Study the effect of kaolin on the electrical properties of polyvinyl acetate-polyol composite

Thamir Salman Bachari

Polymer Research Centre-Material Science Department-Basrah University

Abstract

Polyvinyl acetate and polyol (PVA-Polyol) has been blended in percentage by weight 3:1 and a mixture has been done by mixing different percentages by weight of kaolin for electrical measurements. Diagnosis of kaolin was measured by FTIR spectrophotometer. Quality factor (Q), dissipation factor (D), parallel resistance (R\(_{p}\)), series resistance (R\(_{s}\)), impedance (Z), series capacitance (C\(_{s}\)) and parallel capacitance (C\(_{p}\)) and Phase angle (\(\Phi\)) were measured. The maximum electrical conductivity is found 6794 S.m\(^{-1}\) for samples 1, 3wt% kaolin and the minimum electrical conductivity is 1x10\(^{-5}\) S.m\(^{-1}\) for sample (2) 5wt% kaolin. Dielectric constants (\(\epsilon\)), dielectric loss (\(\epsilon'\)), have been studied and calculated. The frequency dependent ac conductivity (\(\sigma_{\text{ac}}\)) and frequency independent dc conductivity (\(\sigma_{\text{dc}}\)) has studied and investigated. The calculated minimum and maximum ac conductivity (\(\sigma_{\text{ac}}\)) is 3.2x10\(^{-5}\) S.m\(^{-1}\) for samples (3) 6wt % kaolin and 0.45 S.m\(^{-1}\) for sample (2) 5wt % kaolin. The minimum and maximum calculated independent frequency dc conductivity (\(\sigma_{\text{dc}}\)) is -
0.3472 S.m\(^{-1}\) for sample (2) 5wt % kaolin and 1.1671 S.m\(^{-1}\) for sample (1) 3wt % kaolin.

**Keywords:** Composites; FTIR spectroscopy; electrical properties; conductivity.

**Introduction**

Polyvinyl acetate (PVA) is one of the most important commercial polymers, and has many advantages, such as safe operation, low coat and room temperature cure. Therefore, it is suitable for population in birch process. It has other applications such as adhesives, membrane, paper and many other applications (1). PVA is a synthetic resin polymer and due to its non-polar nature, is insoluble in water, oil, fats or gasoline. On the other hand, it is soluble in alcohols, ketones and esters. Kaolinite is one of the abundant aluminosilicate minerals, occurring primarily as clay sized particles with high surface-area to volume ratios. Hence kaolinite weathering may play an important role in controlling the chemical characteristics such as degree of crystalline, concentration of impurities and particles size distribution. The dispersion of the particles differs with particle size as the content is the same. The average inter-particle distance reduces with decrease of particle size afford more connected with the composites (2). Attempts of spectroscopic characterization are still in criterion of study. Clay is widely utilized for different industrial applications and as such any of occurrences is worth proper chemical, mineralogical and technological investigations (3). It is well known that composites can be produced exhibiting enhanced properties that the constituent material may not exhibit. For instance, from the combination of different fibres or fillers with polymer matrices one can produce polymer-matrix composites, a material important to the electronic industry for its dielectric properties in use of capacitors. One of the most attractive features of these filled composites is that their dielectric properties can be widely changed by choice of shape, size, and the conductivity of filled constituents in the polymer matrix. The electrical response of a normal dielectric can be described by its conductance, dielectric constant and loss factor (4). The electric measurements of composites with reinforced fiber were considered the effect of frequency, fiber content and fiber length. The dielectric constant increased steadily with increasing fiber content for all frequencies in the range of 1 to 10\(^7\) Hz. Authors also noted that the dielectric constant was decreased with increase of fiber length and frequency. The composite with 1mm fibers and 30% fiber content had the highest value of dielectric constant (5). Conducting polymeric materials possess great design flexibility together with a number of characteristics that are desirable for a number of specific applications in the
field of catalyst, conversion and storage of energy, chemical and biochemical sensing, microelectronics and optoelectronics. However, experiments have also indicated some general limitations of these materials with respect to the fabrication of devices. Several methods have been proposed to prepare polymer composites, such as sol-gel reaction, interactive polymerization and polymerization via melt processing, depend upon the nature of nanoparticles and types of polymeric matrix. The final properties of these composites depend upon various parameters like size of particles, method of preparation of composites and dispersion of particles into the polymeric matrix (6). The design of polymer composites requires materials that can improve their electrical performance. Polymer filled with non-sized conductive filler can make functional polymer composites. In addition, the attached functional groups may enhance the interfacial interaction between the polymer matrix and the filler (6).

