AC Electrical Properties and AC- Conductivity Model of Ultrafine Aluminum Particles Dispersed in Poly (methyl methacrylate) Polymer

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Abstract

The Polymer Poly (methylmethacrylate) (PMMA) composites with different Aluminum (Al) particle concentration were prepared. The composite have average thickness 100 μm and contain different aluminum particle concentration (0, 1, 2, 4, 6, 8, 10, 15, 20 %wt. %). The electrical properties of the composites as impedance, dielectric constants, dielectric loss, AC- conductivity of the prepared composites were studied at different applied frequency from 10 kHz up to 1200 kHz, and at different temperature (30°C, 40°C, 50°C, 60°C, 70 °C, 80°C and 90 °C) and different aluminum particles concentration. The impedance, dielectric constants, dielectric loss, AC- conductivity was determined from impedance data It was found that the dielectric constant and conductivity increase with applied frequency, temperature and different Al concentrations. Empirical models were used to describe the dependence of the electrical quantities on the frequency and temperature.

Keywords: polymer, particle concentration, impedance, AC-conductivity, dielectric constants, dielectric loss, AC- conductivity model.

1. Introduction

Conductive polymer composites can be controlled by correct choosing the filling components, dispersion state, their shape, interactions and relative concentrations. From this perspective, conductive polymers composite have been the object of wide research in last two decades. The electrical and thermal conductivities of an insulating polymer can be afflicted by adding conductive particles like aluminum, iron, nickel or other conducting filler. In order to obtain electrical conduction in insulating polymeric system, conductive path or ways of dispersed metal particles throughout the polymer matrix are wanted.

Large efforts have been expended in realization of the structure-property relationship, which is requisite for designing and industrialization new materials with desirable properties for particular technological applications. To get polymer composites with suitable thermal, optical, electrical, and mechanical properties needs a smart choice of polymer, as well as that of metal as dispersed component in the polymeric matrix. It has been reported that the choice of polymer host (as matrix) depends fundamentally on presence of polar groups to form electron/ cation coordination, and a low impediment to polymer segmental motion. Polymer complexes with several aluminum particle concentrations have high ionic conductivity. These composites have several characteristic over classical solids, including flexibility, processibility, light weight, ability to absorb mechanical shocks. They can be used in some
applications such as switching devices also as antistatic materials and components for surge protection, for electromagnetic interference shielding of electronic equipments and packing houses (Rothon, 2003; Tritt, 2004). The physical description of this composite can be carried out using a many of analytical techniques as UV- spectroscopy, X- ray diffraction, and AC impedance, besides to DC measurements (Crossman, 2004).

In the present study, polymer with different Aluminum particles concentration was prepared. The AC- electrical properties of that Al/PMMA composite will be determined under different Aluminum particle concentration, temperature and applied field frequency.

2. Experimental works

2.1 Composite preparation

For the samples used in the study, thin films with a thickness of 100 µm thickness were prepared from the poly (methyl methacrylate) compound by casting the poly (methyl methacrylate) solution with the ultrafine particles of aluminum, such as it melted the mixture made of poly (methyl methacrylate) and aluminum particles with different concentrations (0, 2, 4, 6, 8, 10, 15 and 20 %wt.) in an appropriate solvent, methanol. The solution was placed in the room temperature for a few days and doing of the appropriate modulations until we get the mixture in terms of homogeneity and fusibility. The mixture was immediately casted to thin films on to a glass mould (plate) and the methanol allowed evaporating completely at room temperature by waiting for a few days under atmospheric pressure. After that for completely dried samples the oven was used at a temperature of approximately 40 ° C for two days. In composites of Al/PMMA the silane coupling agent acted as a “molecular bridge” to establish chemical bonding between the PMMA matrix and Al. The mechanical properties of prepared Al /PMMA composites have high efficiency to improved strength and hardness. The distribution of Al homogeneous and uniform in the PMMA resins matrix to provide reinforcement effect to the optimal content of Al in the matrix that increase in Al content caused the flexural strength, surface hardness. Thermal stability and other properties are developed to increase until the optimal amount was reached (Zhang et al., 2012).

2.2 Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEMs) were taken for the composites using a K550 Emitech Sputter Coater. Figure (1) shows a micrograph of the fractured surface of the 4 wt% Al/PMMA specimen. The SEM micrograph exhibits good adhesion between the aluminum filler and poly (methyl methacrylate) matrix.

