

## Electrical Conduction Mechanisms of (PMMA-Kaolin) Nanocomposite Films

<sup>2</sup>Hussein A. Noor, <sup>1</sup>Zinah S. Hamad, <sup>2</sup>Fouad Sh. Hashim and <sup>2</sup>Khalid H. Al-Ammar

<sup>1</sup>College of Environmental Sciences, University of Al-Qasim Green, Al Qasim, Iraq

<sup>2</sup>Department of Physics, College of Education for Pure Sciences, University of Babylon, Hillah, Iraq

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**Abstract:** In this study, Kaolin nanoparticles with different percentages (0, 1, 3, 4 and 7) wt.% was used as reinforcing phase in PolyMethyl Methacrylate (PMMA) matrix to form nanocomposite films. PVA solution used as a coated layer covered the nano-kaolin applied as a filler. The DC electrical conductivity ( $\sigma_{dc}$ ) increases with increasing of modified nano-kaolin concentrations and Temperature (T). The AC electrical conductivity ( $\sigma_{ac}$ ) increases with increasing of modified nano-kaolin concentrations and Frequency (F). The dielectric loss and dielectric constant ( $\epsilon'$ ) decrease with increasing of nano-kaolin. The activation Energy ( $E_{act}$ ) decreases with increasing of nano-kaolin content.

**Key words:** PMMA, nano-kaolin, nanocomposites, electrical properties, reinforcing, PVA

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### INTRODUCTION

Polymers form a very important class of materials without which the life seems very difficult. Now a days the enormous use of polymer materials is attributed to their extraordinary combination of properties, low weight and ease of processing. Polymer nanocomposites consist of a polymeric substance and a nanoparticles (particles between 1 and 100 nm in size) reinforcing material. These materials show considerable improvements in different properties in mechanical properties, optical properties, thermal stability, chemical resistance, etc. The requirements of industrial development in the world led to the development of the science and technology of composite materials and the entry into the manufacture of new materials with special specifications determined by the required use (Callister, 2003; Rudko *et al.*, 2015). The improvement of the properties by the addition of particles can be achieved when adequately good interaction between the nanoparticles and the matrix and good dispersion of particles within the matrix. In nanocomposites, covalent bonds, ionic bonds, Vander Waals forces, hydrogen bonding could exist between the matrix and filler components (Camargo *et al.*, 2009; Khadayeir *et al.*, 2018; Habubi *et al.*, 2018). PMMA is an amorphous thermoplastic polymer. It has good optical properties, transitions are indirect (Dakhil and Hashim, 2018) but has a poor scratch resistance and a good weather resistance. This explains that the electron transitions is indirect.

PMMA is stable to alkalis and acid and has a good impact strength higher than that of glass or polystyrene. PMMA is widely used in many technological applications

because of its unique combination of excellent optical properties with chemical inertness, some good mechanical properties, thermal stability, electrical properties and easy shaping (Nahida, 2012). Kaolin as a filler has characteristic of soft white color and has melting point 1770°C in case of purity. Kaolin's structure is composed of silicate sheets (Silica tetrahedral layer)  $Si_2O_5$  bonded to aluminum Oxide/hydroxide layers  $Al_2(OH)_4$  (Al-Octahedral layer) called gibbsite layers. The silicate and gibbsite layers are tightly bonded together with only weak bonding existing between these silicate/gibbsite paired layers (called s-g layers). The weak bonds between these s-g layers cause the cleavage and softness of this mineral (Varga, 2007). Kaolin does not swell because its structure doesn't have interlayer cations and the water  $H_2O$  is chemically-bound in the structure as (OH) ions. These minerals are non expandable in water. Kaolin is widely used in the making of paper, rubber, paint and many other products. In this present research, we studied the effect of addition of nano-kaolin clay on the electrical properties of PMMA.

