

Study the Electrical and Structural Properties of (PMMA-TiO₂) nanocomposites

Raheem G.Kadhim

University of Babylon, College of Sciences, Department of Physics, Babylon, Iraq

Abstract

In this work, we study the effect of nanoTiO₂ particles on electrical properties of polymer PMMA. The samples of (PMMA-TiO₂) nanocomposites were prepared by using casting method. The weight percentages of nano TiO₂ are (0,3,5 and 7) wt.%. The experimental results show that the D.C electrical conductivity for the (PMMA-TiO₂) nanocomposite increase with the increasing temperature, the activation energy for D.C electrical conductivity for (PMMA-TiO₂) nanocomposite decrease with the increasing of concentrations of the (TiO₂) nanoparticles, the dielectric constant, dielectric loss, and the A.C electrical conductivity for (PMMA-TiO₂) nanocomposite are increasing with the increasing of concentrations of the (TiO₂) nanoparticle, the dielectric constant and the dielectric loss of the (PMMA-TiO₂) nanocomposite is decreasing with the increase of frequency of the applied electric field, but the A.C electrical conductivity increasing with the frequency

Keywords : Electrical Properties, Polymethyl methacrylate, TiO₂ nanoparticles.

1. Introduction

Nanocomposites are a new class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range [1]. Nanometer is an atomic dimension and hence the properties of nanoclusters or particles are reflective of atoms rather than bulk materials. An example for nanocomposite in nature is the natural bone consisting of approximately 30 % matrix material and 70 % nanosized mineral. Here the matrix material is collagen fibers (polymer) and the mineral is hydroxyapatite crystals of 50 nm x 25 nm x 3nm size (ceramic). The outstanding reinforcement of nanocomposite is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase. The nanolayers have much higher aspect ratio than typical microscopic aggregates [2]. The three major advantages that nanocomposites have over conventional composites are as follows.

1- Lighter weight due to low filler loading.

2-Low cost due to fewer amount of filler use.

3-Improved properties such as mechanical, thermal, optical, electrical, barrier etc., compared with conventional composites at very low loading of filler.

Three types of nanocomposites can be distinguished depending upon the number of dimensions of the dispersed particles in the nanometer range as follows:

1-Nanocomposites that can be reinforced by isodimensional nanofillers which have three dimensions in the nanometer range. Eg:-Spherical silica nanoparticles obtained by in-situ sol-gel methods or by polymerization promoted directly from their surface.

2-Nanocomposites which can be reinforced by fillers which have only two dimensions in the nanometer scale. Eg:- Carbon nanotube or cellulose whiskers.

3-The reinforcing phase, in the shape of platelets, has only one dimension on a nano level. Eg: - Clays and layered silicates[3].

2.Experimental work

The materials used in this paper is poly methyl methacrylate and nanoTiO₂ particle as filler. The poly methyl methacrylate was dissolved in chloroform. The nanoTiO₂ was added to the polymer by different weight percentages are (0,1,3,5)wt.%. The casting technique was used to prepare the nanocomposites.

The D.C electrical conductivity is measured by measuring the D.C electrical resistance for different temperature range (30 – 55) °C. The sample was placed in the oven and the electrical resistance was recorded after (5 -10) minutes to ensure accurate results. The readings of the Keithley electrometer were taken for different temperatures using the (Keithley electrometer type 2400).

The A.C electrical conductivity was measured by measuring the capacitor and the loss angle tangent as a function to the alternating electric field frequency using the (HIOKI 3532-50 LCR Hi TESTER (JAPAN)). The A.C electrical properties (dielectric constant, loss factor and A.C conductivity) have been studied as a function of frequency, range between 100Hz to 5MHz at room temperature.

3. Results and discussions

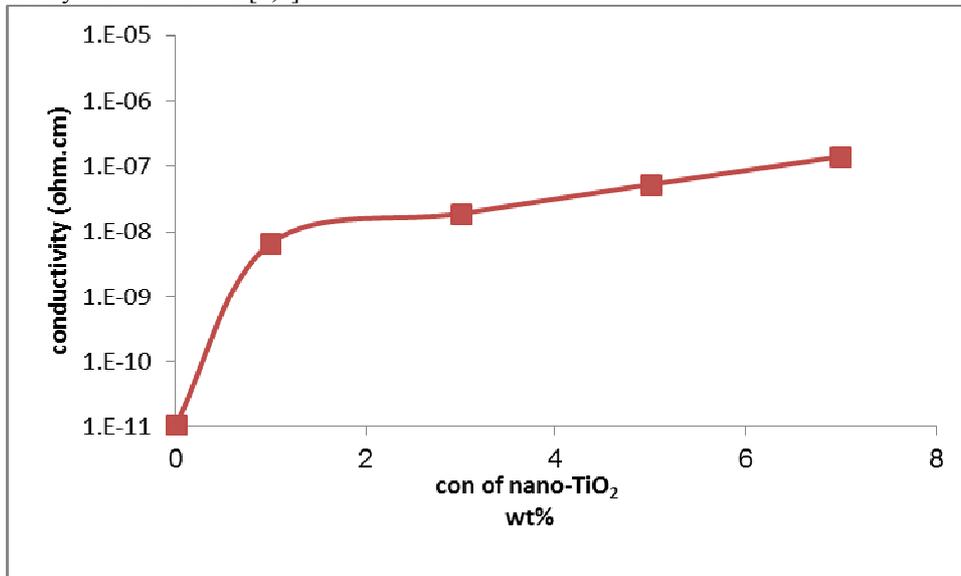
3.1 The D.C Electrical properties of (PMMA-TiO₂) nanocomposites

The surface electrical conductivity σ_v dc is calculated for the prepared films by using equation [4]:

$$\sigma_v = \frac{1}{\rho_v} = \frac{L}{RA}$$

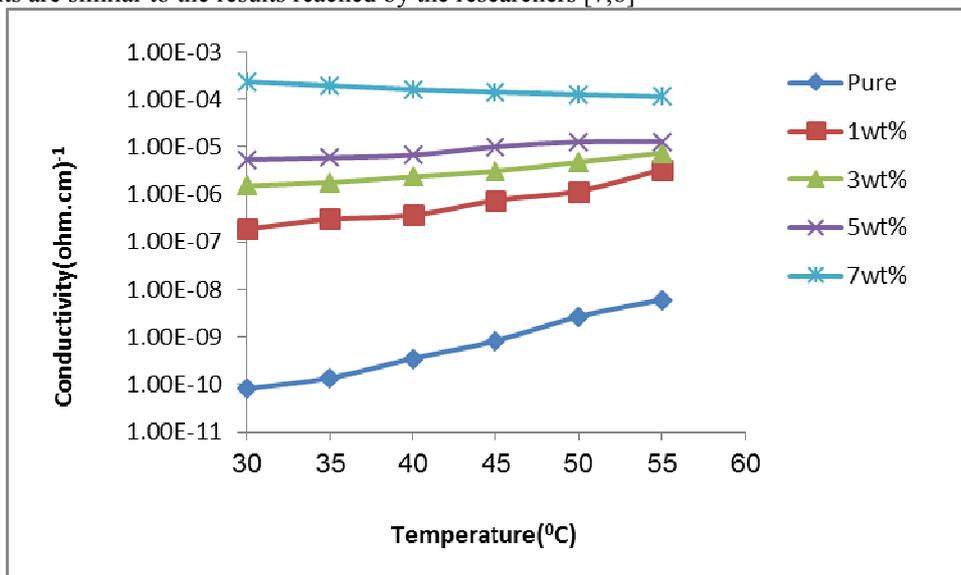
Where ρ_v is the volume resistivity, R the volumetric electrical resistance, (L) the length, (A) the area.