2.3 Impedance measurements

To observe the effects of particle concentration, frequency and temperature on the electrical behaviour of Al/PMMA composites, The electrical measurements (impedence (Z), dielectric constant (ε’), dielectric loss (ε’’) and AC-conductivity (σAC)) have been performed on PMMA/Al composites in the range of frequency from 10 kHz up to 1200 kHz by using the Hewlett Packard (HP) 4192A. The test specimens were set firmly between two copper electrodes connected through cables to the impedance analyzer. The cell was put in an oven
and the temperature measured by thermocouple wires. A period of about 30 min was maintained between successive impedance measurements to allow a steady state of temperature to be reached. The impedance analyzer reads values of impedance and phase angle of the specimen by varying the applied frequency. The mean values and standard deviations were estimated with average error of about 3-5%. Impedance measurements were performed in temperature range (30 °C - 90 °C) (Sbeih and Zihlif, 2009).

The real and imaginary components of the complex impedance $Z$ are given (Ellimat et al., 2008):

$$Z_r = Z \cos \varphi , \quad (1)$$

$$Z_i = Z \sin \varphi , \quad (2)$$

where $\varphi$ is the phase angle.

The dielectric constant $\varepsilon'$ and the dielectric loss $\varepsilon''$ of the sample were calculated from the equations:

$$\varepsilon' = \frac{Z''}{2\pi f C_0 Z^2} , \quad (3)$$

$$\varepsilon'' = \frac{Z'}{2\pi f C_0 Z^2} , \quad (4)$$

where $f$ is the frequency of the applied AC-electric field and $C_0$ is the capacitance of two parallel plates of the cell without sample and is given by:

$$C_0 = \varepsilon_0 A / d \quad , \quad (5)$$

where $A$ is the specimen area, and $d$ is the thickness. The AC conductivity of the composite samples is calculated from the equation:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \quad , \quad (6)$$

And the thermal activation energy ($E_a$) of the conduction process was determined from the Arrhenius equation (Ayesh, 2010):

$$\sigma = \sigma_0 \exp [- E_a / k_B T] \quad , \quad (7)$$

here $\sigma_0$ is a material constant, $T$ is the temperature in Kelvin and $k_B$ is the Boltzmann constant.
3. Results and discussions

3.1 The dependence of electrical properties on the applied field frequency

The electrical measurements (impedance ($Z$), dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and AC conductivity ($\sigma_{AC}$)) have been performed on PMMA/Al composites in the range of frequency from 10 kHz up to 1200 kHz.

Figure (2) shows the dependence of phase angle ($\phi$) (The fraction of a period difference between the peak of voltage and the peak of current), on frequency of the applied field for different Al concentration and neat PMMA. The phase angle ($\phi$) is always negative; for a capacitive circuit since the current leads the voltage (Khazraei et al., 2012).

This figure shows ($\phi$) decreases with increasing frequency and shows that the change of phase angle ($\phi$) toward low negative values with increasing Al content indicating that the films become more resistive than capacitive. The change of phase angle toward higher negative values at high frequencies indicates that the material becomes more capacitive than resistive (Abu-Jamous and Zihlif, 2010).
Figure (2): Phase angle versus frequency for Al/PMMA composite

Figure (3) represents the variation of impedance ($Z$) per unit thickness as a function of frequency at room temperature for specimens of different Al concentration and neat PMMA. The figure clarifies decreasing in impedance with increasing in frequency, and reaching a constant value in the high frequency region, this type of tendency was revealed by all Al/PMMA samples without any anomalous behavior. The high impedance values at low frequency is due to the conductivity across grain boundaries and increases hopping of charge carriers between the localized charge at high frequencies which is might be the underlying factors for this trend (Kaur et al., 2016).

Figure (3): Impedance versus frequency for Al/PMMA composite.
On the other hand, the rapid decrease of impedance values indicates a response of the bulk with alternating electric field. This behavior may be attributed to reduction of the interfacial polarization effect, which may exist at the electrode-specimen surface (Lvovich, 2012); (Sbeih and Zihlif, 2009).

Figure (4) shows the variation of the dielectric constant ($\varepsilon'$) for all specimens with frequency at room temperature. It is observed that with the increase in frequency, the value of dielectric constant decreases, thereafter it becomes almost constant for all the specimens, the appearance of all forms of polarizations probably basic responsible for this type of trend at very low frequency for the specimens. The value of ($\varepsilon'$) increases with increases in space charge polarization, which in turn may be due to a large concentration of defects. But on increasing frequency, some of the polarizations slowly disappear except ionic and electronic polarization, which effects in rapid decrease in dielectric constant (Pattanayak et al., 2013); (Kaur et al., 2016).

