرة من الانابيب الكربونية النانوية داخل المادة المتراكبة.

## 1- Introduction

Nanocomposites can be defined as a composite material in which at least one of the phases (mostly the filler) shows dimensions in the nanometer range. As the fillers size reaches the nanometer level, the interactions at the interfaces become considerable large with respect to the size of the inclusion and thus the final properties show significant changes [1]. A nanocomposite, like a traditional composite has two parts, filler and the matrix. A traditional composite typically uses a fiber such as carbon fiber or fiberglass as the filler, in a nanocomposite the filler is a nanomaterial. Some examples of nanomaterial are CNTs, carbon nanofiber, and nanoparticles such as gold, silver, diamond, copper, and silicon. Of particular interest are CNT nanocomposites because of their high strength and stiffness composites they produce at relatively low CNT volume fraction [2, 3].

An enhancement in a property arises when the length scale of the morphology (i.e., nano) and fundamental physics associated with a property coincide. Two principal factors cause the properties of nonmaterials to differ significantly from other materials: increased relative surface area and quantum effects [4]. Some nanocomposites may show properties predominated by the interfacial interactions and others may exhibit the quantum effects associated with nano dimensional structures [5]. Many of the researchers studied the effect of MWCNTs on the

electrical properties of polymers; in (2011) Estabarak. T. Abdullah and Asama .N. Naje studied AC electrical and dielectric properties of polyvinyl chloride (PVC) with (MWCNT) with different concentrations and different frequency. Electrical conductivity measurements increase with the increasing of the amount of MWCNTs [6]. Also in (2013) J.Jasim studied dielectric properties of (MWCNTs-Epoxy) composites, dielectric constant and dissipation factor of (MWCNTs-Epoxy) was greater for all filler concentration than that of pure Epoxy. Also the dielectric constant and dissipation factor decreased with increasing in frequency [7].

Carbon nanotubes change the properties of the polymers when it is adding to polymers [8-10]. The development of nanotube reinforced polymer composites in recent years make it important due to their attractive applications in various fields. When two and three-dimensional nanofillers are added to a polymer matrix giving large surface area to volume ratios [11].

**2- Theoretical part**

The ratio of the capacitance of a dielectric-filled capacitor ( $C_p$ ) to a capacitor of free space ( $C_0$ ) is called dielectric constant ( $\epsilon$ ). It is very important for AC properties and calculated by using the following equation: [12]

$$\epsilon' = \frac{C_p}{C_0} \dots\dots\dots (1)$$

The dielectric losses ( $\epsilon''$ ) are calculated by followed equation:

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \dots\dots\dots (2)$$

Where  $\tan\delta$  is loss factor.

The AC electrical conductivity is calculated by followed equation:

$$\sigma_{AC} = \omega\epsilon''\epsilon_0 \dots\dots\dots (3)$$

Where  $\omega$  is the angular frequency of the applied field ( $\omega = 2\pi f$ ).

The  $D_{ave}$  is representing the crystalline size calculated by using the Scherrer formula

$$D_{ave} = \frac{0.94 \lambda}{\beta \cos \theta_B} \dots\dots\dots (4)$$

$$\eta = (D \cos\theta)/4 \dots\dots\dots (5)$$

$$\delta = 1/D2 \dots\dots\dots (6)$$

Where  $\lambda$ : Wavelength 1.5406 Å,  $\beta$ : FWHM,  $\theta_B$  (Braagg's angle) = $2\theta/2$ ,  $\eta$ : Strain,  $\delta$  :stress

