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ARTICLE

## Polymer Nanocomposites Based on Graphene and Titanium Oxide for Supercapacitors

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### ABSTRACT

A nanomaterials graphene and titanium oxide (TiO<sub>2</sub>) have been prepared and characterized by IR, atomic force microscopy (AFM) and X-ray diffraction. The different thin films of mixed poly(vinyl alcohol) and polyacrylamide, polymers/nano TiO<sub>2</sub> and polymers/ nano(graphene + titanium oxide) have been prepared and their electrical properties (real and imaginary electrical isolation constants and conductivity) were examined at different frequencies. A super capacitors based on polymer mixtures and polymers mixture with nanomaterials have been prepared and their voltages examined at charging and at different intervals of time (5, 10, 15 and 30 min and 1, 5, 10, 15, 20 and 24 h). The best capacitor was of polymer mixture/nano(graphene + TiO<sub>2</sub>), which is attributed due to the good conductive properties of graphene.

### KEYWORDS

Super capacitors, Graphene, Titanium oxide, Electrical properties.

### INTRODUCTION

Carbon-based nanomaterials used in a small amount as nanofillers with polymers to form polymer nanocomposites and they enhance the mechanical and thermal properties of polymers [1]. Conducting polymers and metal oxides consist a perfect materials, which behave as pseudo-capaciting with high capacity and low stability of cycling [2]. Graphene is a good material for supercapacitors because it has excellent conductivity with large specific surface area, a massive mechanical characteristics and performing of electrochemical process [3].

Recently, there are many efforts to produce a devices for storing energy with reasonably cost [4-7]. Super-capacitors or ultra-capacitors motivate the attention of researchers in recent time as a device for storing energy in electronic devices [4,7]. Super-capacitors can give energy in short time period with a great amount of power density and low energy density. Graphene an attractive material [8], have a thermal conductivity around 5000 W m<sup>-1</sup> K<sup>-1</sup> [9] and a good electrical conductivity which makes an important material in many applications like transparent conductive electrode [10,11]. Graphene form important nanomaterials, which consists of thin layers with a thick of one carbon atom and consider one of carbon allotropes with hexagonal structure gives a distinguished properties over other carbon allotropes [12]. Graphene has a strong structure which make a thin slice from it stronger three hundred times than steel, beside that graphene has a good electrical conductivity better than that of copper [13-16].

Several studies having wide applications achieved on both graphene and graphene oxide through last many years [17-23]. Titanium dioxide represents an important nanomaterial which exist as white nanotubes, low-cost and non-toxic and can be prepared by easy methods [24,25]. TiO<sub>2</sub> nanotubes have high chemical stability and excellent optoelectrical properties, for that properties it used in coating, photosensors, solar cells, *etc.* [26-29].

## EXPERIMENTAL

The materials and chemicals *viz.*, graphite, sodium nitrate, hydrogen peroxide, titanium oxide and sodium sulphate obtained from Sigma-Aldrich. Sulphuric acid and hydrochloric acid were obtained from Riedel-de Haen. Poly(vinyl alcohol) obtained from AFCO, potassium permanganate obtained from Fluka while sodium hydrazine was obtained from Merck.

**Preparation of graphene oxide:** Graphene oxide had synthesized by modified Hummer method [30] by mixing 1 g of graphite powder with 35 mL of conc. sulphuric acid in a beaker of 1000 mL in an ice bath at 0 °C followed by the addition of 1.5 g of sodium nitrate slowly and then 6 g of sodium permanganate with constant stirring to ensure the homogeneity of the mixture and finally left for 1 h. Added 280 mL of hot distilled water in batches with constant stirring for 4 h at a temperature range of 90 °C followed by addition of 20 mL of hydrogen peroxide (35 %). After repeated washing with distilled water, the product was filtered and dried at 70 °C for 24 h.