**Experimental work**

**FT-IR test**

10 mg of Kaolin was Grinded by ceramic mortar to a fine powder with Kbr, this undergoes FT-IR test by JASCO FTIR 4200 spectrophotometer, Japan. The spectra were indicated at the wave number 400-4000 cm\(^{-1}\) as shown in Figure (1). The infrared spectra of kaolin minerals consist of a sheet of corner-sharing tetrahedral, sharing a plane of oxygen and hydroxyls (inner hydroxyls) with a sheet octahedral with every third site vacant (dioctahedral) (8). A typical spectrum of kaolin at 3437.49 cm\(^{-1}\), this is a characteristics band H-O-H stretching absorbed water. The band observed at around 3437.49 cm\(^{-1}\) with band 1650.77 cm\(^{-1}\) could be assigned to the OH vibrationally mode of the hydroxyl molecule, this is observed in almost the natural hydrous silicate. The H-O-H bending of water is observed at 1650.77 cm\(^{-1}\). C-H stretching 1434.78 cm\(^{-1}\) region (9). Main functional
groups were Si-O and Al-OH libration at 935 cm\(^{-1}\). Si-O out of plane stretch 1109 cm\(^{-1}\) (10). Si-O stretching could be observed at 1017.03 cm\(^{-1}\). 799.108 cm\(^{-1}\) and 780 cm\(^{-1}\) is due to Si-O-Si inter tetrahedral bridging bonds in SiO\(_2\) and OH. A compression between the obtained results and previous studied as show in Table (1).

Table (1): FTIR spectroscopy of kaolin compared with previous study.

<table>
<thead>
<tr>
<th>Obtained results wavenumber cm(^{-1})</th>
<th>Functional group</th>
<th>Previous study wavenumber cm(^{-1})</th>
<th>Functional group observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3437.49</td>
<td>H-O-H stretching, Absorbed water</td>
<td>3440-3432</td>
<td>H-O-H Stretching Absorbed water</td>
</tr>
<tr>
<td>660.152</td>
<td>Si-O Quartz</td>
<td>693-696</td>
<td>Si-O quartz</td>
</tr>
<tr>
<td>1650.77</td>
<td>H-O-H bending of water</td>
<td>1642-1632</td>
<td>H-O-H bending of water</td>
</tr>
<tr>
<td>1434.78</td>
<td>C-H stretching</td>
<td>1470-1475</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>1017.03</td>
<td>Si-O out of plane stretch</td>
<td>1109</td>
<td>Si-O out of plane stretch</td>
</tr>
<tr>
<td>799.108-780</td>
<td>Si-O quartz</td>
<td>788-799</td>
<td>Si-O quartz</td>
</tr>
<tr>
<td>463.796-433.423</td>
<td>Si-O-Si bending</td>
<td>470-467</td>
<td>Si-O-Si bending</td>
</tr>
<tr>
<td>935</td>
<td>Al-OH libration</td>
<td>915 and 935</td>
<td>Al-OH libration</td>
</tr>
</tbody>
</table>

Figure (2): FT-IR test of Kaolin
Sample preparation

Glass substrates have been put in flask and have been cleaned with distilled water and rinsed with ethanol for five minutes, and washed again with distilled water, the glass substrates have been put in oven for half hour to be dried. The oven switched off to room temperature and the glass substrates have been taken out of the oven to be ready for use. Kaolin (Available in local market) has been grinded by glass mortar and has been sieved for different particles size. Percentages by weight 3:1 of polyvinyl acetate and polyol were blended on the clean glass substrates by using spatula until the blend become homogeneous. Percentages by weight of prepared kaolin have been dropped on the blend for each sample. The mixtures have been prepared to suitable shapes by spatula to obtain significant dimensions bulk samples as shown in Table (2). Two copper wires were connected at each side of the sample and left over night to be dried (11). The samples were undergoing electrical measurements.

