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Structural and Dielectric properties for (PVC-Ag) Polymer Nanocomposites

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***Abstract*—In this paper, Structural properties of (PVC-Ag) nanocomposites bulk using (AFM, SEM, FT-IR, and XRD) and its dielectric properties have been studied. The (PVC-Ag) nanocomposites were prepared by hot press in different silver nanoparticles volume fraction which were (1%, 2%, 3%,and 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 Ag nanoparticles volume fraction. The FTIR spectrum of samples were measured and shown the type of bond for polymer and the addition of Ag did not affect on the chemical structure of PVC. The experimental results (XRD) showed the samples transmutation from semicrystalline to crystalline because increased volume fraction of Ag nanoparticles. Dielectric properties were measured at room temperature and different frequencies; it was found that the dielectric constant increased with increasing the Ag nanoparticle volume fraction, but decreasing with increasing frequency. This may be due to polarization effects of the nanocomposite. Also the dielectric loss of (PVC-Ag) has been measured. The results refer that the dielectric loss is reduced with increasing of frequency and the AC conductivity is increases with the increasing of the volume fraction of Ag nanoparticles because of the increase of the charge carriers and the formation of a continuous network of Ag nanoparticles inside the nanocomposites.**

Keywords—dielectric constant, dielectric loss, AC conductivity, Structural properties, nanocomposites, silver nanoparticles.

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 nanaocomposite, 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 [2, 3]. The researchers studied the effect of Ag nanoparticle on the electrical properties. In (2011) S. Khairul Anuar, et.al [4] studied the effect of two types of silver (silver A and silver B) with epoxy on the properties of silver/epoxy conductive with different percentage of filler, the experimental results showed that the electrical conductivity and thermal expansion properties of one-part system conductive are higher than those of two part system conductive. Improved electrical conductivity in the one-part system is due to its high crosslink density, which results in high shrinkage during curing which increases electrical conductivity. Many nanofillers can change not less one of important property when are adding to polymers like these nanofiller are Silver nanoparticles [5, 6, 7].The development of nanotube, platelet and particle reinforced polymer composites has grown in importance in recent years due to their attractive applications in various fields. Two and three-dimensional nanofillers into a polymer matrix giving high aspect ratios and large surface area to volume ratios [8].

2-Preparation method:

Polymeric nanocomposites samples have been prepared by weighing an amount of Polyvinyl chloride PVC (supplied as a powder form by Pars Petrochemical with density (1.16) gm/m^3)with Ag nanoparticles (was supplied by (EPRUI) Nanoparticles and Microspheres Company with radius (40) nm and molecular weight (107.86) g/mol) by the liquid mixing as follows ,preparing PVC powder ,then adding to its a solvent as tetrahydrofuran (THF) then adding Ag nanoparticles 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 Ag nanoparticles. 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 Ag nanoparticles to prepare the nanocomposite in the form of a disc with (2) cm diameter and (0.2)cm thickness. Maximum scanning size of the AFM microscope probe was (10x10) μm and its resolution (300x300) pixels; nominal diameter of tip was (10) nm. Atomic force microscopy imaging of nanomaterial is typically performed in tapping mode. Useful information includes the length and diameter distribution of nanotubes in a sample, and the amount of bundling nanotube dispersion. 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^{-1}. The sharply defined transmission peaks that correspond to various vibrational modes of chemical bonds were determined for the prepared samples. All 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

3-Results and Discussion

3-1 Structural properties

a. AFM of Silver (Ag):

An atomic force microscope explorer thermo microscope was used as an indirect method for morphological analysis of the sample. Figure (1) shows structures and nanoparticle size of Ag in three dimensions and particle size distribution of Ag nanoparticles. The surface analysis mode with tapping-mode AFM shows a semispherical shape, good homogenous, roughness average is (1.13)nm and root mean square is (1.31) nm. From this figure can see the range of the particle diameter between (40 -120) nm .The averages of the diameter is (89.43) nm and the grain number is (100).