![Figure 4: Variation of dielectric constant with frequency for Al/PMMA composite](image)

Figure (4): Variation of dielectric constant with frequency for Al/PMMA composite

Figure (5) shows the variation of the dielectric loss ($\varepsilon''$) for all specimens with frequency at room temperature, the nature of the curves is approximately similar with dielectric constant. Generally, a dielectric loss decreases with increasing frequency. This is because the induced charges progressively fail to keep track of the reversing field causing a decrease in the electronic oscillations as the frequency is increased (Singh et al., 2008); (Prasad and Basu, 2013).
Otherwise the dielectric loss becomes less dependent on frequency. This is because the induced charges gradually fail to follow the reversing field causes decreasing in the electronic oscillations as the frequency is increased (Singh et al., 2010).

The AC-conductivity ($\sigma_{AC}$) of the composites as a function of frequency at room temperature is shown in Figure (6). The increase in frequency of the applied field enhances the charge carrier’s jumps between the localized states, which results in increase of conductivity (Pattanayak, et al., 2013); (Kaur, et al., 2016).

**Figure (5):** Variation of dielectric loss with frequency for Al/PMMA composite

**Figure (6):** Variation of AC-conductivity with frequency for Al/PMMA composite
3.2 Dependence of Electrical Properties on Al Concentration

Figure (7) shows the dependence of the AC impedance (Z) (per unit length) on the Al concentration for the prepared composites at different frequencies (200 kHz, 400 kHz, 600 kHz, 800 kHz, and 1000 kHz) at room temperature. It is observed that when the Al concentration increases the impedance (Z) decreases. The Al doped specimens cause consequently decreases the grain boundary thickness.

Since Al is a conductor, its addition in the matrix is expected to reduce the impedance of PMMA host. Moreover, the interfacial polarization inside the composites may also cause these changes. Generally, Al clearly enhances the electrical conductivity and the polar character of PMMA host (Ayesh, 2010).

![Figure 7](image)

**Figure (7):** Variation of the impedance with Al filler concentrations

Figure (8) and figure (9) show the variation of dielectric constant ($\varepsilon'$) and the dielectric loss ($\varepsilon''$) with the increasing concentration. The enhancement in their value is refer to the interfacial polarization effect a phenomenon that clear in a heterogenous system consisting of phases with different dielectric and conductivities, attributed to the piling up of charges at the interfaces. Moreover, increasing in Al content causes the formation of clusters, which leads to the greater average polarization and consequently a greater contribution to the dielectric constant (Singh et al., 2010).
Figure (8): Variation of the dielectric constant with Al filler concentrations

Figure (9): Variation of the dielectric loss with Al filler concentrations

Figure (10) shows the variation of AC-conductivity ($\sigma_{AC}$) with Al concentration. The figure clarify that, The conductivity of the composite increased with the concentration of filler, This is due to the electronic interaction process taking place in the composites and therefore the give rise to composites became more conductive with the increase of the conductive filler content. At low filler content, the conducting particles are separated and electrical charge may flow only by means of hopping or tunneling through nonconducting medium between the neighboring particles. The transport of charge carriers would be inactive.
and the overall conductivity of the composite was observed to be low at a lower concentration). On the other hand, when particle concentration increased, the gap between the particles reduces and conductivity increased due to increase of the conduction path.

The conducting additive is incorporated into polymers at levels that allow the composite to maintain its electrically insulative qualities, as well as at higher levels, which allow the composite to become electrically semiconductive. As the concentration of the Al fillers increases, the bonding to each other to form the conduction paths through the composite, thus causing decreases the resistance and increases the conductivity significantly at a critical concentration, which called percolation threshold (Zhang et al., 2017); (Álvarez et al., 2010)

![Figure (10): Variation of AC-conductivity with Al filler concentrations](image)

For the prepared thin films composite we note from the figure that, The ($\sigma_{AC}$) is nearly constant up to 6 wt. %, after that it increases rapidly with increasing the Al concentration. The concentration value of 6 wt. % filler content can be considered a critical one and called a percolation threshold. On the other hand, at such concentration, mechanical properties of a polymer, such as ductility, toughness and the glass transition temperature are changed (Zhang et al., 2017).

### 3.3 Dependence of Electrical Properties on Temperature

The electrical behavior of PMMA/Al composites is examined at different temperatures (30°C, 40°C, 50°C, 60°C, 70°C, 80°C and 90 °C). The effect of rise in temperature on decreases impedance ($Z$) of the chosen sample 20 wt. % Al filler becomes clearly visible in figure (11). This indicates that the electrical properties of the material arise mainly due to the bulk effects; this may be due to the presence of immobile species at low temperatures and defects at high temperatures. Furthermore, since a decrease on impedance ($Z$) is made at higher temperatures some relaxation species, such as defects, may be responsible for electrical conduction in the material by hopping of electrons among the available localized
sites. And can be explained in terms of certain events such as charge carriers' generation and closing up the energy gap. These processes affect the charge carriers' transport in the composite bulk. Generally, it indicates the presence of space charge polarization. The polarization currents depend on temperature, where as the decay time of polarization is shortened by increasing temperature. This behavior proves that the conductivity increases as temperature increases, similar to semiconducting and ionic solids (Badapanda et al., 2014).