**Preparation of graphene:** A 50 mL of water added to a 250 mL flask contains graphene oxide to form a suspended heterogeneous solution. The mixture then transferred to ultrasonic for 2 h till the clear solution obtained. A hydrazine solution (7 mL) was added to a clear solution and refluxed for 30 h at 100 °C in oil bath, after that the contents of flask poured in a beaker and washed for sometimes till the solution become neutralized. The solution was filtered to get the product which then dried and kept in container for further investigations.

**Preparation of nano-TiO<sub>2</sub>:** Titanium oxide (10 g) added to 50 mL of NaOH solution (10 M) in a conical flask of 250 mL, the reaction mixture then refluxed at 110 °C for 35 h in oil bath. After reflux, 10 mL of conc. HCl added slowly with constant stirring till pH reach 7, after filtration the product dried and kept in container.

**Preparation of polymer nanocomposites:** The polymer composites were synthesized as thin films. The film of PVA was synthesized by dissolving 11 g of PVA in 120 mL of water and left at 60-70 °C until a thick clear homogeneous solution obtained. Then, 25 mL of solution had taken and poured in glass plate to get thin film of PVA. Similarly, 1 g of polyacrylamide dissolved in 40 mL of water under gentle heating to get a thin film of polyacrylamide. The thin film of the mixture of PVA and polyacrylamide have been prepared by mixing a 25 mL of thick solution of PVA and 10 mL of polyacrylamide solution. The polymer nanocomposite film prepared from the solution mixtures of PVA and polyacrylamide doped with 0.2 g of nanoTiO<sub>2</sub>/0.1 g of graphene.

**Preparation of super-capacitors:** A plastic plate of a square shape with a dimensions of 6 cm × 6 cm etched from the center with dimensions of 3 cm × 3 cm. A plastic plate with dimensions of 6 cm × 6 cm having a thickness of 0.5 cm

used as a covers of the etched plates from both sides upper and lower, these plates contained holes connected to the wires of cathode and anode. A plates of polymeric thin films have been prepared with a dimensions of 3 cm × 2 cm, they served as electrodes (anode and cathode). The films of separators with the same dimensions of electrodes have been prepared to separate between the polymeric thin films to prevent electrical contact between the electrodes. A pieces of copper plates with the same dimensions of electrodes attached to them as to serve as collector electrodes in order to provide the system with voltage, they connected with wires going through holes of the covers and also connected to the outer circle. The super-capacitor arrangement is shown in Fig. 1, both sides of capacitor then covered with plastics plates using silicon finally the cell injected with a electrolyte solution of sodium sulphates (0.5 M).

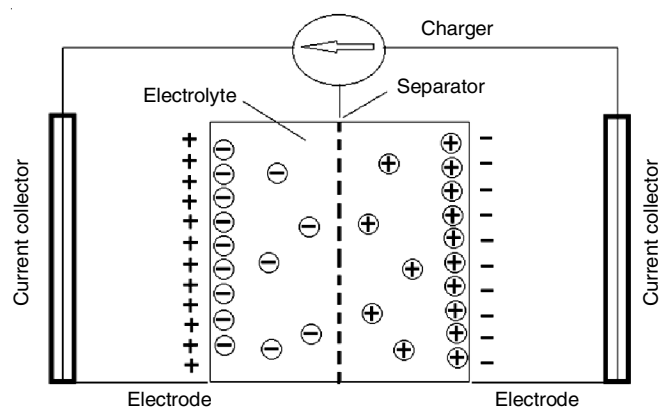


Fig. 1. Internal structure of super capacitor

**Method of super capacitor charging:** The charging of prepared cell (Fig. 1) and measuring the quantity that the cell kept it done as steps. First the capacitor connect to a source of a continuous current of 12 V. Second step involved the charging of the capacitor for 10 s. In the third step, the cell connected to the digital multimeter and the voltages registered at different interval of times after 5, 10, 15 and 30 min, and 1, 5, 10, 15, 20 and 24 h.