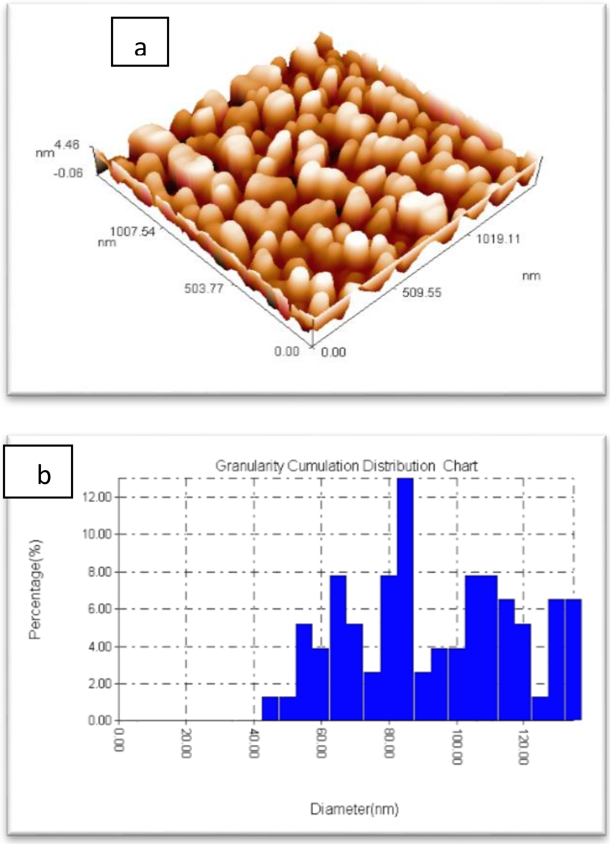

Fig.(1):a: Atomic force microscopy of structures and nanoparticle size in three dimensions , b: particle size distribution of Silver.

b. SEM for (PVC-Ag) nanocomposites:

Scanning electron microscopy has been used to study the compatibility between various components of the polymers and nanomaterial's through the detection of phase separations and interfaces. The sample exhibit uniform density of grain distribution at surface morphology of the composites and show many aggregates or chunks randomly distributed of Ag nanoparticles on the surface samples. The results indicate that Ag nanoparticles tended to form aggregates and good dispersed, from the image observed that the Ag nanoparticles randomly distributed in the (PVC) polymers samples and concluded that small agglomerations is formed in this samples. The result agree with [9]

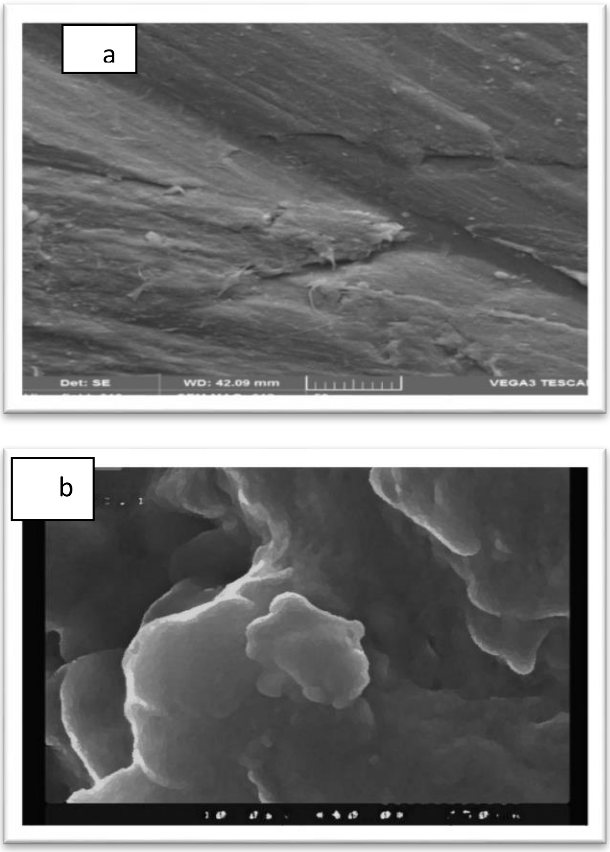

Fig. (2): SEM images; a: PVC: pure
b: (PVC-Ag) nanocomposites for 4vol.% Ag.

