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Coulomb blockade behavior in PVA/PEG/Ag nanocomposite

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ABSTRACT

Poly(vinyl alcohol)/poly(ethylene glycol)/silver nanoparticles (PVA/PEG/ Ag nanoparticles) thin films with different concentrations of silver nanoparticles were prepared using casting technique. properties of samples have been investigated using electrical properties. Increases the electrical conductivity and Coulomb blockade occur by maximum Ag nano particles concentrations in the samples.

Key words: polymers, nanoparticles, electrical properties, Coulomb blockade

تم تحضير العينات وهي شرائح رقيقة مكونة من بولي فينايل الكحل و بولي ايثلين جليكول مع تراكيز مختلفة من جسيمات الفضة النانوية حيث حضرة باستخدام تقنية معينة ، ودرسة الخواص الكهربية للعينات وجد أن التوصلية الكهربية تزداد ويحدث لها زيادة مفاجئة عند اعلي تركيز لجسيمات الفضة النانوية وهو ما يسمي بلوكاد (blockade).

INTRODUCTION

Porous polymeric structures are used in a wide range of applications including wound dressings, vascular grafts, tissue engineering scaffolds, and controlled drug delivery systems. A primary requirement for most of these applications is the ability to control the macroscopic structure in the base polymer[1].Polyvinyl alcohol PVA is an odorless and tasteless, translucent, white or cream colored granular powder[2]. PVA as a hydrophilic polymer is water soluble and the largest volume synthetic resin produced in the world. The excellent chemical resistance, physical properties and biodegradability of PVA have led to the development of many commercial products based on this polymer. PVA is used as an emulsifier, stabilizer for colloid suspensions, sizing agent, coating in the textile, paper industries, and as an adhesive. PVA is a truly biodegradable polymer with the degradation products being water and carbon dioxide. Hence, it is used in many biomedical and pharmaceutical applications, due to its advantages such as: nontoxic, noncarcinogenic, and bioadhesive characteristics with the ease of processing[1].

Polyethylene glycols (PEGs) are family of water-soluble linear polymers formed by the additional reaction of ethylene oxide(EO) with mono ethylene glycols (MEG) or diethylene glycol. There are many grades of PEGs that represents them by theirs average molecular weight. PEGs may be liquid or solid at STD condition. PEGs are widely used in pharmaceutical formulations. As solvent, water soluble, binder, lubricant, plasticizer and use in ointment base, tablet coating, gelatine capsule, liquid oral medications.

Nanoparticles possess a very high surface to volume ratio. This can be utilized in areas where high surface areas are critical for success. Nanoparticles are often in the range 10-100 nm which is the size of human proteins. Silver nanoparticles act as an electron relay, aiding in the transfer of electrons from the BH^{-4} ion to the dyes, and thereby causing a reduction of the dyes. BH^{-4} ions are nucleophilic while dyes are electrophilic. It has been proven that nucleophilic ions can donate electrons to metal particles, while an electrophilic can capture electrons from metal particles.[3] It has been shown that BH^{-4} ions and dyes are simultaneously adsorbed on the surface of silver particles, when they were present together.[3] Silver nanoparticles were a kind of very useful material, which could be used for photocomposition, property of surface enhanced Raman spectroscopy, and catalysts of numerous reactions. It was well known that catalysis depended on the size and shape of the metal nanoparticles, and the size of particles could be critical for their applications. Therefore, it could be important to develop an effective preparation method for making nanoparticles.[4] Single electron tunneling occurs when the capacitance of the nanotube is so small that adding a single electron requires an electrostatic charging energy greater than the thermal energy k_BT. Electron transport is blocked at low voltages, which is called Coulomb blocked.

EXPERIMENTAL

Samples

PVA and PEG used in the present work were supplied by Sigma-Aldrich GMBH. The components, free from impurities, were prepared by melted the PVA in twice-distilled water by warmed to 80^{o} C and stirred thoroughly for about 1 h until the PVA was completely dissolved. PEG solution was prepared by dissolving PEG with in twice-distilled water at room temperature[5]. Preparation of PVA/PEG/Ag nanoparticle thin films with different concentrations of silver nanoparticles by mixed PVA/PEG solution with Ag nanoparticle which was prepared as Noginov and Ziiu did[6], poured onto a level glass plate, and left to dry at room temperature for about 120 h. A thin film of nearly 0.05 mm thickness was formed. The thickness was measured by a thickness gauge Model 11/2704 Ast MD 370 standard which calibrated by Arab British Dynamics.