Electrical measurements

The current-voltage was measured at 10 volt dc. Figure (2) shows a schematic diagram of the electrical circuit. The samples have been put inside enclosure of wood box with front slide window. The samples dimensions were measured by Vernier Capilar made in China as shown in Table (2). The resistivity and the conductivity have been calculated by the following expressions (1).

\[ \rho = \frac{RA}{\tau} \quad (1) \]
\[ \sigma = \frac{\tau}{RA} \quad (2) \]

Where: \( \rho \) is the electrical resistivity of the samples, \( R \) is the electrical resistance of the sample, \( \tau \) is the thickness of the sample, \( A \) is the effective cross sectional area of the sample this is equal to \( \pi D^2/4 \),
The dielectric measurements have been done by LCR meter; sort FLUKE RCL Meter, Automatic 6303 MP, Germany. The measurements include the quality factor (Q), dissipation factor (D), impedance (Z), parallel resistance (R_p), series resistance (R_s), parallel capacitance (C_p), series resistance (C_s)

\[ \varepsilon = \frac{C_s \, d}{\varepsilon_0 \, A} \quad (3) \]

Where: \( C_s \) the series capacitance, \( \varepsilon_0 \) is the permittivity of free space equal to 8.85x10^{-12} \text{ Farad(meter)}^{-1}. \( d \) is the thickness and \( A \) is the effective cross sectional of the electrode = \( \pi \, d^2 / 4 \).

The loss factor is:

\[ \varepsilon'' = \frac{\varepsilon}{R_p \, C_p \, w} \quad (4) \]

Where \( R_p \) is the parallel resistance

\[ R_p = \frac{1}{D \, C_p \, w}, \quad (5) \]

\( C_p \) is the parallel capacitance and \( w \) is the angular frequency equal to \( 2\pi f \).

\( D \) is the dissipation factor (12).

\[ G_s = \varepsilon \, C_0 \, w \quad (6) \]

\[ C_0 = \varepsilon_0 \, A / d \quad (13) \]

\( \varepsilon_0 \) is the frequency dependent ac conductivity of the sample that arises from the motion of charge carrier through the polymer.

The conductance \( G_s \) is calculated by following expression;
Where is the free space capacitance \( C_0 = 4.863 \times 10^{-4} \text{ pF} \) without dielectric, the permittivity of free space \( \varepsilon_0 \), the cross sectional area of the electrode of free space (A) is \( 3.846 \times 10^{-6} \text{ mm}^2 \) and the thickness (d) is 0.07 mm the separation between the electrode is 5 mm.

\[
\sigma' = \sigma_{dc} + \sigma_{ac}
\]

(7)

Where the ac conductivity \( \sigma_{ac} \)

\[
\sigma_{ac} = \varepsilon' \varepsilon_0 \omega
\]

(8)

\( \sigma_{dc} \) is dc conductivity, this is frequency independent conductivity from (7) is equal to

\[
\sigma_{dc} = \sigma' - \sigma_{ac}
\]

The real part of the conductivity can be calculated \( \sigma' \)

\[
\sigma' = (d/A) G_s
\]

(9)

The calculation of the conductivity is as shown in Table 4. The ideal resistance \( R_s \) and an ideal reactance \( X_s \). The real part and imaginary part:

\[
Z = R_s + jX_s
\]

(10)

At that frequency, the impedance behaves like a series of an ideal resistance and an ideal reactance \( X_s \). If \( X_s \) is negative, the impedance is

\[
X_s = -1/2\pi f C_s
\]

(11)

Where \( f \) is the frequency equal 1 KHz.