### MATERIALS AND METHODS

The granular sizes selected for nano-kaolin clay is  $<0.1 \mu m$  and the modified process was performed by additives of PVA at 80°C temperature for 4 h. The PVA addition has pH = 6 is one of the requirements to obtain the best adsorption on the surface of the clay before applied it as filler. The mixture was mixed by a magnetic stirrer type-Sturt-Germany manufacture under 80°C temperature continued to get slurry form and to insure homogeneity with high viscosity, then dried, milled and sieved to granular size  $\sim 0.1 \mu m$ . A solution has been

prepared by solving 1 g of PMMA in 30 mL of the chloroform and using magnetic stirrer to mix the materials to obtain more homogeneous solution at 70-80°C temperature for 30 min. The modified nano-kaolin content of 1, 3, 5 and 7 wt.% were added to PMMA and mixed for 50-60 min even get a homogeneous solution white color. The casting method is used to get the nanocomposites cast on glasses petri dish and left for 2 days to dry. The choice of the casting method in the preparation of PMMA and (PMMA-Kaolin) nanocomposites was due to the require no advanced techniques and complex devices and by which they can prepare samples with a large area and equal thickness.

**Computational details:** The DC electrical properties of nanocomposites were measured by using Keithley electrometer type 2400 source mater. The dielectric properties of samples examined with frequency range from 100 Hz to 5×10<sup>6</sup> Hz by using LCR meter type (HIOKI 3532-50 LCR HI TESTER). The electrical conductivity σ<sub>dc</sub> is (Ahmad *et al.*, 1992):

$$\sigma_{dc} = \frac{1}{\rho} = \frac{L}{R A} \quad (1)$$

Where:

A = A guard electrode effective Area

R = A Resistance

L = A distance between electrodes

The activation Energy E<sub>act</sub> can be calculated by Heitjans *et al.* (2008):

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_{act}}{K_B T}\right) \quad (2)$$

Where:

σ = Electrical conductivity at T Temperature

σ<sub>0</sub> = Electrical conductivity at 0K

K<sub>B</sub> = Boltzmann constant

The dielectric constant ε' calculates by Dube (1984):

$$C_p = \frac{\epsilon' \epsilon_0 A}{d} \quad (3)$$

Where:

C<sub>p</sub> = Capacitance

d = Sample thickness

A = Surface Area

The dielectric loss factor is (Dube, 1984):

$$\tan \delta = \frac{I_p}{I_q} = \frac{\epsilon''}{\epsilon'} \quad (4)$$

where, tan δ is a loss factor. The AC conductivity σ<sub>AC</sub> calculates by Zaky and Hawley (1970):

$$\sigma_{AC} = \omega \epsilon'' \epsilon_0 \quad (5)$$

## RESULTS AND DISCUSSION

Figure 1 shows the DC electrical conductivity (S/cm) as a function of temperature for different wt.% concentration of kaolin nanoparticles. The electrical conductivity is increasing with increase both the temperature and concentration of kaolin nanoparticles.

The increase of electrical conductivity can be explained as follows at low concentration, the kaolin nanoparticles are located in separated groups or cluster inside the polymers (PMMA) while with increasing the amount of nanoparticles form a continuous network inside the polymers. This network has paths where charge carriers are allowed to pass through the paths that have low electrical resistance and also the increase in the charge carriers (Hamood *et al.*, 2018; AL Jubouri, 2013). The increase of conductivity with temperature is attributed to two main parameters, charge carriers and mobility of these charges. The mobility depends on the structure and the temperature (Elaydy and Kraiam, 2007).

Figure 2 shows the relation between Ln σ and the inverse absolute temperature for (PMMA-Kaolin)

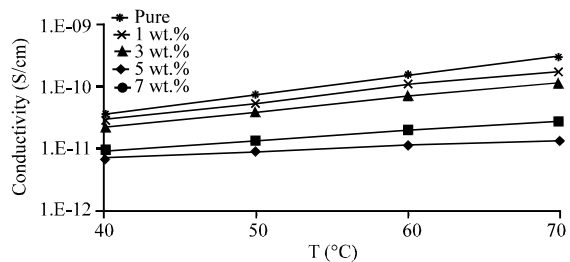


Fig. 1: Variation of DC electrical conductivity with kaolin nanoparticles wt.% concentration for (PMMA-Kaolin) nanocomposite