Scanning Electron Microscope (SEM)

Typical SEM for blank sample (PVA/PEG) is shown in figure1 . The micrographs reveal homogeneous film without any localization of cluster islands. This background helps us to understand the effects of radiation and Ag nano-particles on PVA/PEG samples. In figure 2b the nano-composite reveals an isolated clusters with an average radius of 77.5nm, for Ag nanoparticles concentration equal to 12 %.This structure is reduced with decreasing the nanocomposite of one order as shown in figure 2a for 2 % of concentration Ag nanoparticles with an average radius of 58.5 nm. Figure 2b, that fumed silica is mostly dispersed as small aggregates and even of individual particles. The spacing between the particles is not uniform.

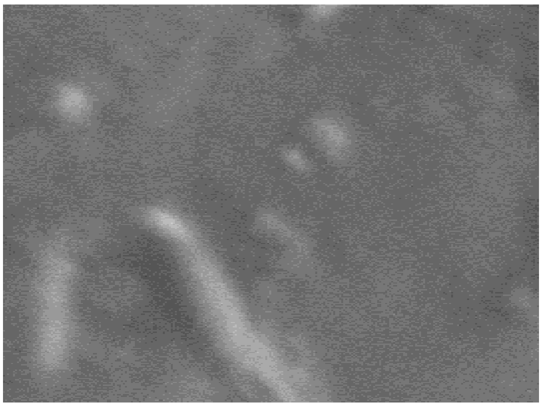

Fig 1 PVA/PEG sample.

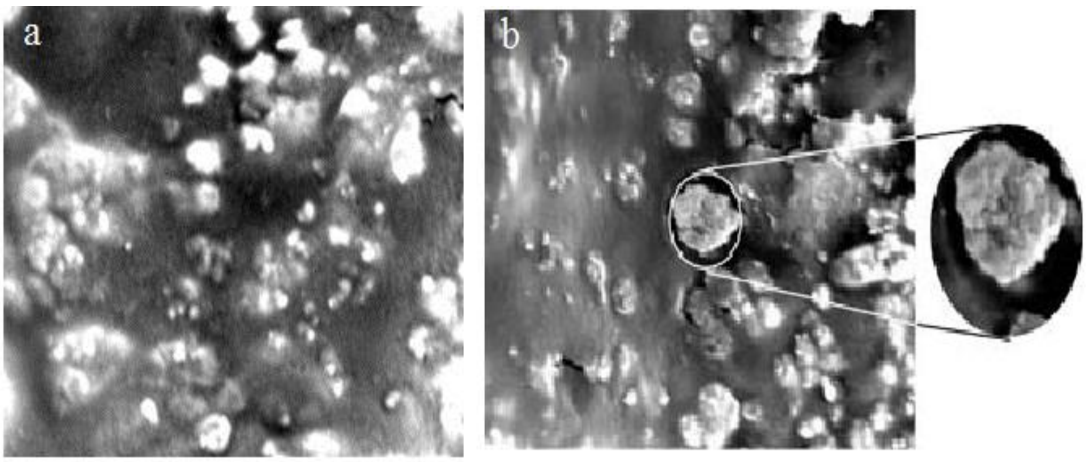

Fig2 PVA/PEG/ Ag nano- composite samples (a) 2 % (b) 12 %.

DC electrical properties

Measured values of current intensity I at different values of the voltage V at temperatures T ranging from room temperature up to 80°C for samples.

Blank PVA/PEG thin film

The relationship between the electric field and the current density at temperatures ranging from room temperature up to 80°C was studied and represented as in the figure 3. From this figure, a direct proportion between the electric field and current density occur. While figure 4, representative of the relationship between logarithm of current density and square root of the electric field.

By using the equation $\mathbf{J = \sigma_{dc}\ E}$, the values of the dc conductivity of PVA/PEG samples were calculated, and then the relationship between the values of logarithm of dc conductivity and 1000/ T in Kelvin^{-1} are shown in the figure 5.