Figure (1) show the D.C surface electrical conductivity as a function of the concentration for (TiO₂)nanoparticle samples at a temperature of (30 °C). From this figure we note that the electrical conductivity is increasing with the increase of the concentrations of (TiO₂) nanoparticles. These results are similar to the results reached by the researchers [5,6].



Figure(1):Variation of D.C electrical conductivity with the Concentration of NanoTiO₂ Particles fo(PMMA-TiO₂) nanocomposites at 30 °C

Figure (2) show the variation of the electrical conductivity for (PMMA-TiO₂) nanocomposite with temperature. From this figure we note that the bulk electrical conductivity increases with the increase of the temperature of(PMMA-TiO₂)nanocomposite at low concentrations .This means that these materials have resistance of negative thermal coefficient; that is having the resistance decrease with the increase of temperature . These results are similar to the results reached by the researchers [7,8]



Figure(2):Variation of D.C electrical conductivity with temperature for(PMMA-TiO₂) nanocomposites

The activation energy was calculated by using equation[8]:

$$\sigma = \sigma_0 \exp(-E_{act}/K_B T)$$

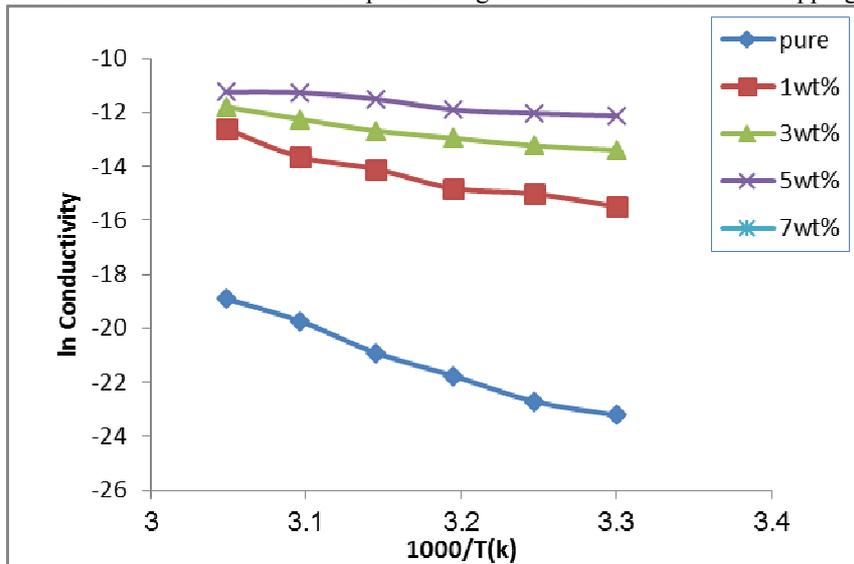
Where:

σ = electrical conductivity at T temperature

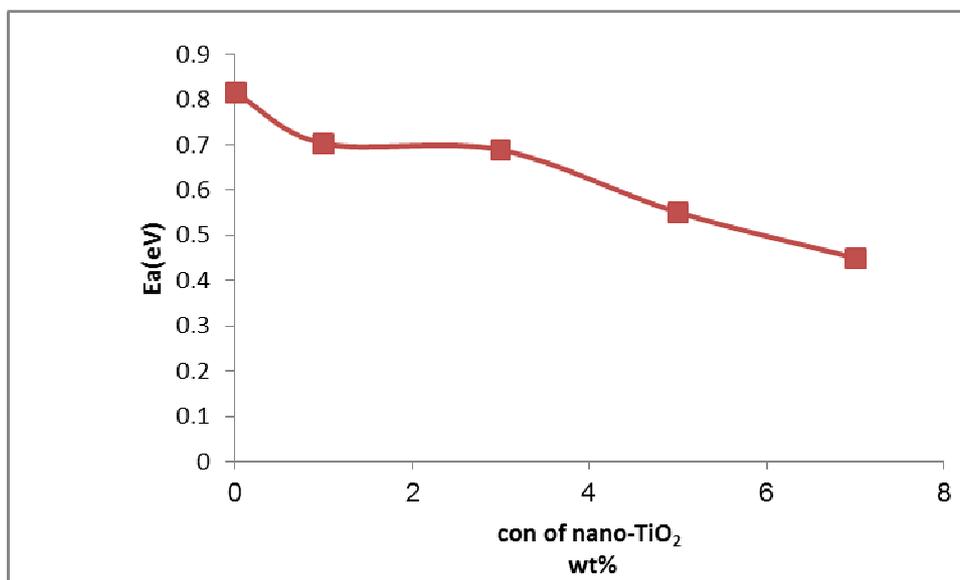
σ_0 = electrical conductivity at absolute zero of temperature

K_B = Boltzmann constant
 E_{act} = Activation Energy

Figure (3) show the relation between $\ln\sigma$ and the inverse absolute temperature for (PMMA-TiO₂)nanocomposite, it can be seen that there are high values of activation energy ranging from (0.816) eV to (0.45) eV for (PMMA-TiO₂)nanocomposites, By adding low concentrations of TiO₂ nanoparticles the values of the activation energy are decreasing for all (PMMA-TiO₂)samples as a result of the impact of space charge. The addition of low concentrations creates local energy levels in the forbidden energy gap which act as traps for charge carriers, which move by hopping among these levels. By increasing the TiO₂ nanoparticles concentrations, the activation energy decreases as a result of the increase of local centers ,as shown in figure (4), Thus ,the mechanism of conduction in the samples having low concentrations is the hopping [9,10].



Figure(3):Variation of D.C electrical conductivity with inverse absolute temperature for ((PMMA-TiO₂) nanocomposites



Figure(4):Variation activation energy for D.C electrical conductivity with the Concentration of NanoTiO₂ Particles for (PMMA-TiO₂)nanocomposites

3.2 The A.C Electrical properties of (PMMA-TiO₂)nanocomposites.

The A.C electrical properties for the (PMMA-TiO₂) nanocomposites were studied within frequency ranging from (100-5×10⁵)Hz. The dielectric constant, which is the most important A.C properties, was calculated by using the equation (1) which gives the ration of the capacitance of a dielectric-filled capacitor (C_p) to a capacitor of free space (C_0). The dielectric loss was calculated by equation (2), using the measured dielectric constant and

$\tan\delta$, while the A.C electrical conductivity σ_{AC} was calculated by equation (3) after substituting the measured values of ϵ [11].