c-FT-IR of (PVC-Ag) nanocomposite

In Figure (3) for pure (PVC) shows the peaks (665.44)cm^{-1} correspond to (C-Cl), (744.52,806.25,839.03,900.76 and 968.27) cm^{-1} correspond to the (C-H) aromatic, the peaks (1064.71,1116.78,1172.72 and 1257.59) cm^{-1} correspond to the (C-O-C) of ethers groups, the transimission around (1373.32) cm^{-1} characterize the asymmetric bending vibrations of ($C-CH_3$) and ($C-CH_2$) bonds respectively, the peak (1452.4cm^{-1}) correspond to the band stretching (C=C) aromatic rings, the peaks (2835.36,2866.22, 2916.36 and 2964.59) cm^{-1}correspond to the (C-H) stretch aliphatic**.** From the table (1) and the figure (3), it was noted that there are two peaks (1064.71 and 2131.34) cm^{-1} refers to Ag nanoparticles appeared in all samples, and all other peaks as the same for pure PVC polymer, the intensity of transmission for (PVC-Ag) samples more than (PVC) pure and all peaks are compared with the result of other reserarch [9] .

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

Active Band		**volume fraction (Ag)**		
	0 wt.%	**1 vol.%**	**3 vol.%**	**4 vol.%**
C-H Out of phase bending (625-970) cm^{-1}	665.44 cm^{-1} 839.03 cm^{-1} 968.27 cm^{-1}	665.44cm^{-1} 839.03cm^{-1} 968.27cm^{-1}	665.44 cm^{-1} 839.03 cm^{-1} 968.27 cm^{-1}	665.44 cm^{-1} 839.03 cm^{-1} 968.27 cm^{-1}
C-O-C ethers (1000-1300) cm^{-1}	1116.78cm^{-1} 1172.72 cm^{-1} 1257.59 cm^{-1}	1064.71cm 1111cm^{-1} 1172.72cm^{-1} 1253.73cm^{-1}	1060.85cm^{-1} 1118.71 cm^{-1} 1163.08 cm^{-1} 1249.87 cm^{-1}	1064.71 cm^{-1} 1114.86 cm^{-1} 1170.79 cm^{-1} 1253.73 cm^{-1}
$O-CH_3$ deformation	1373.32 cm^{-1}	1375.25cm^{-1}	1375.25 cm^{-1}	1373.32 cm^{-1}
$C-CH_3$ $C-CH_2$	1452.4 cm^{-1}	1454.33cm^{-1}	1454.33 cm^{-1}	1438.98 cm^{-1} 1479.59cm^{-1}
C=O asters (1600-1800) cm^{-1}	1730.15 cm^{-1}	1732.08cm^{-1}	1730.15 cm^{-1}	1732.08 cm^{-1}
C-H aliphatic (2800-3200) cm^{-1}	2835.36 cm^{-1} 2866.22 cm^{-1} 2916.36 cm^{-1} 2964.59 cm^{-1}	2839.22cm^{-1} 2866.22cm^{-1} 2924.09cm^{-1} 2964.59 cm-1	2837.29 cm^{-1} 2866.22 cm^{-1} 2906.73cm^{-1} 2956.87 cm^{-1}	2835.36 cm^{-1} 2872.01 cm^{-1} 2895.15 cm^{-1} 2954.95 cm^{-1}