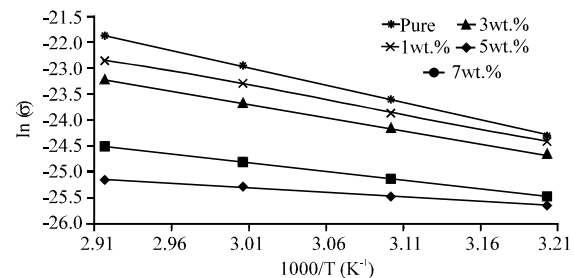


Fig. 2: Variation of Ln DC electrical conductivity (σ) with inverse absolute temperature for (PMMA-Kaolin) nanocomposites

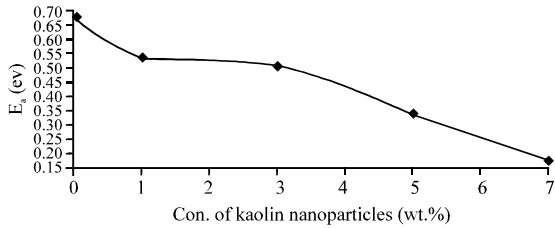


Fig. 3: Variation of activation energy for DC electrical conductivity with concentration of kaolin nanoparticles wt.% for (PMMA-Kaolin) nanocomposites

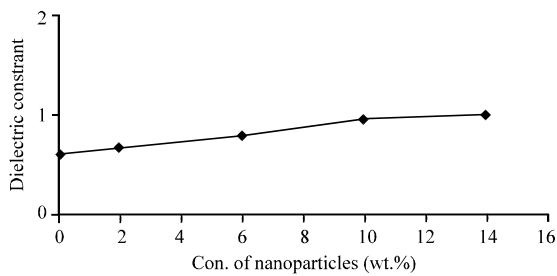


Fig. 4: Variation of dielectric constant with concentration of kaolin nanoparticles wt.% at 100 Hz for (PMMA-Kaolin) nanocomposites

nanocomposites. Results show that the values of activation energy ranging from 0.654-0.157 eV for (PMMA-Kaolin) nanocomposites, the high values existence for activation energy in state pure polymers. By adding low concentrations of kaolin nanoparticles, the values of the activation energy are decreasing for all 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 kaolin nanoparticle concentrations, the activation energy decreases as a result of the increase of local centers as shown in Fig. 3 for (PMMA-Kaolin) nanocomposites. Thus, the mechanism of conduction in the samples having low concentrations is the hopping (Khissi *et al.*, 2011).

Figure 4 shows the effect of adding the kaolin nanoparticles on the dielectric constant at 100 Hz and 25°C. It is clear that the dielectric constant increases with increasing the concentration of kaolin nanoparticles. This attributed to the formation of a continuous network of kaolin nanoparticles inside the nanocomposite at high concentrations and because the increase of  $C_p$  for the storage charges.

Figure 5 shows the variation of the dielectric constant of (PMMA-Kaolin) nanocomposites with angular

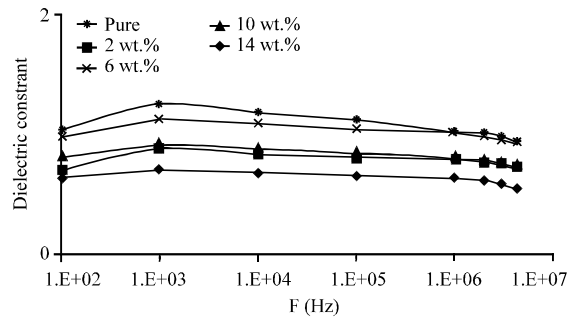


Fig. 5: Variation of the dielectric constant of (PMMA-Kaolin) nanocomposites with frequency

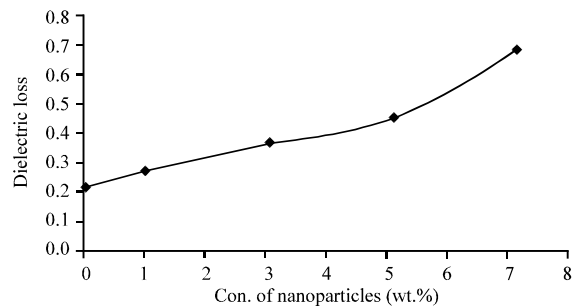


Fig. 6: Variation of dielectric loss with concentration of kaolin nanoparticles at 100Hz for (PMMA-Kaolin) nanocomposites

frequency. Figure shows that the dielectric constant values decrease with increasing applied frequency due to decrease the space charge polarization and because the dipolar, ionic and electronic polarization (Abbas and Hasan, 2014).