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

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

$$\sigma_{A.C} = w \epsilon'' \epsilon_0 \dots\dots\dots(3)$$

Figure (5) shows the variation of the dielectric constant of (PMMA-TiO₂) nanocomposites with the frequency. The figure shows that the dielectric constant is decreased with increasing of frequency which attributed to decrease the space charge polarization [12]. Also, we can see the dielectric constant is increased with increase of nanoTiO₂ concentration which due to carries numbers[13], as shown in figure(6).

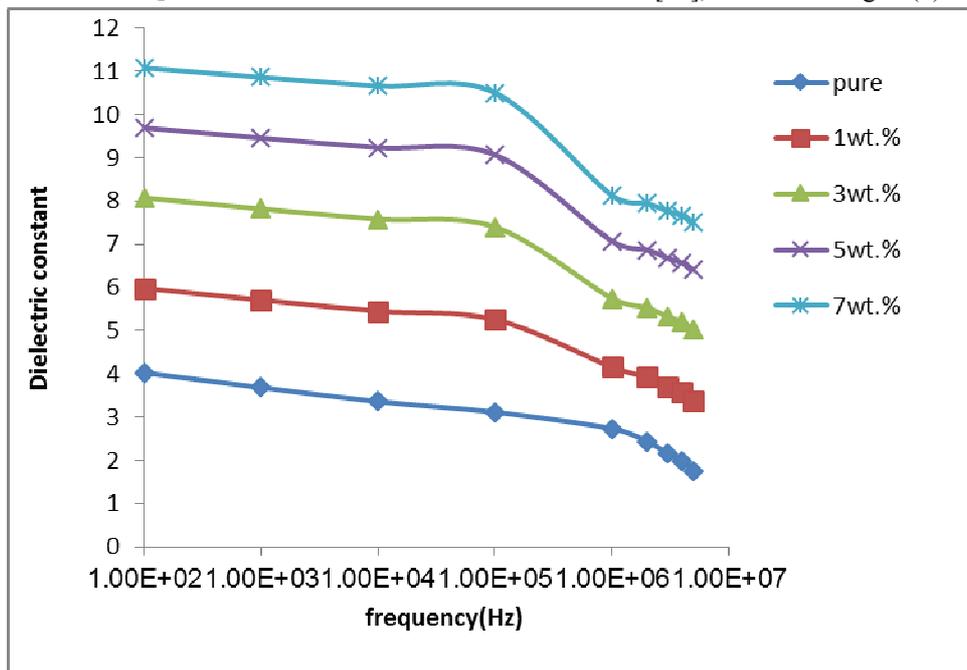


Figure (5): Variation of the Dielectric Constant of (PMMA-TiO₂)Nanocomposites with the Frequency

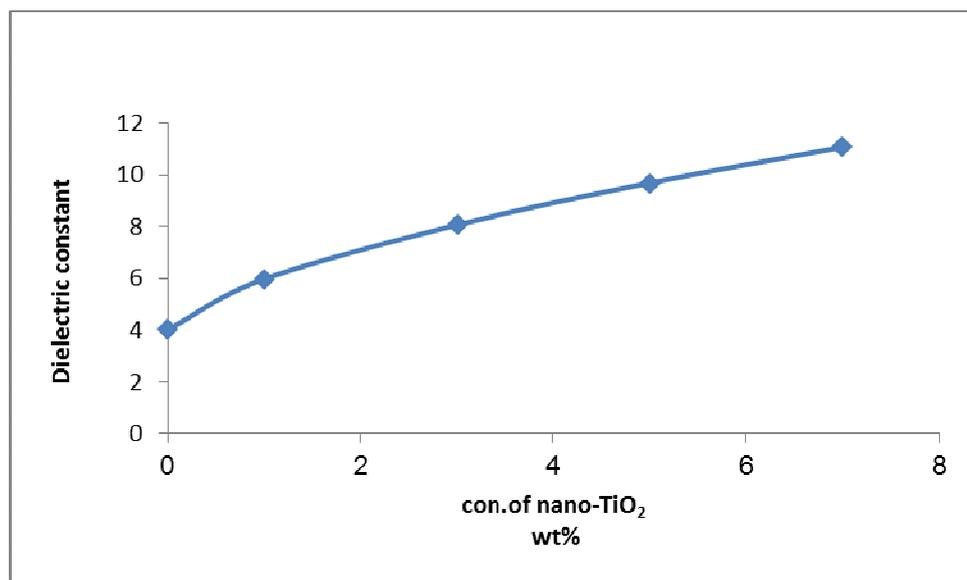


Figure (6): Variation of the Dielectric Constant of (PMMA-TiO₂) Nanocomposites with the Concentration of NanoTiO₂ Particles

The effect of frequency on the dielectric loss of (PMMA-TiO₂) nanocomposites for different concentration of nanoTiO₂ particles is shown in figure (7). The dielectric loss is decreases with increasing the frequency which due to decrease the dipoles in nanocomposites [14]. The dielectric loss is increased with the increase of the weight percentages of nanTiO₂ particles which attributed to increase the numbers of electrons in nanocomposites which is increase the electrical conductivity of polymer[15],as shown in figure (8).

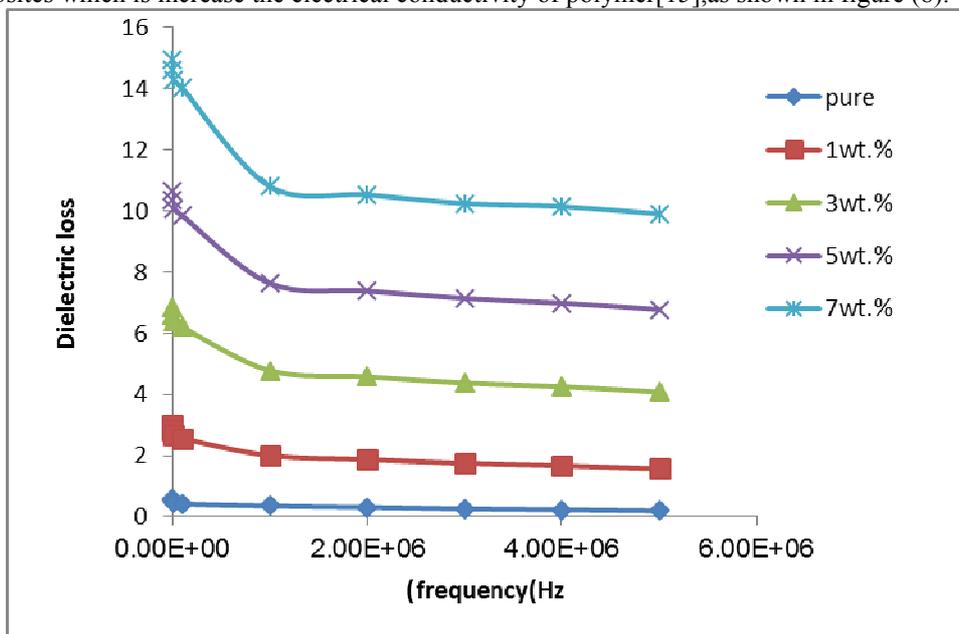


Figure (7): Variation of the Dielectric Loss of (PMMA-TiO₂)Nanocomposites with the Frequency