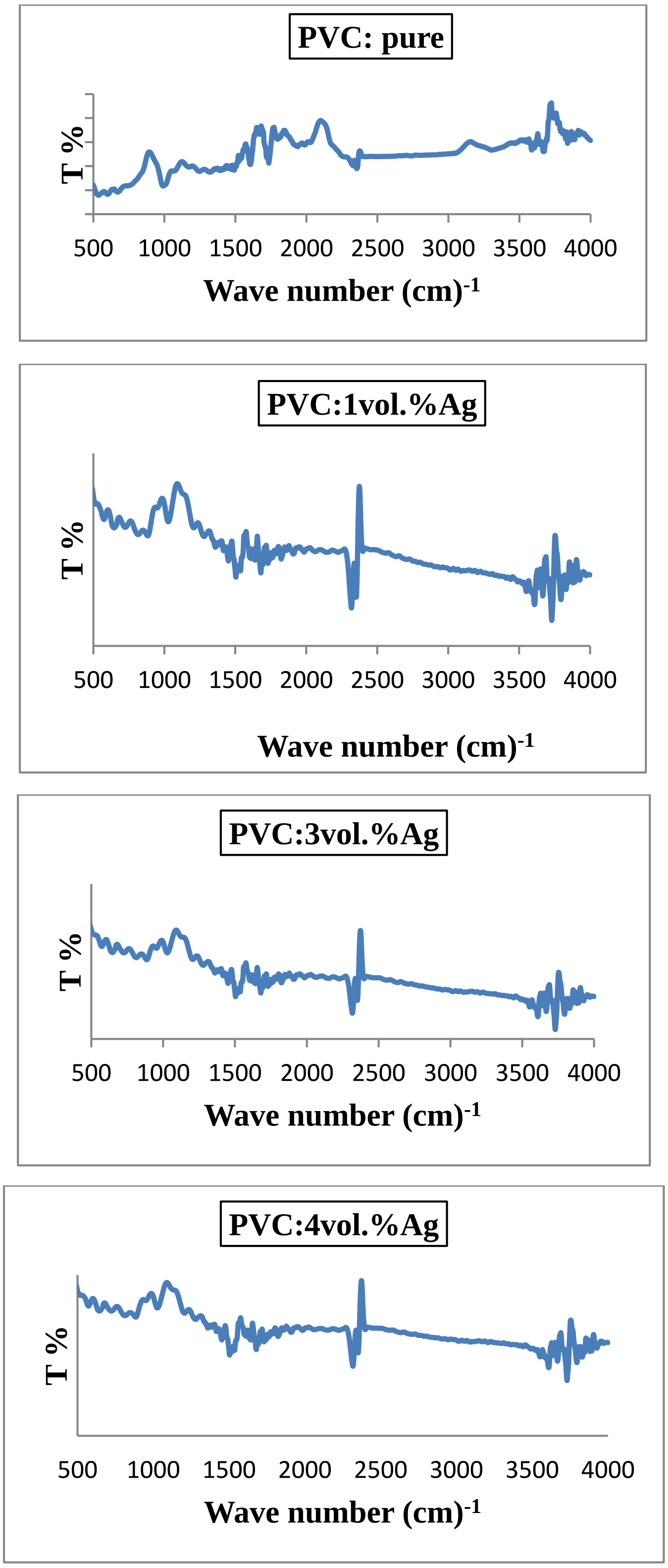

Fig. (3): FT-IR of (PVC-Ag) nanocomposites samples with different volume fraction

d. XRD of (PVC-Ag) nanocomposites:

The X-ray diffraction peaks of Ag nanoparticles occur at 2θ=(37.80°, 43.42 ° and 64.14°) for sharp peaks only corresponding to reflections from the (111), (200) and (220) planes of Ag FCC lattice structure respectively, as shown in Figure(4) which were in good agreement with reference of FCC structure from joint committee of powder diffraction standard (JCPDS) card No-087-0720. Figure (4) shows the (XRD) of (PVC-Ag) nanocomposites for (4vol. %Ag) has three sharp peaks that represent peaks of (Ag) that means this sample became crystalline because increased volume fraction of Ag nanoparticles. The D_{ave} is representing the crystalline size calculated by using the Scherrer formula

$$D_{ave} = \frac{0.94\ \lambda}{\beta \cos\ \theta_B} \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \ (1)$$

Where λ: Wavelength 1.5406 Å, β: FWHM, $\theta_B = 2\theta/2$ .The crystalline size was increased by adding (Ag) as shown in table (2) which is emerged by adding (Ag) to (PVC) enhanced the structural properties of (PVC-Ag) nanocomposites, that meaning the degree of crystalline increase because the particles of Ag nanoparticles.The results agree with [10].

Table (2): Some properties structure of X-ray characterization

sample	*2Theta (deg)*	*hkl plane*	*d observed (Å)*	*FW HM (deg)*	*D (nm)*	*δ × 10^14 lines .m^-2*
(PVC-Ag) 4vol.%Ag	37.80 43.42 64.14	(111) (200) (220)	0.0038 0.0213 0.0468	0.12 0.14 0.14	61.96 52.12 47.52	4.95 5.67 5.17