![Graph showing impedance variation with temperature](image1)

**Figure (11):** Variation of the impedance with temperatures for 20 wt. % Al

The dielectric loss \( \varepsilon'' \) curve versus temperature at different frequency is shown in the figures (12). Increasing in dielectric loss as temperatures is due to the perturbation of phonon system by an electric field, the energy transferred to the phonon is dissipated in the form of heat (Singh et al., 2010).

![Graph showing dielectric loss variation with temperature](image2)

**Figure (12):** Variation of the dielectric loss with temperatures for 20 wt. % Al
Dielectric constant $\varepsilon'$ of specimens at various temperatures is similar to the behavior of dielectric loss. It display an increasing tendency in dielectric constant on increasing the temperature, this behave is explained from the occurrence of two process of attitudes, which would yield effects on dielectric constant of the specimens by varying the temperature. One of them, increasing temperature which would cause improves the segmental mobility of the polymer and simplifies the orientation of dipoles such that, the dipole molecules cannot orient themselves in the lower temperature region. However, owing to thermal expansion, the ration of the number of molecules to effective length of dielectric decreases when the temperature increases, and as the temperature increases, the orientation of dipoles is facilitated then, consequently, increase dielectric constant this process is represent the dominant process in the present case. On the other hand, the clear thermal amplification of the Al filler and polymer that can disrupt the clusters of Al filler, which causes decrease in the dielectric constant, whereas the thermal expansion coefficient of the polymer PMMA is greater than that of the Al metal (Yadav et al., 2010); (Singh et al., 2010).

The variations of AC- conductivity ($\sigma_{AC}$) for chosen samples (pure PMMA and 20 wt. % Al) as a function of the reciprocal of the absolute temperature at different frequencies were shown in figures (13 and 14). It is clearly seen that the nature of variation in temperature altered the nature of the conductivity curve as a function of temperature particularly at higher temperatures. A weak dependence of conductivity in low temperature region shows a short range of hopping of defects but, when increased temperature the conductivity is increased, this behavior can be explained by indicating that the electronic charge must hop between the metal particles. In other words, the increase in temperature provides an increase in free volume and partial mobility. These entities then allow charging charges from one location to another, thus increasing conductivity (Singh et al., 2010); (Prasad and Basu, 2013).

![Figure (13): Variation of Ln ($\sigma_{AC}$) versus 1000/T for pure PMMA composites at different frequency](image-url)
Figure (14): Variation of \( \ln(\sigma_{AC}) \) versus \( 1000/T \) for 20 wt. % Al sample at different frequencies.

The values of activation energy \( (E_a) \) which represent the minimum amount of thermal energy that is required to activate ions, atoms, and molecules to conduction, in which they can undergo physical transport were evaluated from the slopes of the approximated straight lines obtained from the figure and by using of the Arrhenius equation:

\[
\sigma = \sigma_0 \exp \left[ -\frac{E_a}{k_B T} \right],
\]

where \( \sigma \) is the electrical conductivity, \( \sigma_0 \) pre-exponential factor for the material conductivity, \( T \) is the temperature in Kelvin, \( k_B \) is the Boltzmann constant, and \( E_a \) is the activation energy in eV.

The \( E_a \) values at different frequencies were determined for chosen sample (neat PMMA and 20 wt. % Al) and inserted in tables (1 and 2). It was found that the \( E_a \) decreases with increasing the applied frequency. The decrease in \( E_a \) reflects higher electron mobility and enhancement in electrical conduction in the thin composite films membranes (Ahmad et al., 1991).