## RESULTS AND DISCUSSION

**FT-IR studies:** The FT-IR spectrum of nanographene oxide showed some of the absorption bands *viz.*, stretching of OH appeared at 3510 cm<sup>-1</sup>. Distinguished band of nanographene oxide represents stretching of carbonyl group (enriched with these groups, some of them singles and other with hydroxyl groups on the surface layer) appeared at 1708 cm<sup>-1</sup>. The double stretching of C-O appeared at 1193 cm<sup>-1</sup>. These bands didn't appear in the graphite which used as a starting material to prepare graphene oxide. After the reduction of graphene oxide, stretching band of C=O disappeared, the band of 1660 cm<sup>-1</sup> belongs to stretching of C=C in the skeleton of graphene. The vibrational stretching at the range 1590-1530 cm<sup>-1</sup> appeared in the spectra of graphene and graphene oxide referred to the presence of C-C bond considered an essential bond in the skeleton of graphene, graphene oxide and graphite. IR spectrum of nano-TiO<sub>2</sub> showed two essential bands at 678-424 cm<sup>-1</sup>, which attributed to the stretching of Ti-O bond. Another two bands at 3442 cm<sup>-1</sup> of ν(OH) and 1614 cm<sup>-1</sup> of δ(OH) of water

absorbed from atmosphere by nano-TiO<sub>2</sub> due it active nano size [30-33].

**XRD studies:** The X-ray diffraction patterns of graphene and graphene oxide are depicted in Figs 2 and 3, which are coincided with the literature values [34,35]. Fig. 2 shows a strong diffraction ( $2\theta = 13^\circ$ ), a distinguished peak of graphene oxide, internal distance of this peak is (6.35303 Å). The other peaks were at  $2\theta = 25^\circ$  with internal distance (5.30621 Å) and  $2\theta = 43^\circ$  with internal distances (3.51396 Å), these peaks belong to carbon skeleton of the plate. The X-ray diffraction of graphene (Fig. 3) with wide peak at angles  $2\theta = 24.5813^\circ$ , with distance of 3.78358 Å,  $2\theta = 24.2525^\circ$  with distance of 3.57992 Å and  $2\theta = 23.4940^\circ$  of internal distance 3.6669 Å. The disappearance of band at  $2\theta = 13^\circ$  in the measurements of graphene and the appearance of new band give an evidence to the transformation from graphene to graphene oxide. From the results of internal distances between the layers of graphene and graphene oxide, it is noticed that the distance between graphene oxide layers bigger than that of graphene which was due to the exfoliation and the reduction of graphene oxide which displace the water molecules out of the areas between the layers which connected to oxygen atoms of oxide groups between layers and increase the distance between the layers of graphene oxide.

