Influence of Water Absorption on Volume Resistivity and the Dielectric Properties of Neat Epoxy Material

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Anwar Ali Sulaimani

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The thesis of Anwar Ali Sulaimani is approved by the examination committee

Committee Chairperson: Gilles Lubineau / Matthieu Mulle
Committee Member: Marco Alfano
Committee Member: Sigurdur Thoroddsen
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Epoxy resins are widely used materials in the industry as electrical insulators, adhesives and in aircraft structural components because of their high mechanical stiffness, strength and high temperature and chemical resistance properties. But still, the influence of water uptake due to moisture adsorption is not fully understood as it detrimentally modifies the electrical and chemical properties of the material. Here, we investigate the influence of water moisture uptake on the neat epoxy material by monitoring the change in the volume resistivity and dielectric properties of epoxy material at three different thickness configurations: 0.250 mm, 0.50 mm and 1 mm thicknesses.

Gravimetric analysis was done to monitor the mass uptake behaviour, Volume Resistivity was measured to monitor the change in conductivity of the material, and the dielectric properties were mapped to characterise the type of water mechanism available within the material during two ageing processes of sorption and desorption.

Two-stage behaviours of diffusion and reaction have been identified by the mass uptake analysis. Moreover, the plot of volume resistivity versus mass uptake has indicated a non-uniform relationship between the two quantities. However, the analysis of the dielectric spectrum at medium range of frequency and time has showed a change
in the dipolar activities and also showed the extent to which the water molecules can be segregated between bonding to the resin or existing as free water.
ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

\( E \) Electric Field
\( D \) Electrical Flux Density
\( \sigma \) Electrical Conductivity
\( \rho_V \) Volume Resisitivity
\( \varepsilon_r \) Relative Permittivity
\( \varepsilon' \) Dielectric Constant
\( \varepsilon'' \) Dielectric Loss Factor
\( D \) Dissipation Factor
\( \delta \) Phase Angle
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Chapter 1

Introduction

1.1 Thermosets, Applications and Problem

Thermoset is defined as the petrochemical material that is made by mixing Resin with Hardener and irreversibly cures, by adding heat generally above 150 °C. The resins may be reacted with themselves or with poly functional hardeners like: amines, acid anhydrides, phenols, alcohols, etc. to form thermosetting polymer that has strong mechanical properties as well as high temperature and chemical resistance properties. Because of their explicit properties in addition to the ease in processing, epoxy resins are used in a wide range of applications in industry including: metal coatings, electronic components, electrical insulators, structural adhesives and aircraft frame structural components.

However, unavoidable water ingress can creates serious degradation to the mechanical properties of thermosets and can modify their structural performance. It was reported that water uptake could decrease the glass transition temperature , reduce the maximum operating temperature, and decrease the fracture toughness of different epoxy systems [3][4][5].

Therefore, understanding of the behavior of water absorption in epoxy material and its consequential modifications to material structure is an essential step to predict micro-mechanical damage that could happen under the same ageing conditions.
1.2 Behavior of Water Absorption in Epoxy Material

In the last decades, many studies were conducted to understand the kinetics of water absorption into the bulk of neat epoxy and epoxy composite materials [6][7][8][9][10]. Most of them have monitored the mass uptake that accounts for the overall amount of water molecules absorbed by the material using gravimetric analysis. The results have shown a common gravimetric curve behaviour for water absorption represented by three-stage process as shown in Fig 1: (a) A sharp linear increase at the beginning of the curve represents water sorption through the bulk of the material and follows the first part of the pseudo-Fickian behavior explained by Grave and McEwan [1]. (b) A subsequent linear increase of sorption but in a slower rate deviated from Fickian model without stabilisation of the mass uptake for the considered time window, and (c) A sudden decrease in the water content happens due to desorption or if wet sample is lifted to dry for a period of time more than the sorption period.

Many studies have proposed distinctive explanations for the behavior shown in Fig.1 using several identification methods and technologies, while others provide models that can produce such behavior. [6][7][8][9][10][11][12]

There are two groups of explanations and models. The first group has attributed the deviation from classical Fickian behavior to the variation in the diffusion rate and water concentration represented by the diffusion parameter. Bhattacharyya et al.[6] and Wong et al.[7] provided a model for diffusion parameter that is changing at different levels of relative humidity. Weitsman et al.[8] also proposed a model for two kinds of sorption behavior based on the viscoelasticity properties of the material. However, this group of explanation was quite good in imitating the sorption process but failed to match the experimental findings related to the desorption process.

A second group of explanations came out with a new rationalisation for the devia-
Figure 1.1: Gravimetric curve of water uptake on epoxy during sorption and desorption from Grave et al. [1]