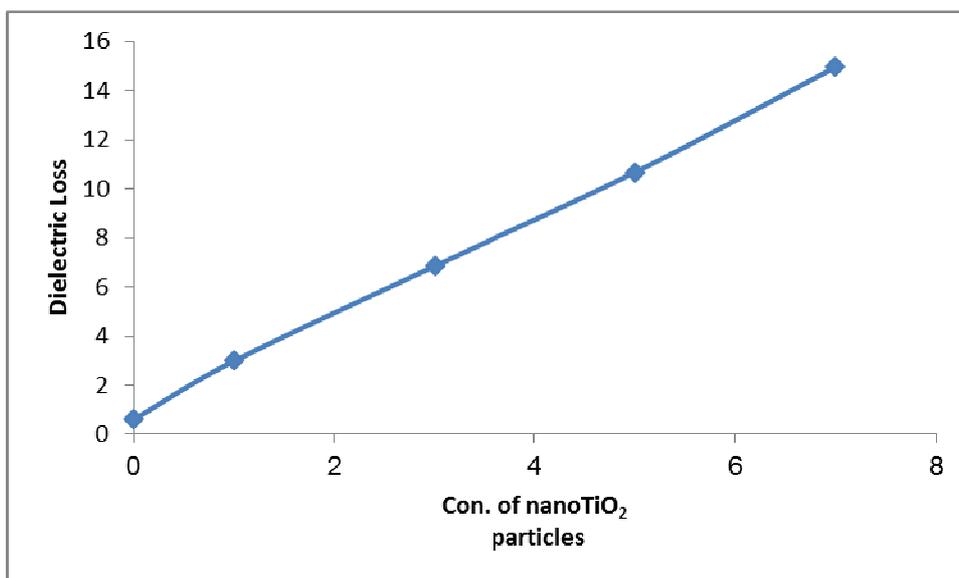


Figure (8): Variation of the Dielectric Loss of (PMMA-TiO₂) Nanocomposites with the Concentration of NanoTiO₂ Particles

The variation of A.C electrical conductivity of nanocomposites as a function of frequency is shown in figure (9). The A.C electrical conductivity is increased with increase of the frequency which attributed to the electronic polarization and the charge carriers which travel by hopping[16]. The A.C electrical conductivity is increased with increase of the concentration of nanoTiO₂ particles, as shown in finger(10), which attributed to increase the numbers of charge carries[16].

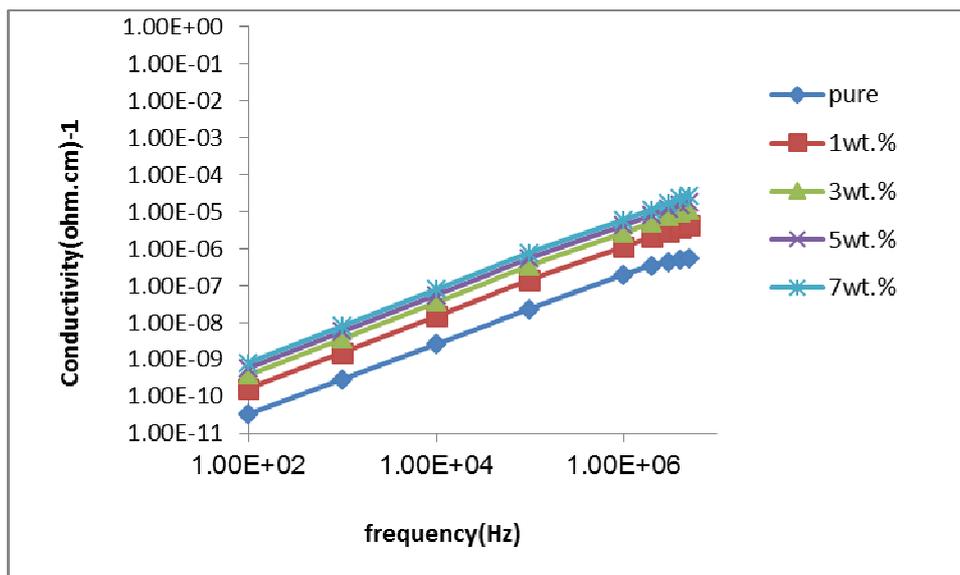


Figure (9): Variation of the Electrical Conductivity of (PMMA-TiO₂) Nanocomposites with the Frequency