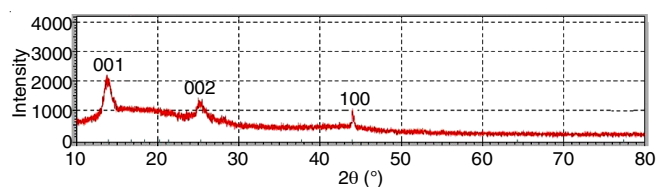


Fig. 2. X-ray diffraction pattern of nano graphene oxide

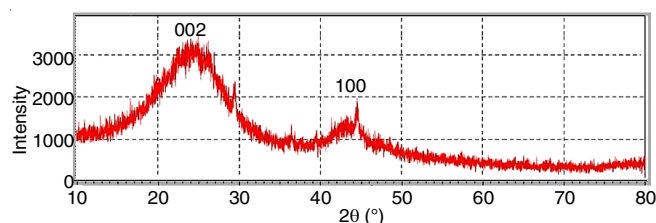


Fig. 3. X-ray diffraction pattern of nano graphene

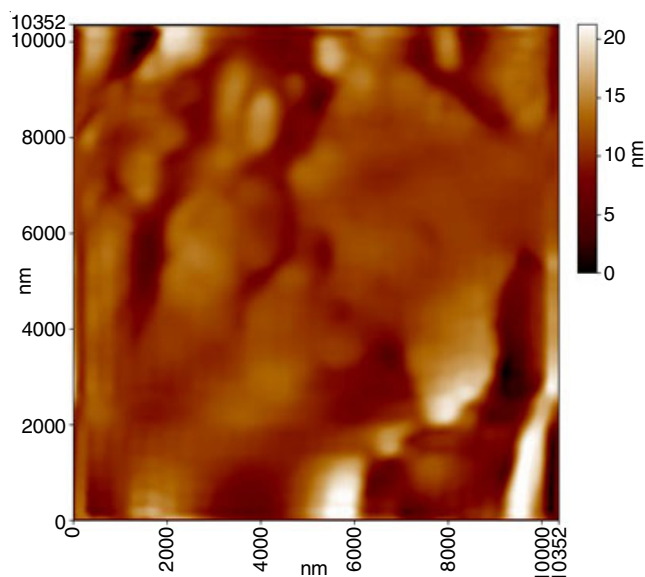


Fig. 4 shows X-ray diffraction pattern of titanium oxide nanotubes. The size of particles have been calculated from Debye-Scherrer equation [35]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D represents the size of particle, K is a constant a unit less quantity and depend on the crystal shape and equal to 0.94, B represents the width of the peak at high intensity and  $\lambda$  represents the wave length of X-ray (1.456 nm).

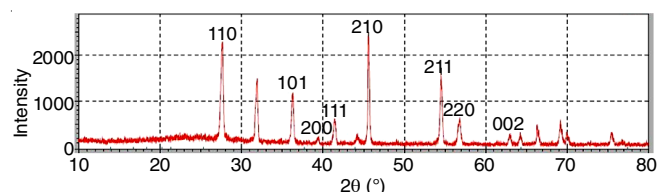


Fig. 4. X-ray diffraction pattern of titanium oxide nanotubes

From the above equation, it is found that the particle size of the prepared titanium oxide was 8.97 nm. This give good match with the results of X-ray diffraction of titanium oxide nanotubes. The band at  $2\theta = 32.6^\circ$  belong to the remaining of starting materials [36,37].

**Atomic force microscope measurements:** The results of AFM measurement of graphene (Fig. 5) shows that graphene consists of plates one over each other. The high value of plates thickness was 21.2 nm. The length of nanoplates fall in the range 300-2600 nm and the average plates lengths was about 948.56 nm. About 90 % nanoplates were in the length of 1400 nm. These long lengths and the low values of thickness represent a good properties of graphene. Fig. 6 shows the AFM image of titanium oxide, from the image we noticed that titanium oxide with the lengths fall in the range 60-120 nm with average length of 89.14 nm and 90 % of titanium oxide nanotubes were in the length of 105 nm.

**Electrical properties of pure polymers and polymer nano-composites:** Fig. 7-10 show the relation between the real electrical isolation constant and imaginary electrical isolation constant