### Table (2): Sample preparation

<table>
<thead>
<tr>
<th>No.</th>
<th>Weight of PVA gm.</th>
<th>Weight of polyol gm.</th>
<th>Percentage of added kaolin gm.</th>
<th>Total weight gm.</th>
<th>Thickness of sample mm.</th>
<th>Length of sample mm.</th>
<th>Width of sample mm.</th>
<th>Electrode effective area mm².</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.18</td>
<td>0.06</td>
<td>3%</td>
<td>0.2472</td>
<td>10</td>
<td>22</td>
<td>12.5</td>
<td>7.85X10⁻¹</td>
</tr>
<tr>
<td>2</td>
<td>0.18</td>
<td>0.06</td>
<td>5%</td>
<td>0.252</td>
<td>11</td>
<td>21.5</td>
<td>12.4</td>
<td>1.96X10⁻¹</td>
</tr>
<tr>
<td>3</td>
<td>0.18</td>
<td>0.06</td>
<td>6%</td>
<td>0.2544</td>
<td>10</td>
<td>22</td>
<td>12.5</td>
<td>7.85X10⁻¹</td>
</tr>
<tr>
<td>4</td>
<td>0.18</td>
<td>0.06</td>
<td>8%</td>
<td>0.2592</td>
<td>8</td>
<td>21.4</td>
<td>13</td>
<td>7.06X10⁻²</td>
</tr>
<tr>
<td>5</td>
<td>0.18</td>
<td>0.06</td>
<td>10%</td>
<td>0.264</td>
<td>15</td>
<td>19</td>
<td>11.2</td>
<td>3.84X10⁻¹</td>
</tr>
</tbody>
</table>
Figure (3): I-V characteristics of PVa-Polyol with 3wt% kaolin.

Figure (4): I-V characteristics of PVa-Polyol with 5 wt% kaolin

Figure (5): I-V Characteristics of PVa-Polyol with 6wt% kaolin.

Figure (6): I-V characteristics of PVa-Polyol with 8wt% kaolin.

Figure (7): I-V characteristics of PVa-polyol with 10wt% kaolin.
Table (3): The dielectric and electrical properties of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q As</th>
<th>Cp F</th>
<th>CsP F</th>
<th>Rp MΩ</th>
<th>Rs MΩ</th>
<th>Z MΩ</th>
<th>Dissipation factor</th>
<th>Φ deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.57</td>
<td>3</td>
<td>2</td>
<td>8</td>
<td>8</td>
<td>55</td>
<td>0.11</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>0.73</td>
<td>65</td>
<td>10^2</td>
<td>2</td>
<td>1.3</td>
<td>1</td>
<td>13.6</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>8.03</td>
<td>2.9</td>
<td>2.9</td>
<td>318*</td>
<td>6.7</td>
<td>54</td>
<td>0.145</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>2.35</td>
<td>4</td>
<td>3</td>
<td>135</td>
<td>13.8</td>
<td>51</td>
<td>0.366</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>0.81</td>
<td>2.9</td>
<td>2.8</td>
<td>2</td>
<td>7.5</td>
<td>55</td>
<td>0.137</td>
<td>82</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Φ</th>
<th>ε′</th>
<th>Gs S</th>
<th>σ_ac Sm⁻¹</th>
<th>σ′ Sm⁻¹</th>
<th>σdc Sm⁻¹</th>
<th>σ** Sm⁻¹</th>
<th>Xs Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3x10³</td>
<td>3.3x10⁴</td>
<td>5x10⁻⁴</td>
<td>1.8x10⁻¹</td>
<td>1.1672</td>
<td>1.1671</td>
<td>3522.4</td>
<td>-7.6x10⁻⁷</td>
</tr>
<tr>
<td>2</td>
<td>6x10⁷</td>
<td>8.1x10⁹</td>
<td>1.8x10⁻⁶</td>
<td>4.5x10⁻¹</td>
<td>0.1028</td>
<td>-0.3472</td>
<td>1.044</td>
<td>-1.5x10⁸</td>
</tr>
<tr>
<td>3</td>
<td>4x10³</td>
<td>5.8x10⁸</td>
<td>1.2x10⁻⁸</td>
<td>3.2x10⁻⁵</td>
<td>1.5x10⁻⁴</td>
<td>1.5x10⁻⁴</td>
<td>27.229</td>
<td>-5.4x10⁷</td>
</tr>
<tr>
<td>4</td>
<td>3.8x10⁴</td>
<td>1.4x10⁵</td>
<td>6.2x10⁻⁵</td>
<td>7.7x10⁻⁴</td>
<td>0.0122</td>
<td>0.0121</td>
<td>20.58</td>
<td>-5.3x10⁷</td>
</tr>
<tr>
<td>5</td>
<td>1.2x10⁴</td>
<td>1.6x10⁵</td>
<td>3.6x10⁻⁸</td>
<td>3.8x10⁻⁵</td>
<td>1.4x10⁻⁵</td>
<td>0.00136</td>
<td>467.248</td>
<td>-5.6x10⁷</td>
</tr>
</tbody>
</table>