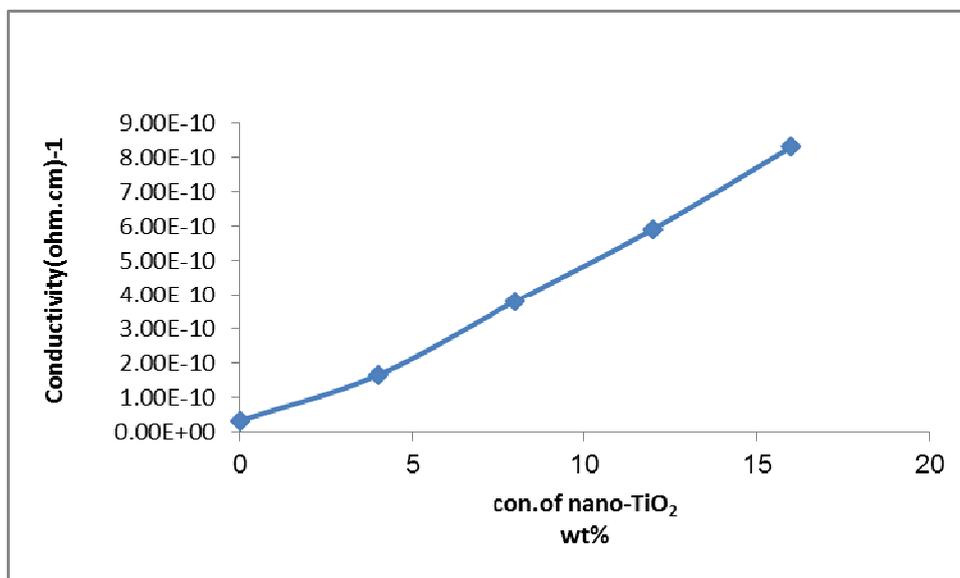
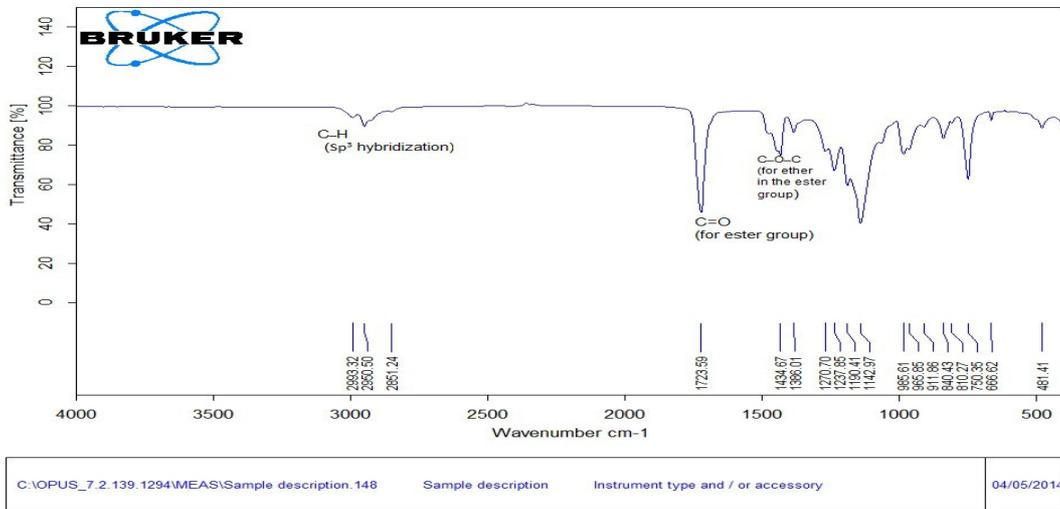


Figure (10): Variation of the Electrical Conductivity of (PMMA-TiO₂) Nanocomposites with the Concentration of NanoTiO₂ Particles

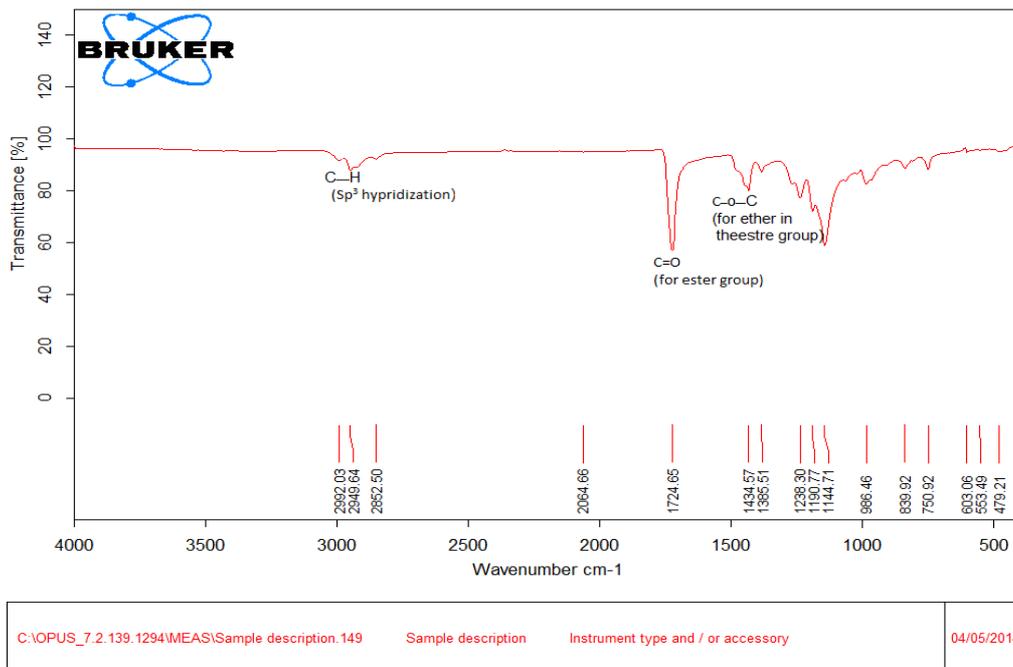
4.4 FTIR measurement:

The Fourier transform infrared spectroscopy (FTIR) spectra of pure (PMMA) composite as show in Fg.(4.16) and added concentration (TiO₂) nano particles to the films are shown in figures (11,12,13,14,15) .All spectra exhibit the characteristic absorption bands of pure (PMMA) composite ; are (2993.32,1723.59,1434.67) .It can be noticed that these elements cause some observable changes in the spectra features of the simples apart from new absorption bands and slight changes in the intensities of some absorption bands. The new bands may be correlated like wise with defects in deuced by the change transfer reaction between The polymer chain and the dopant .The appearance of the package(2993.32) at the absorption sites dating back to the stretching bond that C H its hybridized type is (SP³) (this meaning all bonds of C H The appearance of the package(1723.59) at the absorption sites dating back to the stretching bond that(C=H)(Carbonyl) return to the ester group in the polymer.The appearance of the package(1434.67) at the absorption sites dating back to the stretching bond that (C O C) Ether existing within the group in the polymer Asturian. After addition TiO₂ nanoparticlea, some polymer chain have been broken and some other chains have been formed instead. we notice through FTIR if presence (TiO₂) nanoparticales lead to restricted of moleculer vibrational motion and special vibration motion at three dimation for(PMMA) composite and which most probably be affected of IR energy and this restricted of moleculer polymers move reason occurance apparent distortion for some the parts functional for polymers