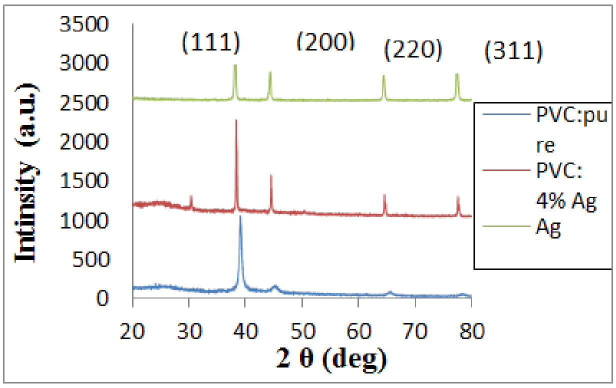

Fig. (4): XRD pattern of (PVC-Ag) nanocomposites

3-2 Dielectric constant

The ratio of the capacitance of a dielectric-filled capacitor (C_p) to a capacitor of free space (C_0) is called dielectric constant (ὲ). It is very important for AC properties, was calculated by using the equation (1) [11]

$$\varepsilon' = \frac{C_p}{C_o} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \ (2)$$

At room temperature the dielectric constant (ὲ) is determined with different frequencies. Dielectric constant of (PVC-Ag) nanocomposites values decrease with increasing the electric field frequency as shown in figure (5). In low and high frequency region, this figure shows that the dielectric constant is decreasing when the applied field frequency increases. In the middle frequency region the dielectric constant is approximately 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 (PVC-Ag) nanocomposites with the increase of the electric field frequency (f) [11].

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 in 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 [12].

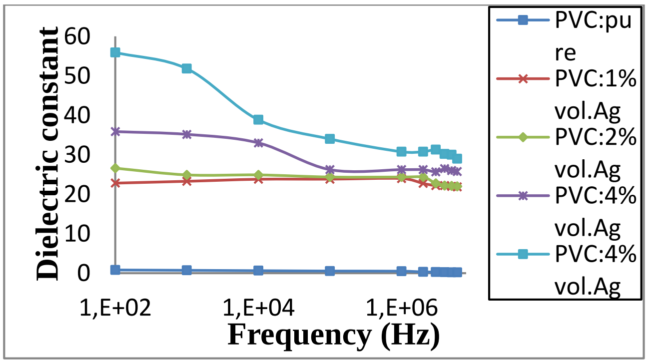

Fig. (5): Variation of the dielectric constant of (PVC-Ag) nanocomposites with frequency

Figure (5) show the dielectric constant increases with the increasing of the volume fraction of Ag nanoparticles [13]. The reason for this increase in the value of dielectric constant is the formation of a continuous network of Ag nanoparticles inside the nanocomposites; at low volume fraction of Ag nanoparticles of additive like pure (0, 1, 2) vol. % take the form of clusters or separated groups; hence, the dielectric constant becomes approximately low, while at high volume fraction of Ag nanoparticles like 3vol. % and 4vol. % 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 the Ag nanoparticles. The results agree with [14, 15].

3-3 Dielectric loss

The dielectric losses (ε″) are calculated by followed equation:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where $\tan\delta$ is loss factor .

Dielectric loss increases to the highest value of (f=100 KHz) of (PVC-Ag) nanocomposites as shown in figure (6).

This value represents the highest dielectric loss at certain frequency; that is the highest absorption of applied field. [16]. When the frequency (f) is increases to 3 MHz, the dielectric loss is approximately constant of (PVC-Ag) nanocomposites.

This is attributed to the mechanisms of other types of polarization that occurs at high frequencies. The value of dielectric loss increases by increasing the volume fraction of Ag nanoparticles; this is due to the increase of the charge carriers caused by the increase of the volume fraction of Ag nanoparticles. The results agree with [13, 17].

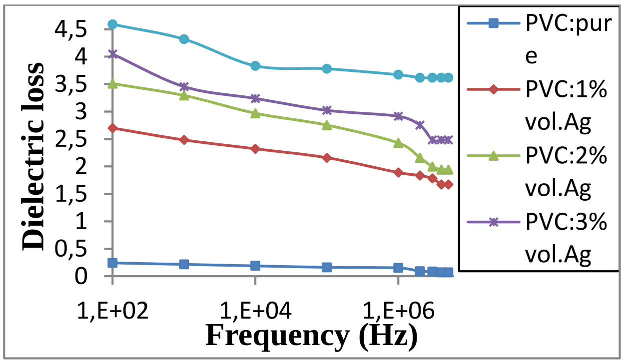

Fig.(6): Variation of the dielectric loss with frequency of (PVC-Ag) nanocomposite

3-4 The A.C electrical conductivity

The AC electrical conductivity is calculated by followed equation (3)

$$\sigma_{Ac} = \omega\varepsilon''\varepsilon_{\circ} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Where ω is the angular frequency of the applied field (ω =2πf).