Table (1): The activation energy for pure PMMA

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Activation Energy ( E_a \times 10^{-2} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>12.76</td>
</tr>
<tr>
<td>400</td>
<td>9.72</td>
</tr>
<tr>
<td>600</td>
<td>9.23</td>
</tr>
<tr>
<td>800</td>
<td>8.31</td>
</tr>
</tbody>
</table>
Table (2): The activation energy for pure PMMA

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Activation Energy $E_a \times 10^2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>6.90</td>
</tr>
<tr>
<td>400</td>
<td>4.36</td>
</tr>
<tr>
<td>600</td>
<td>4.57</td>
</tr>
<tr>
<td>800</td>
<td>4.90</td>
</tr>
</tbody>
</table>

The $E_a$ values of all samples at specific frequency ($f = 600$ kHz) were also determined and inserted in table (3), it was found that The activation energy decreases with the aluminum filler in the polymer matrix, which means that composites have better electrical conduction. The observed behavior opposes the AC-conductivity ($\sigma_{AC}$) behavior of the samples (neglecting the frequency). The highest AC-conductivity ($\sigma_{AC}$) value and the lowest $E_a$ was observed at 20 wt. % Al /PMMA composite (which have the largest Al concentration), where the lowest AC-conductivity ($\sigma_{AC}$) value and the highest $E_a$ was that of the pure PMMA sample.

Table (3): The activation energy values for all samples at ($f = 600$ kHz)

<table>
<thead>
<tr>
<th>Composites</th>
<th>Activation Energy $E_a \times 10^2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>9.23</td>
</tr>
<tr>
<td>2 wt.% Al</td>
<td>8.01</td>
</tr>
<tr>
<td>4 wt.% Al</td>
<td>7.78</td>
</tr>
<tr>
<td>6 wt.% Al</td>
<td>7.32</td>
</tr>
<tr>
<td>8 wt.% Al</td>
<td>6.90</td>
</tr>
<tr>
<td>10 wt.% Al</td>
<td>5.08</td>
</tr>
<tr>
<td>15 wt.% Al</td>
<td>4.78</td>
</tr>
<tr>
<td>20 wt.% Al</td>
<td>4.57</td>
</tr>
</tbody>
</table>

3.4 AC-Conductivity Model

It is known that an AC-conductivity ($\sigma_{AC}$) of a wide range of materials dependence on frequency that clarify by relation which called power low and takes the following form:

$$\sigma_{AC}(f) = \sigma_{DC} + A f^n$$  (9)

where A and n are coefficients, $f$ is the frequency of the applied field (Hz), $\sigma_{DC}$ is the DC conductivity.
conductivity of the material and $\sigma_{AC}$ is the AC-conductivity of the material in $(\Omega \cdot m)^{-1}$ which is usually identified with the dc conductivity of the material. At higher frequencies, the conductivity increases as a power of the frequency, in this case $A$ and $n$ are temperature dependents. Therefore the above equation can be simplified to the form:

$$\sigma_{AC}(f) \approx Af^n$$  \hspace{1cm} (10)

From this equation and figure (15) we can estimate the coefficients $A$ and $n$ for 20 wt. % Al sample at different temperatures and tabulated in table (4). It was found that the power exponent ($n$) taking values near one and decreases linearly with increasing temperature (Atta, 2003; Singh et al., 2010).

![Figure (15): Variation of log($\sigma_{AC}$) versus log(frequency) for 20 wt. % sample](image)

**Table (4):** Estimated A and n coefficients for 20 wt. % Al/PMMA

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$A \times 10^{-3}$ $(\Omega \cdot m)^{-1}$ (Hz)$^{-n}$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>11.09</td>
<td>0.963</td>
</tr>
<tr>
<td>40</td>
<td>11.29</td>
<td>0.948</td>
</tr>
<tr>
<td>50</td>
<td>11.49</td>
<td>0.942</td>
</tr>
<tr>
<td>60</td>
<td>11.58</td>
<td>0.940</td>
</tr>
<tr>
<td>70</td>
<td>11.66</td>
<td>0.937</td>
</tr>
<tr>
<td>80</td>
<td>11.78</td>
<td>0.933</td>
</tr>
<tr>
<td>90</td>
<td>11.92</td>
<td>0.93</td>
</tr>
</tbody>
</table>

4. Conclusions

In the present study, the AC electrical properties of The Polymer Poly (methylmethacrylate) (PMMA) composites with different aluminum (Al) particle
concentrations were investigated as a function of applied field frequency, temperature and different Al particle concentrations. The AC quantities as dielectric constant, AC conductivity, and activation energy, were determined from analysis of impedance data. It was found that the dielectric constant and conductivity increase with applied frequency, temperature and different Al concentrations. The charge transfer in the Al/PMMA composite is enhanced by increasing the amorphous phase when temperature composite become higher. Some reported empirical equations were used to fit the measured AC quantities of the prepared composite.

5. References


Ayesh, A. S. (2010), Electrical and optical characterization of PMMA doped with Y 0.0025 Si 0.025 Ba 0.9725 (Ti (0.9) Sn 0.1) O 3 ceramic. Chinese Journal of Polymer Science, 28, 537-546.