*calculated from \( R_p = \frac{1}{DwC_p} \).

** The average values of electrical conductivity are calculated from Table

Figure (8): Effect of wt% kaolin on the electrical conductivity (σ).

Figure (9): the dependence of conductance on the wt% kaolin.
Results and discussion

FTIR test of kaolin as shown in Figure (1). Table (1) indicates the improvement of chemical composition of kaolin because the functional groups become evident with respect to the wave numbers. Investigates OH vibrations whose transitions band appears at different frequencies depending on the cations directly linked to the hydroxyls. These are permit the determination of cation distribution around hydroxyls and thus allows assessing short-range cation ordering. The structure of kaolin mineral consist of tetrahedral sharing a plane of oxygen and hydroxyls (inner hydroxyl), with a sheet of edge-sharing octahedral and every third site vacant(dioctahedral)(8). I-V curve measurements by using the electric circuit in Figure (1) and the calculated resistivity and electrical conductivity of the samples. These are depending on the variations of current as a function of time (16). According to these variations the conductivity is varied for several orders of magnitude (17). The sizes of particles of small aspect ratio of kaolin have great effect on the conductivity (18). For example, sample
1 at 3%wt kaolin the variation is nearly the same there is no change in orders of magnitude as shown in Figure (3). For sample (3), 6wt% kaolin the conductivity raised by three orders of magnitude and sample (4), 8wt% kaolin the change is five orders of magnitude. The I-V curve measurements of PVA-polyol for 3wt% kaolin is shown in Figure (3) the variation of current with voltage is rather unstable in time interval 2760 seconds, because the straight line either to obey Ohm law (16). In Figure (4) the percentage is 5w% kaolin there is a reverse bias in voltage this makes the current in same direction in time interval 3300 seconds. At PVA-polyol with 6wt% kaolin as shown in Figure (5), the direction is also unstable as in Figure (3) and the measurement is done in time interval 2280 seconds. In Figure (6), PVA-polyol with 8wt% kaolin, The I-V curve measurement is rather stable and Ohm law can be applied in time interval 3480 seconds. For 10wt% kaolin the I-V curve measurement as shown in Figure (7) the change in current values to µA rather than in direction, this is let the current flow steep directions in time interval 2040 seconds. The size effect of electrical conductivity originates from the electrical conductivity decrease as the film thickness increased at constant wire diameter. The experimental values indicate that bulk electrical conductivity reduces along with increasing grain size. The calculated maximum electrical conductivity is found (6794, 2.287, 131.89, 263.52 and 1284.4) Sm⁻¹. In Figure (8) shows the effect of wt(3, 5, 6, 8 and 10)% kaolin of the bulk samples on the average electrical conductivity (σ), there is decreased in the electrical conductivity with increasing at wt5% kaolin and the electrical conductivity is increased again at wt10% kaolin. In Table (3), the dielectric behavior of polymer determined by the charge distribution and also by statistical motion of its polar group. The dielectric measurements were done in frequency 1 KHz. The effect of kaolin content on the dielectric constant (ε) (is the ability of a material to store an electric charge) and dielectric loss (ε') of PVA-Polyol