### **3-Preparation method**

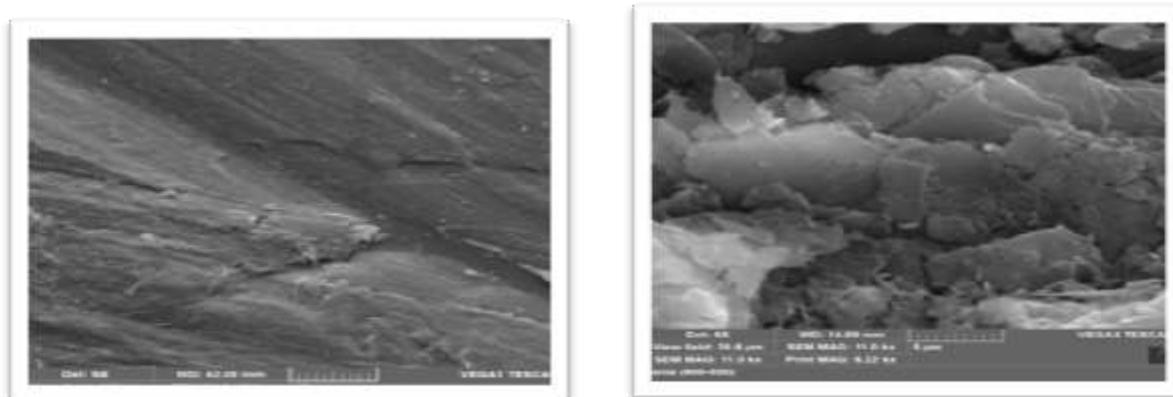
Polymeric nanocomposites samples have been prepared by weighing an amount of Low density polyethylene LDPE (supplied as a powder form by Pars Petrochemical with density 912 kg/m<sup>3</sup> ) with MWCNTs(were supplied by Material and Electrochemical Research (MER) Corporation, U.S.A, the diameter of (MWCNTs) was (140 ± 30) nm and a length of (7 ± 2) microns) by the liquid mixing as follows ,preparing LDPE powder ,then adding to its a solvent as tetrahydrofuran (THF) then adding MWCNTs that have a little from tetrahydrofuran (THF) . Then mixing well by constant stirring for half an hour until the mixture is homogenous. Then putting the mixture in a glass bowl and using an Ultrasonic device for an hour for the purpose of homogeneity of the polymer with MWCNTs. Then leave the mixture to dry, or dried by drier at a temperature 343k until it becomes as the dry block, after that the process of grinding begins to a very fine powder up to 3 μm or less, then being the hot press process at temperature (353-363)k according to the rate of MWCNTs to prepare the nanocomposite in the form of a disc with (2)cm diameter and (0.2)cm thickness. The SEM study had been carried out by Hitachi (S-4160). FT-IR spectra were recorded by (SHIMADZU), the wave number range is (400- 4000) cm<sup>-1</sup>. The sharply defined transmission peaks that correspond to various vibrational modes of chemical bonds were determined for the prepared samples. Crystal structures of the preparation polymeric composites have been studied by using the XRD (6000) diffraction device supplied by the Japanese company (SHIMADZU) .It has the following properties: Target: Cu., wavelength: 1.5406 Å, Voltage: 40 KV, Current: 30 mA

### **4-Results and Discussion**

#### **4-1 Structural properties**

##### **a. SEM for (LDPE-MWCNTs) nanocomposites:**

Figure (1) shows randomly distributed of MWCNTs in the (LDPE) polymer samples and concluded agglomerations formed in these samples. The result agree with [13]