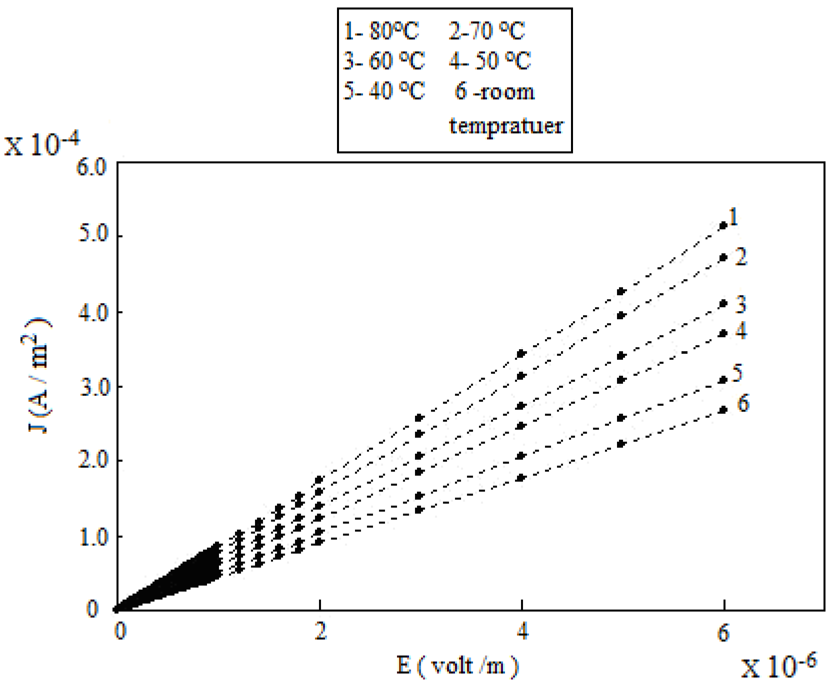

Fig 3 Variation of J with E for PVA/PEG sample at different temperatures.

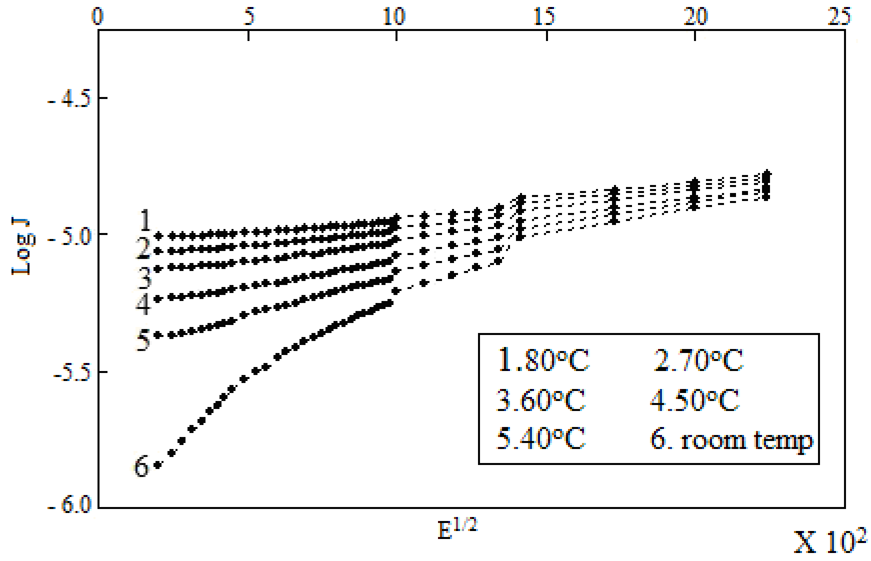

Fig4 Variation of Log J with $E^{1/2}$ for PVA/PEG sample at different temperatures.