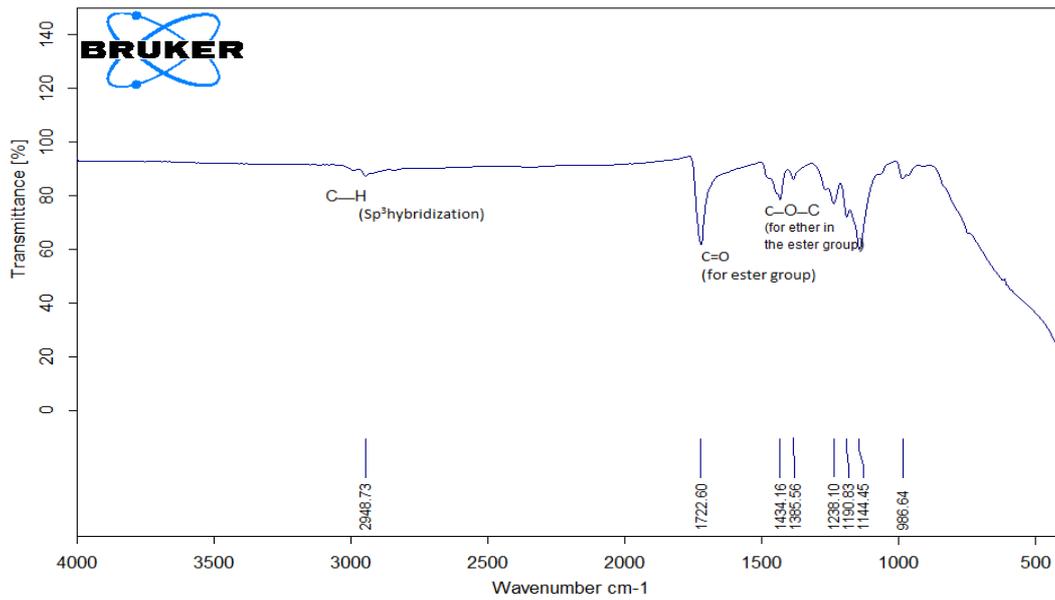
(functional groups) therefore that films nanocomposites has characteristic nano approximately being restricted or issemble all functional groups for polymers when apparent at IR as shown in Fig's.(11,12,13,14,15) The Fourier transform infrared spectroscopy (FTIR) spectra of pure (PMMA) and doped (TiO₂) nanoparticles films these results are similar to the results reached by the research [17,18].



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Fig (11): FTIR spectrum of poly (methyl methacrylate) (PMMA).



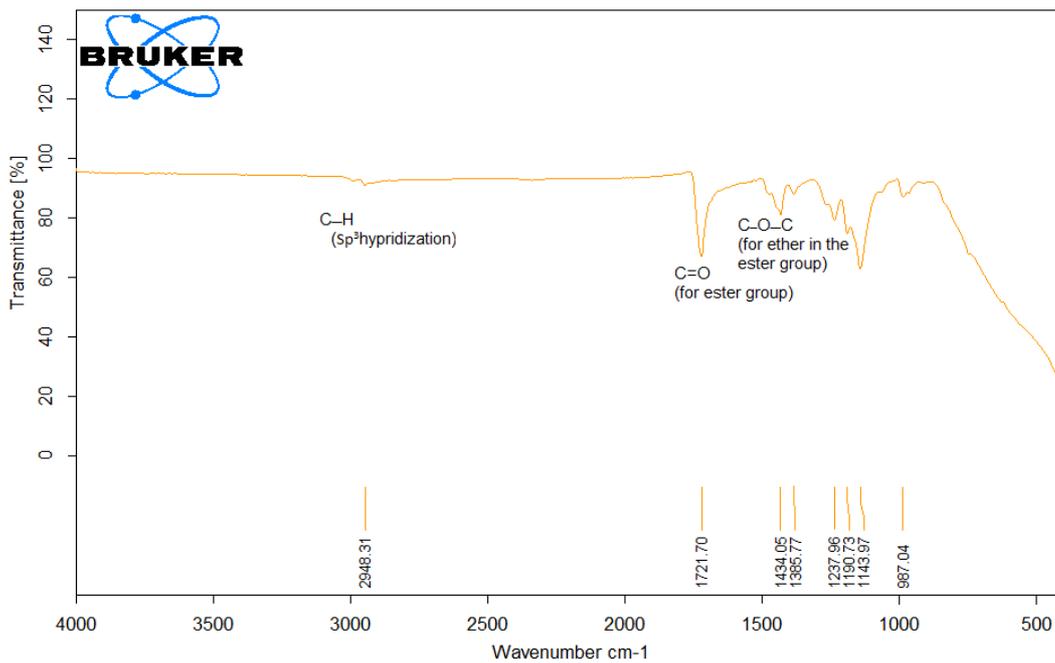
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Fig (12): FTIR spectrum of (PMMA-TiO₂) nanocomposite (1wt.%).



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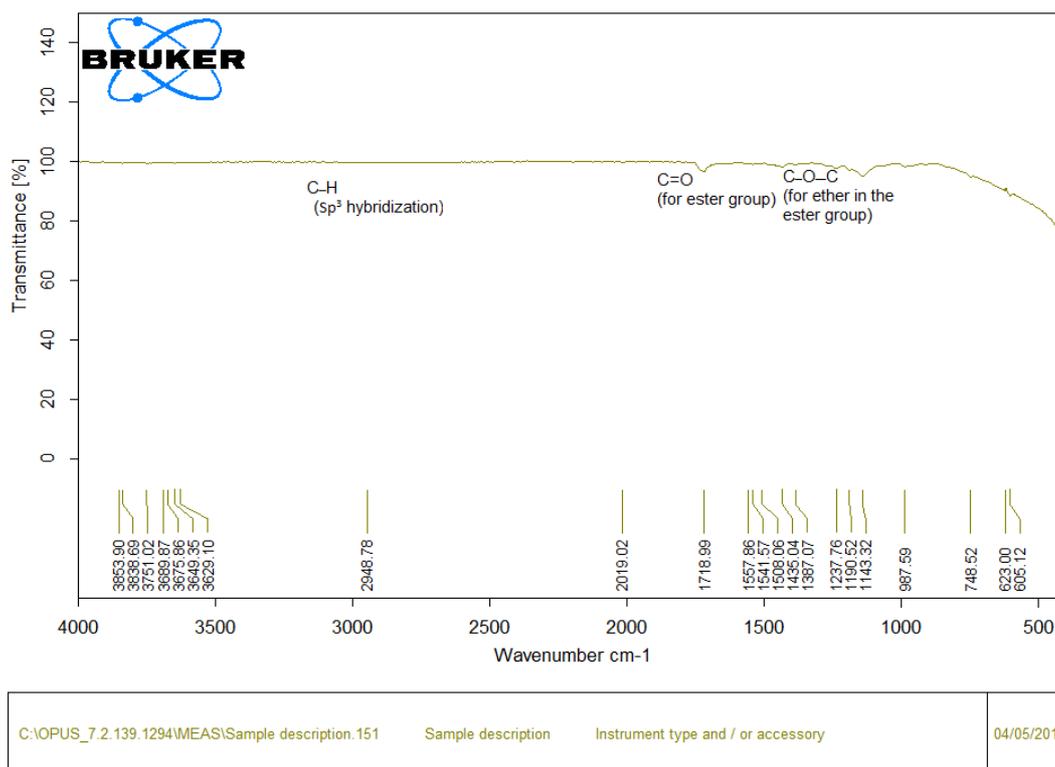
Fig (13): FTIR spectrum of (PMMA-TiO₂) nanocomposite (3wt.%).



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Fig (14): FTIR spectrum of (PMMA-TiO₂) nanocomposite (5wt.%).



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Fig (15): FTIR spectrum of (PMMA-TiO₂) nanocomposite (7wt.%).