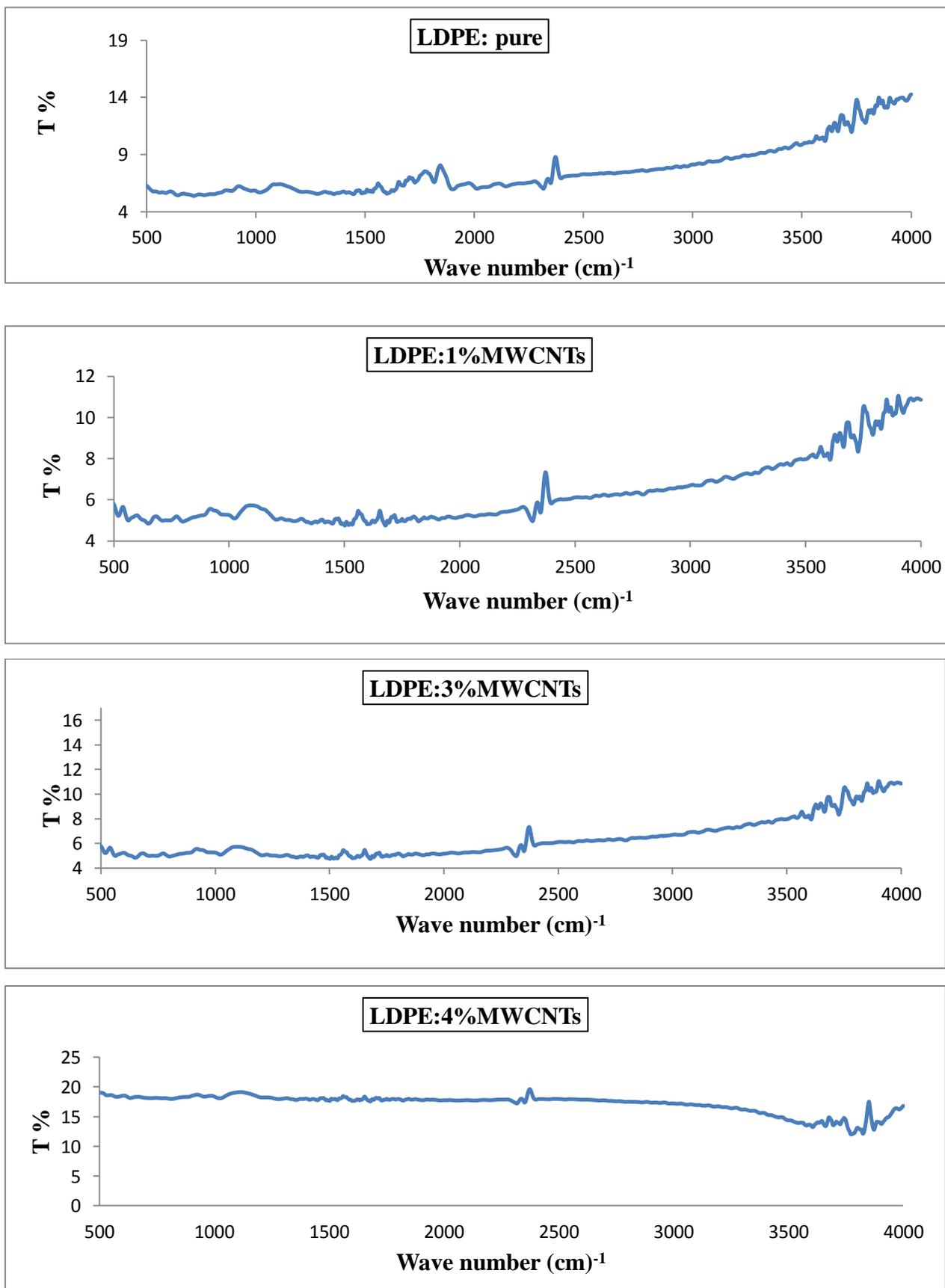
**Figure (1): SEM images; a: LDPE: pure  
b: (LDPE-MWCNTs) nanocomposites for 4vol.% MWCNTs**

#### **b-FT-IR of ( LDPE-MWCNTs) nanocomposite**

In Figure (2), pure (LDPE) shows the peaks ( $715.59$  and  $887.26\text{cm}^{-1}$ ) correspond to the (C-H) aromatic, the peaks ( $1018.41$  and  $1282.66\text{cm}^{-1}$ ) correspond to the (C-O-C) of ethers groups, the transimission around ( $1381.03^{-1}$ ) characterize the asymmetric bending vibrations of (C-CH<sub>3</sub>) and (C-CH<sub>2</sub>) bonds respectively, the peaks ( $1517.98$ ,  $1533.41$  and  $1598.99\text{cm}^{-1}$ ) correspond to the band stretching (C=C) aromatic rings, the peaks ( $2974.23\text{cm}^{-1}$ ) correspond to the (C-H) stretch aliphatic and the peak ( $3979.15\text{cm}^{-1}$ ) correspond to the band stretching (O-H) and in this figure,we note that there are two peaks ( $1028.05$  and  $3824.84\text{cm}^{-1}$ ) refers to MWCNTs appeared in high volume fraction samples , and all other peaks as the same for pure LDPE polymer .The results agree with [14,15] .