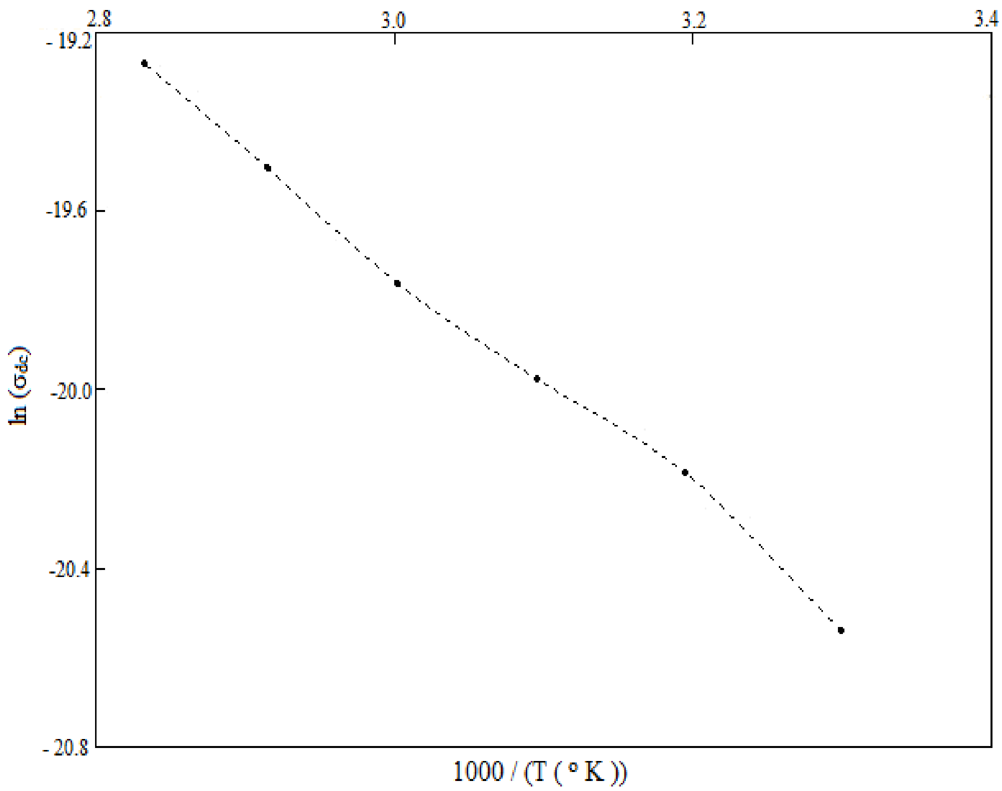

Fig5 Temperature dependence of σ_{dc} for PVA/PEG sample.

PVA/PEG/Ag nanoparticle thin films with different concentration of Ag nanoparticle

The relationship between the electric field (E) and the current density (J) at temperatures ranging from room temperature up to 80^{o}C is shown in the figure 6. A direct proportionality between the electric field and current density, as well as the direct proportionality between the concentration of Ag nanoparticles and the current density occur. The current density the relationship between the square root of the electric field and logarithm current density representative in the figures 7 and 8 .

By using equation **J= σ_{dc} E,** the values of dc conductivity were calculated, and relationship between the 1000/(T) (Kelvin)$^{-1}$ and the logarithm of the dc conductivity is shown as in figure 9. It shows as inverse proportion. This figure also, illustrates the direct proportion with the concentration of Ag nanoparticles, which proves that as the concentration of Ag nanoparticle increases the dc conductivity incraes as well.