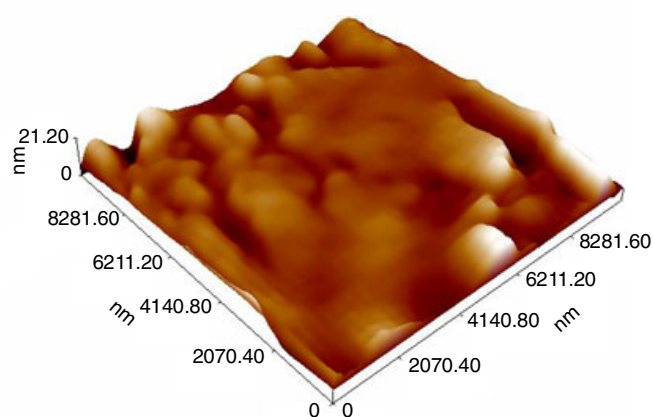


Fig 5. AFM image of graphene

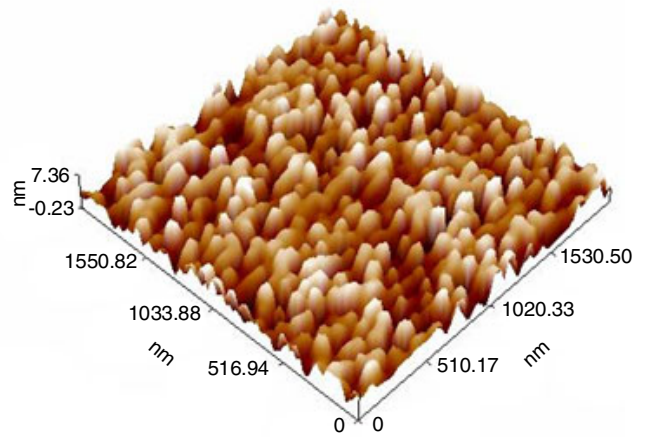
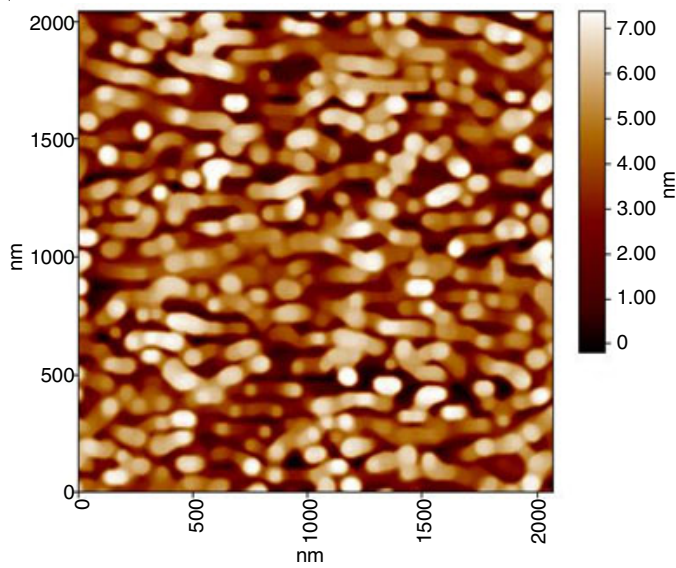


Fig. 6. AFM image of  $\text{TiO}_2$

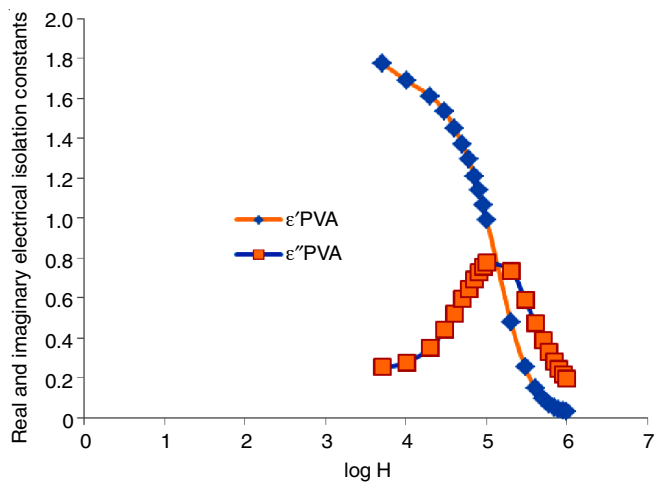


Fig. 7. Relation between real and imaginary electrical isolation constant ( $\epsilon'$  and  $\epsilon''$ ) and frequency (H) logarithm of PVA