**Table (1 ): FTIR transmittance bands positions and the spectral data of the (LDPE-MWCNTs) nanocomposite for (0, 1, 3,4vol. %)**

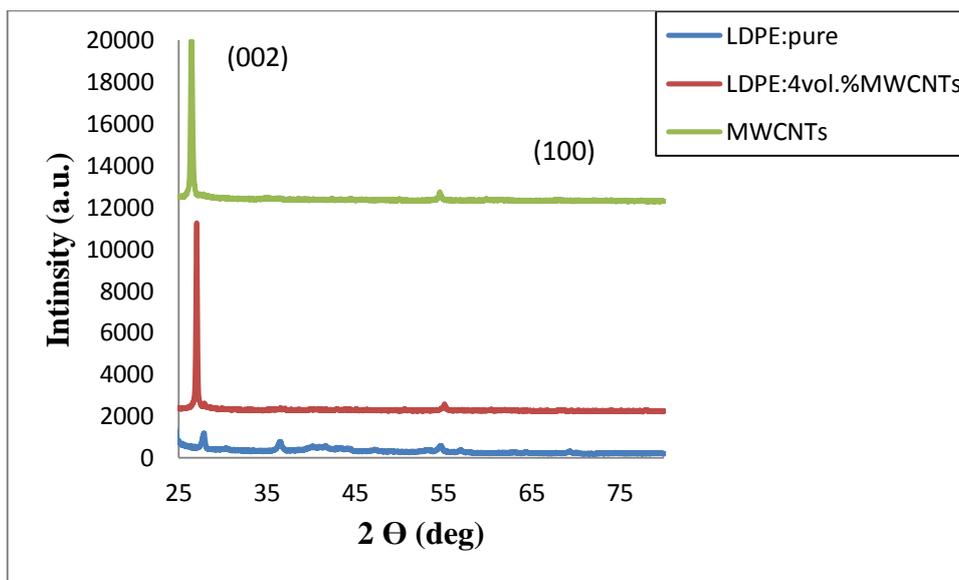
Active Band	(MWCNT) vol.%			
	0 vol.%	1 vol.%	3vol.%	4vol.%
C-H Out of phase bending (675-970) cm <sup>-1</sup>	715.59cm <sup>-1</sup> 889.26 cm <sup>-1</sup>	713.66cm <sup>-1</sup> 800.46cm <sup>-1</sup>	713.66 cm <sup>-1</sup> 800.46cm <sup>-1</sup>	723.31cm <sup>-1</sup> 813.96cm <sup>-1</sup>
C-O-C ethers (1000-1300) cm <sup>-1</sup>	1018.41 cm <sup>-1</sup> 1282.66 cm <sup>-1</sup>	1024.2cm <sup>-1</sup> 1282.66 cm <sup>-1</sup> 1028.05 cm <sup>-1</sup>	1024.2 cm <sup>-1</sup> 1282.66cm <sup>-1</sup> 1028.05 cm <sup>-1</sup>	1024.2 cm <sup>-1</sup> 1280.73cm <sup>-1</sup> 1028.05 cm <sup>-1</sup>
O-CH <sub>3</sub> deformation	1381.03 cm <sup>-1</sup>	1382.96cm <sup>-1</sup>	1382.96cm <sup>-1</sup>	1382.96 cm <sup>-1</sup>
C-CH <sub>3</sub> C-CH <sub>2</sub>	1517.89 cm <sup>-1</sup> 1533.41 cm <sup>-1</sup>	1517.98cm <sup>-1</sup> 1533.41cm <sup>-1</sup>	1517.98cm <sup>-1</sup> 1533.41cm <sup>-1</sup>	1519.91 cm <sup>-1</sup> 1537.27cm <sup>-1</sup>
C=O asters (1600-1800) cm <sup>-1</sup>	1712.79 cm <sup>-1</sup>	1730.15 cm <sup>-1</sup>	1730.15 cm <sup>-1</sup>	1730.15 cm <sup>-1</sup>
C-H aliphatic (2800-3200) cm <sup>-1</sup>	2974.23 cm <sup>-1</sup>	2958.8 cm <sup>-1</sup>	2958.8cm <sup>-1</sup>	2981.95 cm <sup>-1</sup>