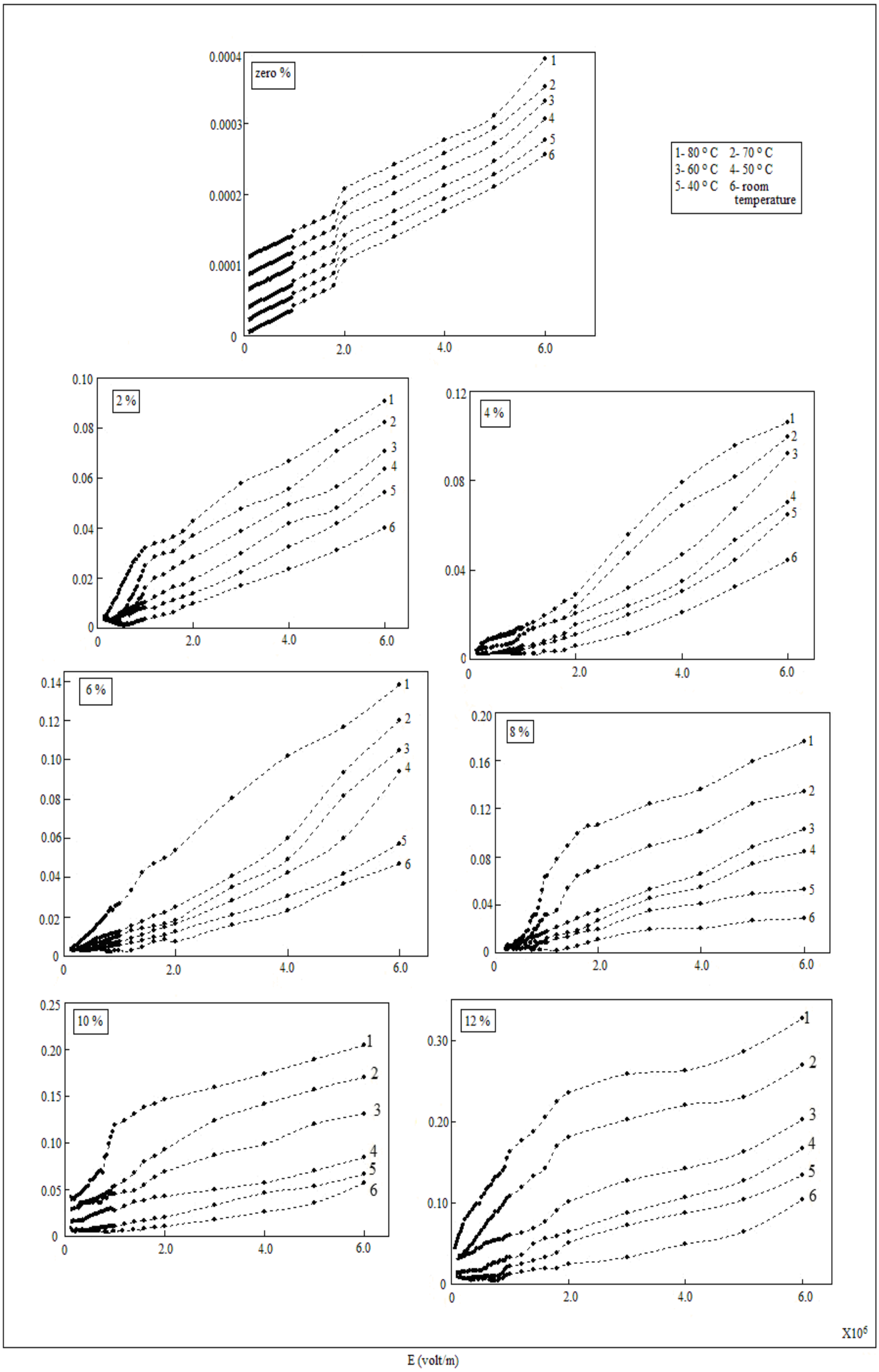

Fig 6 Variation of J with E for PVA/PEG/Ag nanocomposite samples with different concentration of Ag nano-particles and different temperatures.