4.5 SEM measurement:

The SEM shows the very detailed three dimensional images at very high magnification . the surface structure of (PMMA) and (TiO₂) can be imaged through SEM with high clarity. SEM images depict the surface morphology of (PMMA) before and after addition concentration of (TiO₂) nanoparticles which are shown in fig's.(16,17,18,19,20).The films exhibit uniform density of grain distribution at surface morphology. The surface morphology of the (PMMA-TiO₂) nanocomposit .films shows many aggregation or chunks randomly distributed of (TiO₂) nanocomposites on the top surface of the films. The results indicated that the (TiO₂) particles tend to form aggregation and good dispersed at (PMMA-TiO₂) nanoparticl films. From the Fig's.(16,17,18,19,20).It was observed that (TiO₂) nanoparticles are randomly distributed in the PMMA composites films and it was concluded that small agglomerations is formed these films , these results are inagreement with results of research[19,20,21].

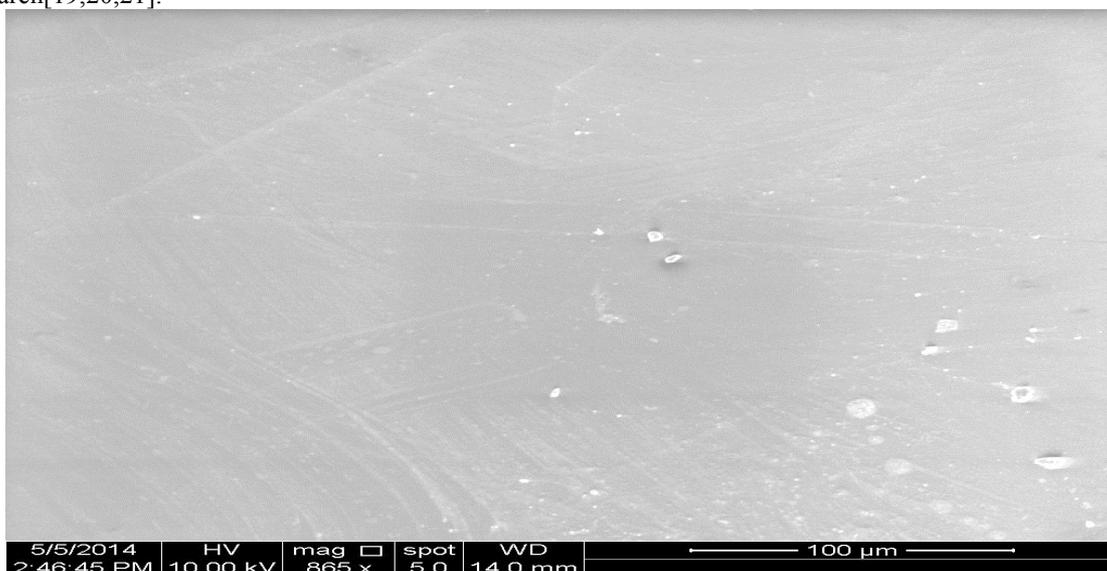


Fig (16): SEM measurement of (PMMA) .

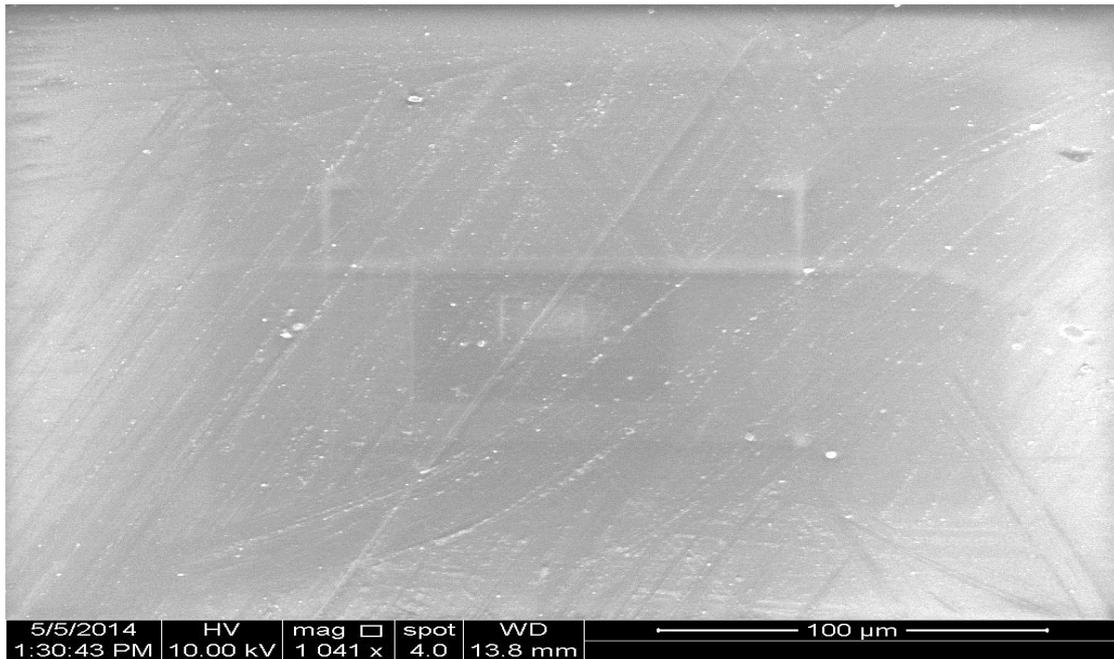


Fig (17): SEM for (PMMA-TiO₂)(1wt.%).