**Fig. (2): FT-IR of (LDPE-MWCNTs) nanocomposites samples with different volume fraction**

**c. XRD of (LDPE-MWCNTs) nanocomposites:**

X-ray diffraction peaks of MWCNTs occur at  $2\theta = (26.8577^\circ$  and  $54.8394^\circ)$  corresponding to reflections from the (002) and (100) planes of MWCNTs respectively. Peaks indexed to (002) and (100) reflected hexagonal structure (according to ICDD N 1997 and 2011 JCPDS) .The presence of (002) in the (XRD) data, suggests multiwall nature of carbon nanotubes. Figure (3) shows (XRD) of (LDPE-MWCNTs) nanocomposites for (4vol. %MWCNTs), there are two sharp peaks belong to (MWCNTs), from the observation of this XRD it can be conclude that synthesis of the composites with MWCNTs in LDPE was successful and crystalline size was increased by adding (MWCNTs) ,which is emerged by adding (MWCNTs) to (LDPE) enhanced the structural properties of (LDPE-MWCNTs) composites, that meaning the degree of crystalline increase because the particles of ((MWCNTs)). Table (2) shows some properties of (LDPE-MWCNTs) nanocomposites. The result is a good agreement with [15]



***Fig.(3): XRD of (LDPE-MWCNTs) nanocomposites.***

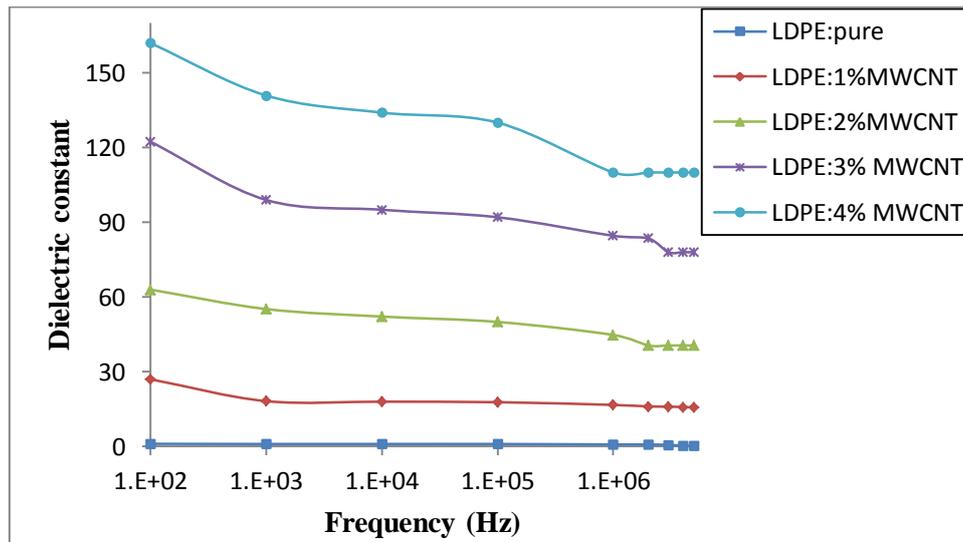
**Table (2): Some properties structure of (LDPE-MWCNTs) nanocomposites.**

<i>sample</i>	<i>2θ</i> (deg)	<i>hkl</i> <i>plane</i>	<i>d</i> <i>observed</i> ( $\text{Å}$ )	<i>FWHM</i> (deg)	<i>D</i> (nm)	$\delta \times 10^{14}$ <i>lines.m</i> <sup>-2</sup>	$\eta \times 10^{-4}$ <i>lines</i> <sup>2.m</sup> <sup>-4</sup>
(LDPE-MWCNTs)	26.85	(002)	.,.17	.,.9	80,30	1,37	3,83
4 vol.%MWCNTs	54.83	(100)	.,.30	0.07	100.05	0.99	2.72