as composite films there is increased at 5wt% kaolin to the value 6x10⁵ in sample (2) and 3wt% kaolin to the value 3x10⁴ as in sample (1), these are for (ε). For (ε') there is increased at 5wt% kaolin to the value 8.1x10⁶ sample (2) and 3wt% kaolin to the value 3.3x10¹⁰ for sample (1). These are due to the weak magnetization at low percentage by weight of kaolin (19). The investigations of the dielectric properties of the composite films are depend on the percentages by weight of kaolin. The dissipation factor (D) (is the degree of the dielectric loss) is increase slightly with increasing percentages by weight of kaolin accept at 5wt% kaolin there is increased to 13.6. The dc conductivity is frequency independent has been calculated different percentages by weight of kaolin in Table (3). The samples were exhibited variation of dc conductivity range using formula (7) and (8). Figure (9) shows the dependence of the conductance on the applied wt% kaolin there is increased in the conductance 5x10⁻⁴ S at wt3% kaolin sample (1) and the conductance is decreased to
1.2x10⁻⁸ S at 6 wt% kaolin. Figure (10) shows the effect of (3, 5, 6, 8 and 10) wt% kaolin of the bulk samples on the frequency dependant ac conductivity (σ_ac), is increased the ac conductivity with increase 5wt% kaolin to 0.45 S.m⁻¹ at sample (2), and is decreased at wt6% kaolin sample (3) to 3.2x10⁻⁵ Sm⁻¹, 8 wt % kaolin to the value 7.7x10⁻⁴ S.m⁻¹ in sample (4) and 10 wt % kaolin to the value 3.8x10⁻⁵ S.m⁻¹ in sample (5). Figure (11) shows the effect of wt (3, 5, 6, 8 and 10) wt% kaolin on the frequency independent (σ_dc), that is increased first at 3 wt % kaolin to the value 1.1671 S.m⁻¹ sample (1) and is decreased at 5wt% kaolin to -0.347 S.m⁻¹ in sample (2), at weight of kaolin at sample (2) and is decreased at sample (3) and sample (5) 6- The dielectric constant (ε) is increased at 5wt% of kaolin and 10wt% of kaolin.7- The dc conductivity (σ_dc) decrease with increasing the percentages by weight of kaolin accept at sample (1) is increased to 1.167 S.m⁻¹. 8- The ac conductivity (σ_ac) depends on the calculated loss factor increase at a certain percentage by weight of kaolin. This is 5 wt % of kaolin to 0.45 S.m⁻¹. 9-The minimum calculated conductance is at 6 wt% kaolin 1.2x10⁻⁸ S and maximum at 3wt% kaolin 5x10⁻⁴ S.

Conclusion

1- The electrical characterization and the dielectric properties depend on the functional groups of the kaolin.

2- The electrical characterization and dielectric properties depend on particles size and percentage by weight of kaolin.

3- Frequency dependent (σ_ac) and frequency independent (σ_dc), dielectric constant (ε) and dielectric loss (ε') in PVA-Polyol and kaolin samples composite has been studied at frequency 1 KHz.

4- Kaolin mineral has properties that make it a functional Ingredient in industrial applications such as paper industry, paint, rubber and plastics.

5- The dielectric Loss is increased with increasing the percentages by

6 wt % kaolin to 1.5x10⁻³ S.m⁻¹, at 8wt% kaolin to 0.0121 Sm⁻¹ in sample (4) and is decreased at wt10% kaolin to 0.00139 S.m⁻¹ in sample (5). The frequency dependent conductivity (σ_ac) representation is a most prominent representation to relate the macroscopic measurements to the microscopic movement of the ions (20). Ac conductivity has been calculated from expression (7), at constant frequency 1 KHz as shown in Table 3. Figure (13) shows the variation on impedance in ohm vis the calculated reactance X in ohm.
References