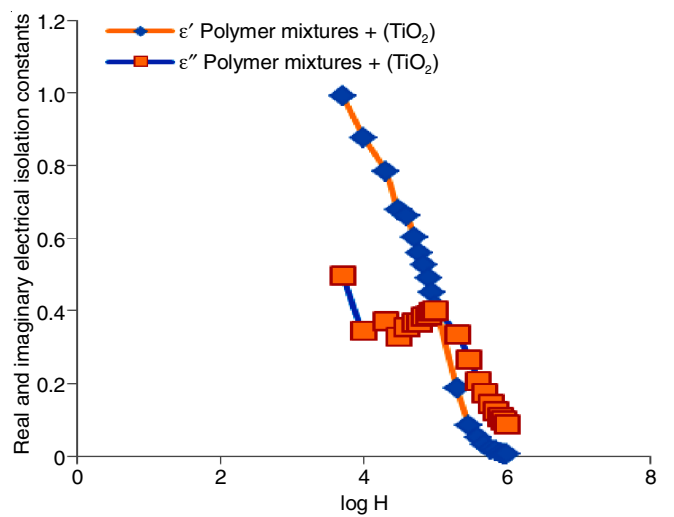


Fig. 9. Relation between real and imaginary electrical isolation constant ( $\epsilon'$  and  $\epsilon''$ ) and frequency (H) logarithm of polymer mixtures composite containing nano titanium oxide

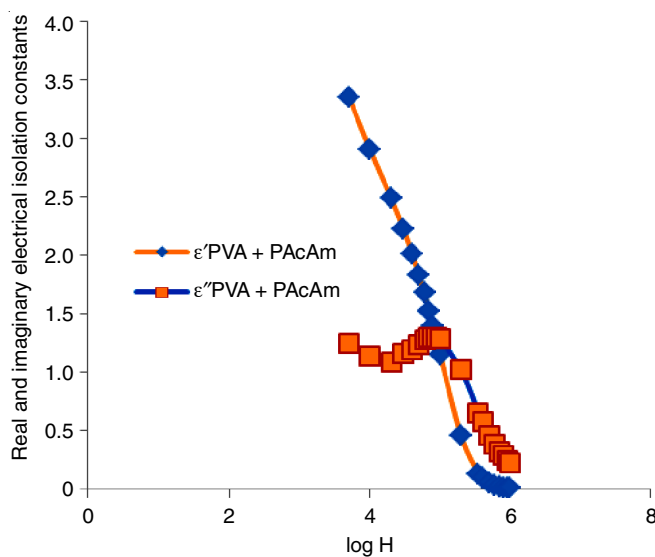


Fig. 8. Relation between real and imaginary electrical isolation constant ( $\epsilon'$  polymer mixtures +  $\text{TiO}_2$  and  $\epsilon''$ ) and frequency (H) logarithm of polymer mixture (PVA + PAcAm)

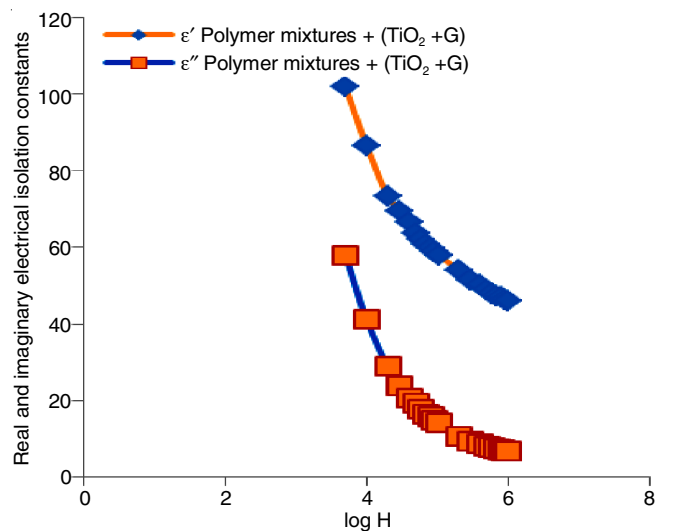


Fig. 10. Relation between real and imaginary electrical isolation constant ( $\epsilon'$  and  $\epsilon''$ ) and frequency (H) logarithm of polymer composite containing nano graphene and titanium oxide