#### 4-2 Dielectric constant

The variation of the dielectric constant of (LDPE-MWCNTs)nanocomposites with frequency at room temperature is shown in Figure (4). In low and high frequency region, this figure shows that the dielectric constant values decrease when the applied field frequency increases, while in the middle frequency region it is nearly constant. Increasing of the frequencies cause decreasing of space charge polarization (interfacial polarization) to the total polarization. The space charge polarization becomes the more contributing type of polarization at low frequencies, and less contributing with the increase of frequency; this caused decreasing of dielectric constant values for all samples of (LDPE-MWCNTs) nanocomposites with the increase of the electric field frequency (f) [16].

The other types of polarizations appear at high frequencies, the ionic polarization reacts slightly to the variation in the field frequencies compared to the electronic polarization because the mass of ion is greater than that of the electron. Electronic polarization is demented at high frequencies due to its low mass of electron. This makes the dielectric constant approximately constant for all samples at high frequencies. The results agree with [17].



**Fig.(4): Variation of the dielectric constant of (LDPE-MWCNTs) nanocomposites with frequency**

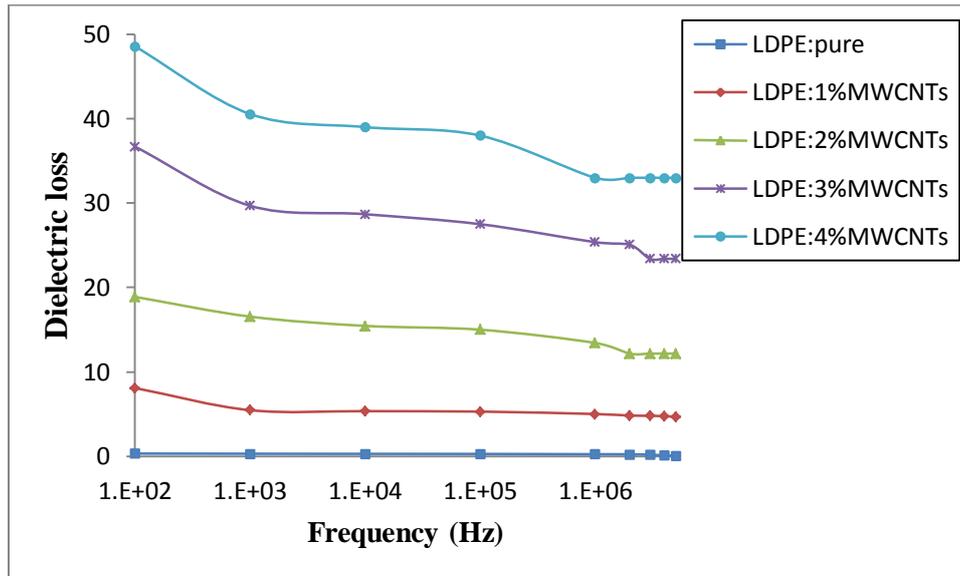
Figure (4) show the dielectric constant increases with the increasing of the volume fraction of MWCNTs [18].

The reason for this increase in the value of dielectric constant is the formation of a continuous network of carbon nanotube inside the nanocomposites; at low volume fraction of additive like pure (1%) take the form of clusters or separated groups; hence, the dielectric constant becomes approximately low, while at high volume fraction like 2%, 3%, and 4% form a continuous network inside the nanocomposites.

( $C_p$ ) is increase for the storage charges and increased the value of dielectric constant increases with the volumetric rate of MWCNTs. The results good agreement with [19, 20].