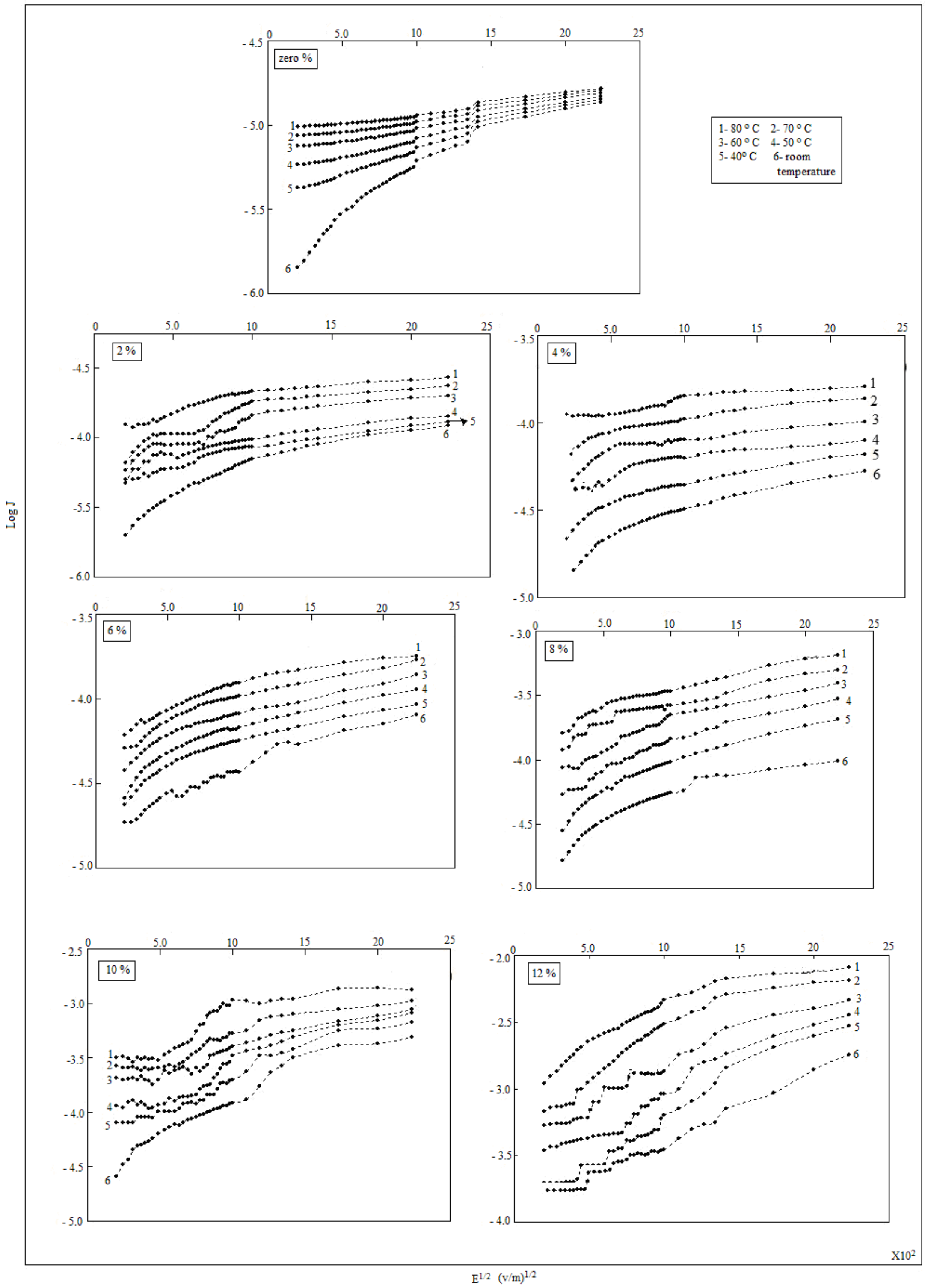

Fig7 Variation of Log J with $E^{1/2}$ for PVA/PEG/Ag nanocomposite samples at different concentration of Ag nano- particles and at different temperatures.

The measurements different temperatures on a single nano-particle lying across two metal electrodes show the steps occur at voltages which depend on the voltage applied to a third electrode that is electrostatically coupled to the nano-particle. This resembles a field effect transistor made from a silver nano-particle. This coulomb blockade (CB) behavior observed with the sample doped with maximum Ag nano particles concentration which corresponding to the production of homogeneous thin film.

In figure 8 the Log J- $E^{1/2}$ curve observed the CB- voltage and temperature action in a disordered conductor. Our report is, therefore, also the first observation of the CB co-oper-voltage. As one of some interesting problems, which geometry part of the wire is effective for the parasitic capacitance of the CB is discussed proposing an electric field propagation model[7]. This conclusion is verified by SEM in which the Ag nanoparticles form aggregates with nonuniform distribution according to the concentration of Ag nano particles. The radius of these aggregates ranges from 58.5 to 77.5 nm.