with the logarithm of frequency of PVA, polymer mixtures (PVA + PAcAm) and polymer mixture composites/nanomaterial. At low frequencies, the values of real electrical isolation constant become high while that of imaginary electrical isolation constant become low. The pure polymers give a low values of real electrical isolation constant compared to that of polymer composites containing nanographene with  $\text{TiO}_2$  and polymer composites containing nanotitanium oxide alone. Figs. 7-10 showed that the values of real electrical isolation constant follow the series put the polymer composite mixtures containing nanographene and  $\text{TiO}_2$  in first level followed by polymer mixtures composite with titanium oxide alone, the least value was found for PVA. The polymer mixtures composite of nanographene and titanium oxide have high conductivity due to the plates of graphene, which help significantly in the transfer of charge carrier, while titanium oxide, a semiconductor and has moderate energy band gap which reduce the conductance and give lower real electrical isolation constant with polymer composite mixtures. The high value of real electrical and low value of imaginary electrical isolation constant of polymer composite containing nanographene and titanium oxide give it a high efficiency in electrical energy storage super capacitors.

Electrical conductance of polymers and composites have been studied by using alternative current at different frequencies ranged from 5 to 100 KHz and calculated from eqn. 2 :

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \quad (2)$$

where  $\sigma$  represents the electrical conductance,  $\omega$  is the angular frequency and  $\epsilon$  is the frequency used in the measurement.

The electrical conductivities of polymers and composites containing nanomaterials were low at low frequencies and increase with the increasing of frequency as depicted in Figs. 11 to 14. As mentioned above, the conductivity of composite containing nanographene and titanium oxide higher than that of composite with nanotitanium oxide alone and pure polymer. The graphene increase the distance between the internal surfaces and lead to spread the nanoparticles resulted increasing the number of electrons on electrodes, so this composite will be suitable for the manufacturing of capacitors.

**Supercapacitors voltage measurement:** Table-1 shows the voltages values of prepared capacitors at different interval of times. The capacitor of polymer composite with nanographene and titanium oxide give a voltage of 1.277 volt at the beginning

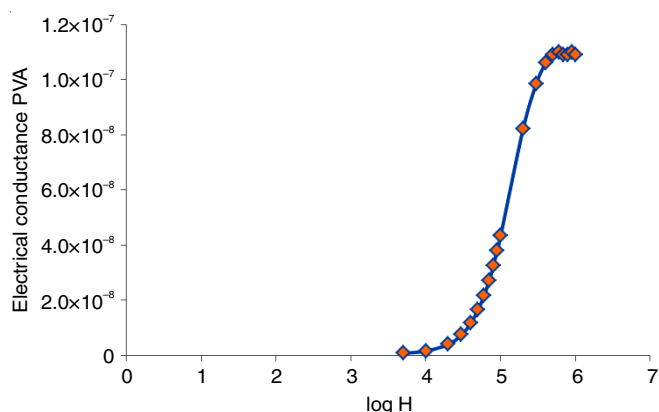


Fig. 11. Relation between electrical conductance ( $\sigma$ ) and the logarithm of frequency (H) of PVA

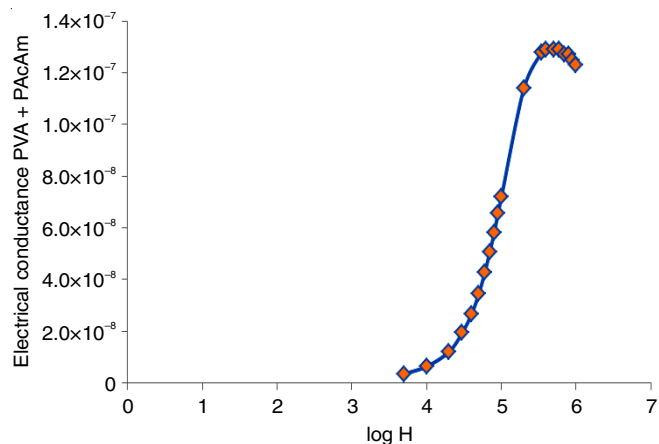


Fig. 12. Relation between electrical conductance ( $\sigma$ ) and the logarithm of frequency (H) of polymer mixtures (PVA + PAcAm)