#### 4-2 Dielectric loss

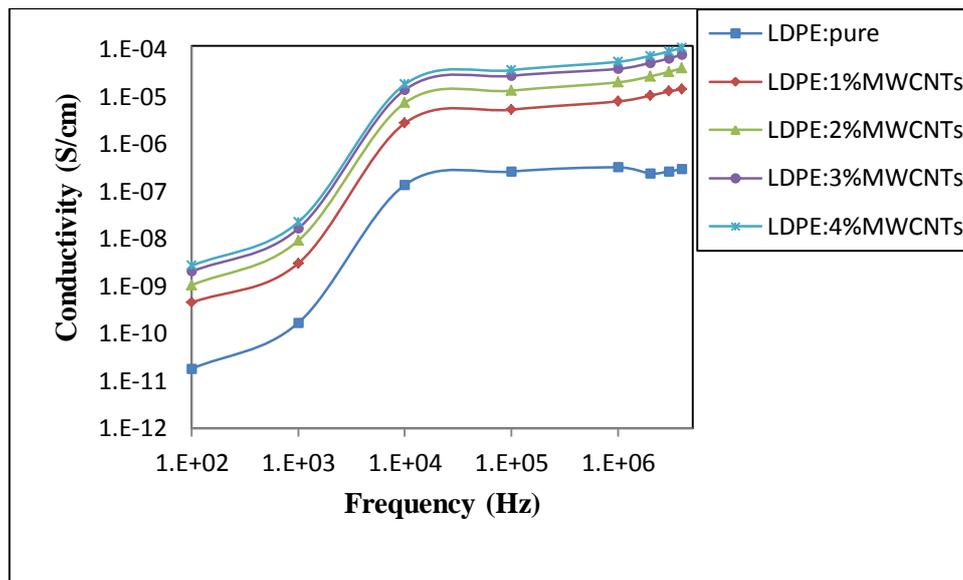
The behaviour of the dielectric loss for various volume fraction of the filler as a function of frequency at room temperature is shown in Figure (5) . In the low and high frequency region ,it was shown that the dielectric loss is decreasing . This is attributed to the decrease of the space charge polarization (interfacial polarization) contributes when the frequency increases . In the intermediate frequency region from ( $f= 10^3$  ) Hz to ( $f= 10^6$ ) Hz the dielectric loss is approximately constant of (LDPE-MWCNTs) nanocomposites.From this figure it was noted that the value of dielectric loss increases by increasing the volume fraction of MWCNT; this is due to the increase of the charge carriers caused by the increase of MWCNTs vol.%. This is consistent with the results of researchers [18,21].



**Fig. (5): Variation of the dielectric loss with frequency of (LDPE-MWCNTs) nanocomposites**

### 4-3 The AC electrical conductivity

The behaviour of AC conductivity of (LDPE-MWCNTs) nanocomposites for various volume fraction of MWCNT as a function of frequency at room temperature is shown in Figures (6). It was shown from this figure that the AC conductivity increases considerably when the frequency range from 100 Hz to  $1 \times 10^4$  Hz, above this value the AC conductivity is nearly constant. This is attributed to the space charge polarization that occurs at low frequencies and to the motion of charge carriers by hopping process. The increases of the conductivity are small at high frequencies; this is attributed to the electronic polarization and the charge carriers, which travel by hopping process [21]. It was observed that the AC electric conductivity increased sharply with the increasing of the volume fraction of MWCNTs. The conductivity is increases with the increasing of the volume fraction of MWCNTs because of the increase of the charge carriers and the formation of a continuous network of MWCNTs inside the nanocomposites. This is consistent with the results of researchers [18].



**Fig. (6): Variation of AC electrical conductivity with frequency of (LDPE-MWCNT) nanocomposites.**

### 3-4 conclusions

The values dielectric constant were decreasing with increasing of frequency and increasing with MWCNTs vol.%, this effect may be due contribute the polarization and form network inside the polymer, the dielectric loss of the (LDPE-MWCNTs) nanocomposites decrease with the increase of frequency of the applied electric field and the AC conductivity is increases with the increasing of the MWCNTs vol.% because of the increase of the charge carriers and the formation of a continuous network of MWCNTs inside the nanocomposites.

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