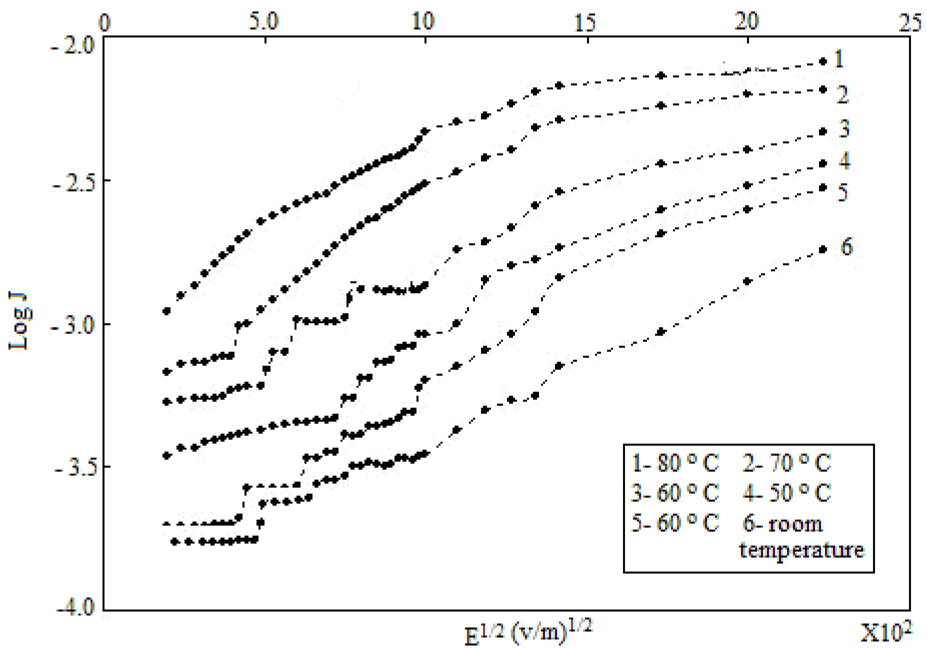

Fig8 Variation of Log J with $E^{1/2}$ for PVA/PEG/Ag nanocomposite concentration of Ag nano-composite e 0.12 grams at sample at different temperatures.

The values of the dc conductivity of PVA/PEG/ Ag nanocomposite at different concentration of Ag nanocomposite sample were calculated, and then the relationship between the values of logarithm of dc conductivity and 1000/ T in Kelvin^{-1} are shown in the figure 9.

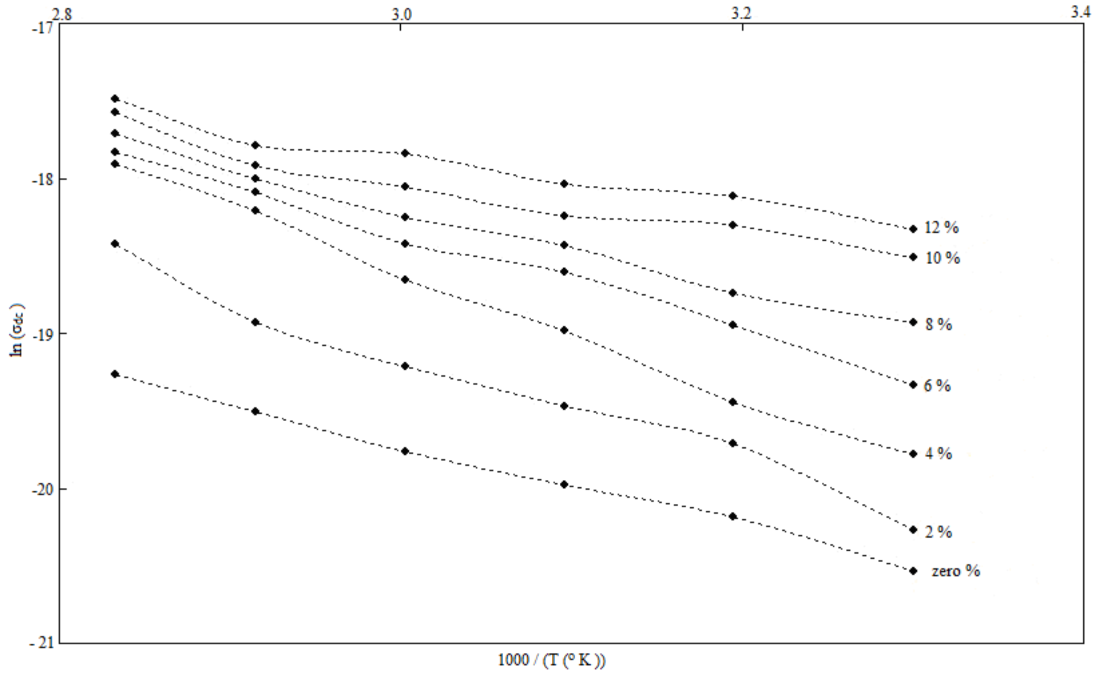

Fig9 Temperature dependence of σ_{dc} for PVA/PEG/Ag nanocomposite samples at different concentration of Ag nanocomposite.

Conclusion

Adding nanoparticles increases the electrical conductivity by approximately 2- orders magnitude as a result of increasing the electrical paths between the polymer chains. Low concentrations and at low- grade heat causes an increase in the electrical conductivity due to the electrical behavior of Ag nanoparticles. This is known as blockade. This Coulomb blockade occur for samples doped with maximum Ag nanoparticles concentrations.

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