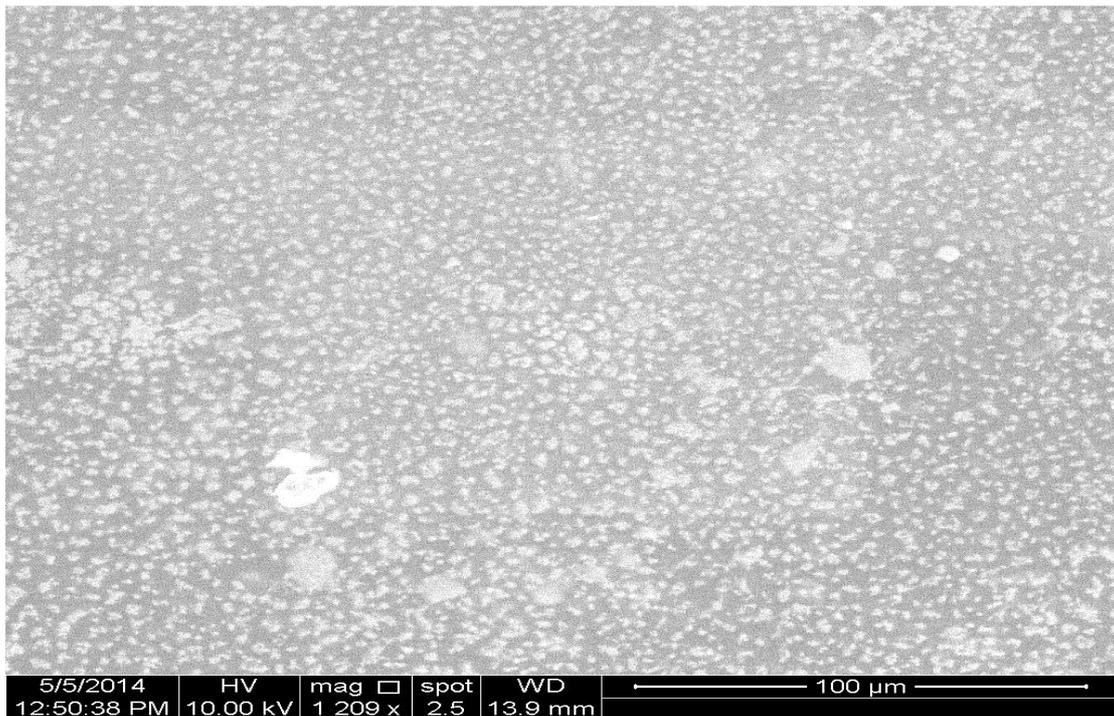


Fig (18): SEM for (PMMA -TiO₂)(3wt.%).

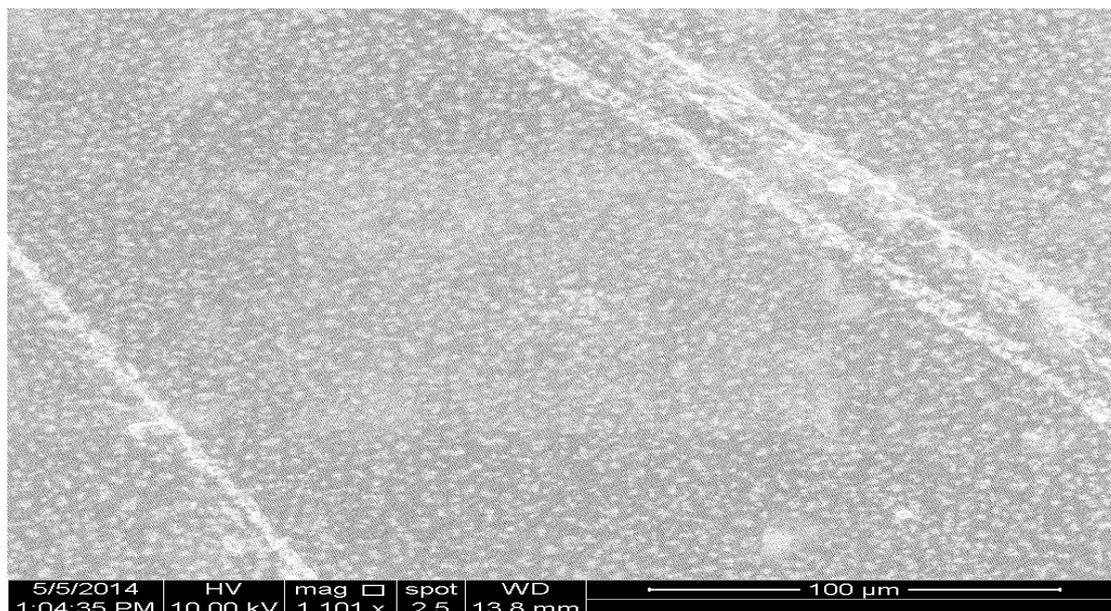


Fig (19): SEM for (PMMA-TiO₂) nanocomposite (5wt.%).

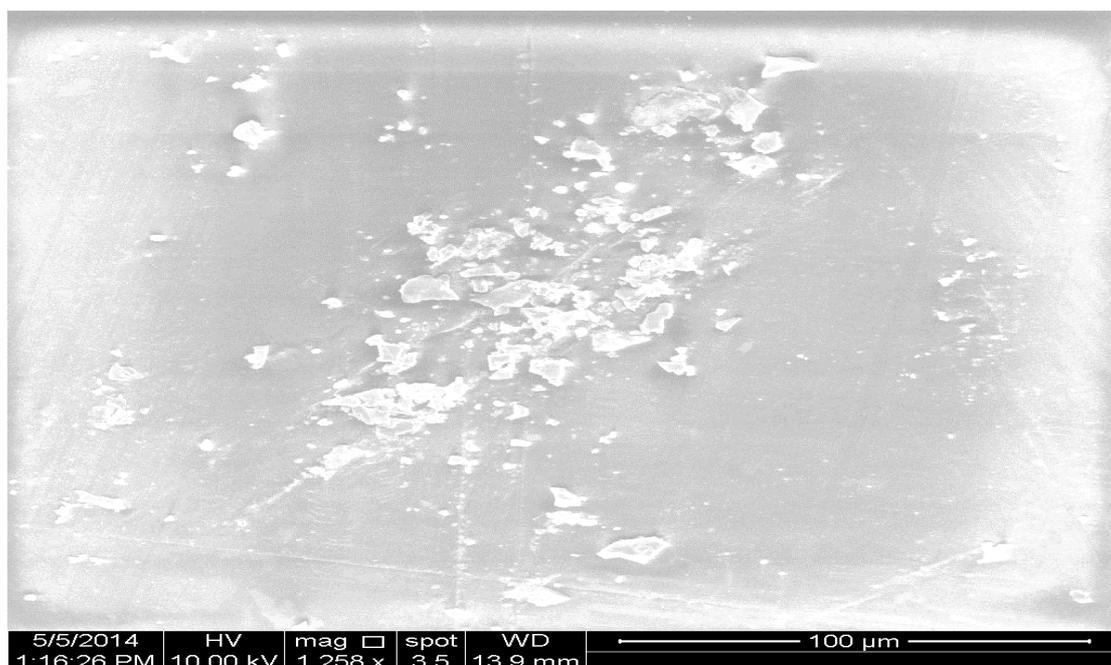


Fig (20): SEM for (PMMA-TiO₂) nanocomposite(7wt.%).

4. Conclusions

The summarized results from this work are the following:

- 1.The D.C electrical conductivity for the (PMMA-TiO₂) nanocomposites increases with the increasing temperature .
- 2.The activation energy for D.C electrical conductivity (PMMA-TiO₂). nanocomposites decreases with the increasing of concentrations of the (TiO₂) nanoparticles.
- 3.The dielectric constant, dielectric loss, and the A.C electrical conductivity for (PMMA-TiO₂)) nanocomposites are increasing with the increasing of concentrations of the (Ag) nanoparticles .
- 4.The dielectric constant and the dielectric loss of the (PMMA-TiO₂) nanocomposites is decreasing with the increase of frequency of the applied electric field, but the A.C electrical conductivity increasing with the increase of the frequency.

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