Figure 6 shows the dielectric loss with concentration of kaolin nanoparticles at 100 Hz. It is clear that the dielectric loss increases with increasing the concentration of kaolin nanoparticles which is due to increase the electronic charge (Liang and Tjong, 2008).

Figure 7 shows the dielectric loss with the frequency of (PMMA-Kaolin) nanocomposites at RT. It is clear from the figure that dielectric loss decreases with frequency. The larger value of dielectric loss at low frequency could be due to the mobile charges within the polymer backbone. When the frequency is increasing, the dielectric loss are of low loss up to a roughly constant value, due to the mechanisms of other types of polarization that occur at high frequencies (Satapathy *et al.*, 2008).

Figure 8 shows the AC conductivity  $\sigma_{ac}$  (S/cm) of (PMMA-Kaolin) nanocomposites with kaolin concentration at 100 Hz and 25°C. The conductivity is increasing with

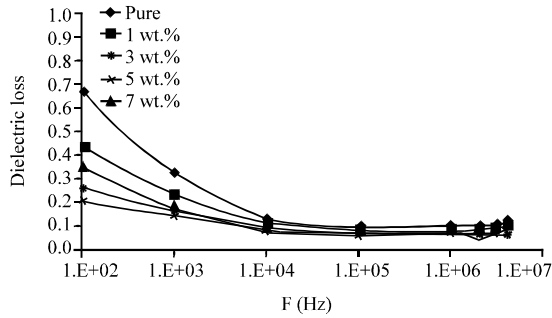


Fig. 7: Variation of the dielectric loss with frequency for (PMMA-Kaolin) nanocomposites

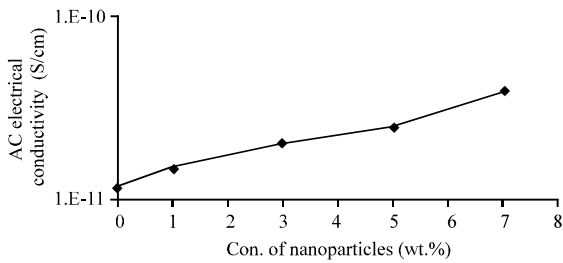


Fig. 8: Variation of AC electrical conductivity with concentration of kaolin nanoparticles at 100 Hz for (PMMA-Kaolin) nanocomposites

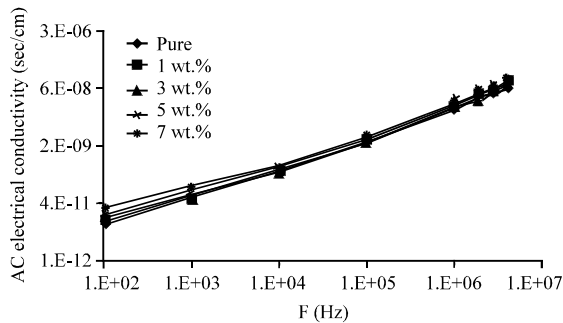


Fig. 9: Variation of AC electrical conductivity with frequency for (PMMA-Kaolin) nanocomposites

increase the concentration of kaolin nanoparticles. This increase is due to increase the charge carriers (Palin, 1973).

Figure 9 shows the variation of the AC conductivity for (PMMA-kaolin) nanocomposites with frequency. Figure shows that AC conductivity increases considerably with the increase of frequency due to the motion of charge carriers by hopping process and the excitation of charge carriers to upper states in the conduction band (Palin, 1973).

## CONCLUSION

The DC electrical conductivity ( $\sigma_{dc}$ ) increases with increasing of modified nano-kaolin concentrations and Temperature (T). The AC electrical conductivity ( $\sigma_{ac}$ ) increases with increasing of modified nano-Kaolin concentrations and Frequency (F). The dielectric loss, dielectric constant ( $\epsilon'$ ) and activation energy ( $E_{act}$ ) decrease with increasing of nano-kaolin content.

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