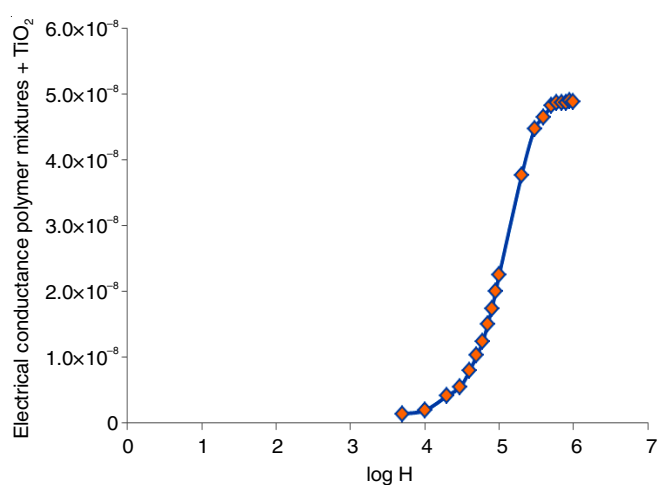


Fig. 13. Relation between electrical conductance ( $\sigma$ ) and the logarithm of frequency (H) of PVA + PAcAm with nano titanium oxide

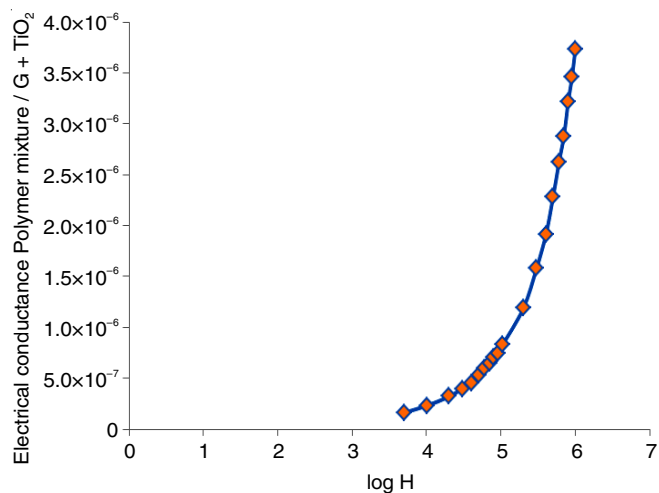


Fig. 14. Relation between electrical conductance ( $\sigma$ ) and the logarithm of frequency (H) of PVA + PAcAm with nano graphene and titanium oxide

of charging and kept the electrical energy after 24 h with a voltage of 0.248 volt while that of composite with nano titanium oxide give 1.141 volt with a lower voltage after 24 h. The capacitor of polymer mixture [poly(vinyl alcohol) and poly(acrylamide)] without nanomaterials give a voltage value of 0.514 volt at charging and gave the least value of voltage 0.002 after 24 h.

TABLE-1  
VOLTAGE OF CAPACITORS AT DIFFERENT TIMES

Time	Capacitor of PVA + AcAm (G + TiO <sub>2</sub> )	Capacitor of PVA + AcAm (TiO <sub>2</sub> )	Capacitor of PVA + AcAm
At charging	1.277	1.141	0.514
After 5 min	1.253	0.916	0.468
After 10 min	1.170	0.603	0.375
After 15 min	1.126	0.497	0.172
After 30 min	0.992	0.265	0.107
After 1 h	0.568	0.196	0.098
After 5 h	0.410	0.182	0.032
After 10 h	0.399	0.178	0.011
After 15 h	0.390	0.152	0.009
After 20 h	0.277	0.058	0.005
After 24 h	0.248	0.048	0.002

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