Figure (7) shows the variation of the conductivity for (PVC-Ag) with frequency. The figure shows that the AC conductivity increases slightly with the increase of frequency (f) from $1*10^{2}$ Hz to $1*10^{6}$ Hz, above this value the AC conductivity increases sharply. 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 [14]. Consequently, the conductivity is increasing when the frequency increases for all different rates of Ag nanoparticle for (PVC-Ag) nanocompósities.

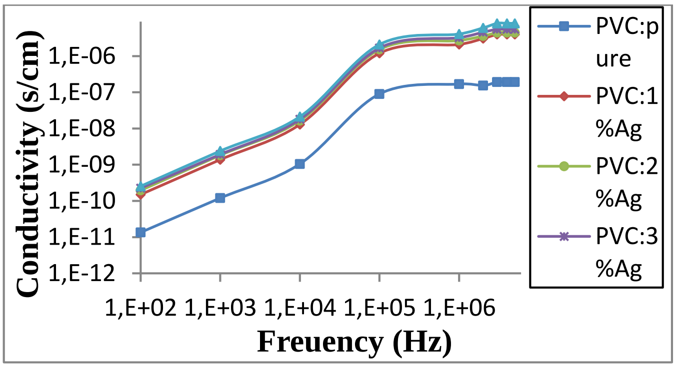

Fig. (7): Variation of A.C electrical conductivity with frequency of (PVC-Ag) nanocomposites.

Figure (8) shows the variation of A.C conductivity of (PVC-Ag) nanocomposites, with the volume fraction of Ag nanoparticles at 100 Hz under room temperature (30^0C). The A.C conductivity slightly increases at low volume fraction of Ag nanoparticles this increase is due to the effect of the space charge. The Ag nanoparticles take the form of clusters or separated groups. The conductivity is increases with the increasing of the volume fraction of Ag because of the increase of the charge carriers and the formation of a continuous network of Ag inside the nanocomposites. Consequently, the conductivity is increases with the increasing of the volume fraction of Ag for (PVC-Ag) nanocomposites. The results agree with [18].

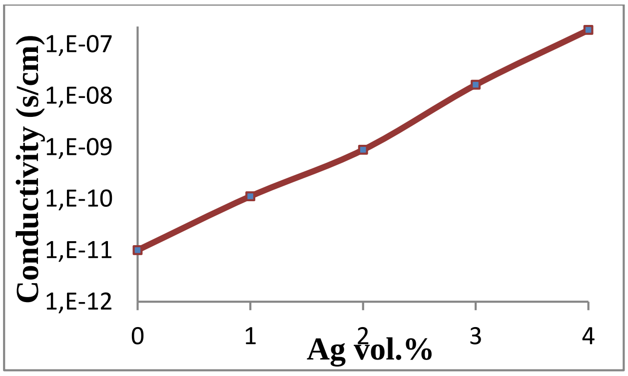

Fig.(8): Variation of A.C electrical conductivity with silver nanoparticles vol % at 100 Hz of (PVC-Ag) nanocomposites

3-5 conclusions

Images Scanning Electron Microscope (SEM) shows grain distribution at surface morphology of (PVC-Ag) nanocomposites and grain aggregates with increasing of the volume fraction of Ag nanoparticles. The FTIR showed that the addition of Ag nanoparticles did not effect on the chemical structure of PVC. The experimental results (XRD) showed the samples transmutation from semicrystalline to crystalline because increased ratio particles of Ag nanoparticles. Dielectric properties were measured at room temperature and different frequencies; it was found that the dielectric constant behaviors decreasing with increasing of frequency and increasing with the volume fraction of Ag nanoparticles, this effect may be due contribute the polarization and form network inside the polymers, the dielectric loss of the (PVC-Ag) nanocomposites decrease with the increase of frequency of the applied electric field and the AC conductivity is increases with the increasing of the volume fraction of Ag nanoparticle because of the increase of the charge carriers and the formation of a continuous network of Ag nanoparticles inside the nanocomposites.

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