tion from classical behavior of the Fickian model based on partitioning of water uptake into two types: “bonded” and “free” water. Adamson et al. [9] evaluated thermal expansion and swelling on epoxy resin and graphite/epoxy composites. He determined that some water molecules interacted by forming hydrogen bonds with hydrophilic groups in epoxy resin while others are retained in free volume of the material. Apicella et al. [10] investigated water absorption in glassy epoxy resin and proposed that the transport of moisture below transition temperature is a three stage process: (i) diffusion of water through the bulk of the polymer network, (ii) absorption of moisture on the surface voids, and (iii) hydrogen bond formation between hydrophilic groups associated with hydroxyl or amine groups attached to the polymer chain and the water molecules. Zhou and Lucas [11] studied the nature of sorbed water and the related hygrothermal effects in three epoxy systems using solid state nuclear magnetic resonance (NMR). He found that two types of bound water were identified:
desorption rate of absorbed moisture was rapid. However, the desorption rate slowed with time. Also, it can be seen that the moisture desorption becomes quickly as the temperature increases. Most of absorbed moisture can be easily removed from the material studied, and there are small residual moisture content (0.12%) in the studied epoxy resin system when the desorption temperature was not high enough. Moreover, the desorption dynamic experiment at relative low exposure temperature, show that the residual moisture content can be removed regardless of the time that the specimens were soaked in thermal conditions. However, when temperature was 155°C, especially 175°C, the amount of residual moisture can be continually removed with time. The moisture content becomes more and more small and final to almost zero. The existence of residual moisture in the epoxy resin system was also reported by Ciriscioli [15], Moy [16] and Marsh [17]. But, they didn’t give further interpretation for this phenomenon. In this Letter, the experimental results reveals that desorption from high moisture saturation tended to leave small residual moisture content, which could only be removed by heating at relative high temperature. The further interpretation of this phenomenon will discussed below from the activation of bound waters by experiments and molecular dynamic simulations.

After the NPT and NVE MD simulations, many useful results can be obtained from the atom trajectory files. In this study, the mean-square displacements (MSD) of water molecules are concerned. Fig. 3 shows the MSD plots of water molecules at 65, 85, 125, 155, 175 and 195°C cases, respectively. They follow a general trend observable in glassy polymers [8–11]. It is obvious that the plots of MSD versus time are indeed linear over a period of time of about 1.5 ns. At longer times, however, the plots deviate from linearity due to the increasing statistical error involved in the calculations of MSD.

Figure 1.2: Imaginary cell structure for epoxy material (White and Gary) with bonded water molecules (red and blue)

(i) Type I bonding corresponds to a water molecule which forms a single hydrogen bond with the epoxy resin network. This water molecule possesses lower activation energy and is easier to remove from the resin. (ii) Type II bonding is as a result of a water molecule forming multiple hydrogen bonds with the resin network. Carter and Kibler [12] have proposed the Langmuir-type model and defined “bonded”water as molecules that create low energy bonds with hydrophilic sites while unbounded water are molecules that transport in the free volume of material.

Although there is a substantial agreement between second group explanations on the concept of partitioning of water, but considerable disagreement is still there on the definition of what is called “bonded water” and also on the number of hydrogen bonds that is created between the water molecules and the hydrophilic groups in epoxy resins. Therefore, other methods of characterisation were needed to investigate the type of water molecules and the type of chemical bonds created between water and
epoxy under certain mass uptake adsorption.

El Yagoubi et al.[2] proposed a fully-coupled diffusion-reaction model that unifies and extends the approaches mentioned above to create a framework that can reproduce both sorption and desorption behavior on samples of various thicknesses. This model describes the 3D distributions of the diffusing water and the reacted species based on assuming two basic mechanisms: Diffusion and Reaction. Both COMSOL and MATLAB genetic algorithm functions were used to estimate the values of the seven parameters used in the model.

1.3 Dielectric Spectroscopy Characterisation

Over the last few years, the interactions of water with the surrounding polymer have been carefully studied using a diverse range of spectroscopic techniques. The dielectric relaxation spectroscopy method (DRS), that also known as electrochemical impedance spectroscopy (EIS), is an experimental method for characterising electrochemical systems by measuring the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. This technique measures the permittivity of a system over a very wide range of frequencies and the frequency response of the system including the energy loss and dissipation factor. The technique is sensitive to orientation motions of permanent dipoles fixed within the material and the translational contribution of ions through the bulk material and within inclusions due to the applied electric field.

Several studies have utilized the dielectric spectroscopy as an analysis tool for identifying the state of water available within the epoxy resin or for investigating certain effects on the structure of the epoxy. The influence of moisture on the dielectric relaxation behaviour of an imidazole cured epoxy system was reported by Maxwell and
The results suggest that water exists both as hydrogen bounded phase dispersed throughout the resin matrix and as a free phase, which is absorbed within the micro-voids of epoxy matrix. Dielectric analysis done by Pethrick and Hollins on the effect of curing temperature on water absorption of tris-epoxy-propoxy-phenyl methane over frequency range from $10^{-1}$ to $10^9$ Hz revealed that proportion of water molecules bound to chemical functions of resin at low frequency, while another portion of free water molecules clustered in micro-cavities at high frequency. Both types are changed with cure temperature. Grave and McEwan have studied the effect of having three different stoichiometric ratios of epoxy:amine on the water absorption by measuring dielectric permittivity and loss factor at frequency range of $10^{-3}$ to $10^{10}$ Hz. The dielectric analysis shows the existence of bounded water indicated by a peak in loss factor noticed at 10 KHz associated with the relaxation of hydroxyl group in amine hardener. Moreover, a relaxation in dielectric loss factor at $10^9$ Hz was a solid indication that clusters of free water molecules have formed mobile phase within micro voids. Reid and Laurence have studied the dielectric relaxation behaviour of a glass-epoxy composite and could indicate three effects of moisture interaction: For moisture uptake less than 0.1%, they noticed a decrease in dielectric loss and attributed it to the change in resin chemistry. From 0.1% to 1.4%, they associate the decrease in the activation energies and the peak in dielectric loss to the plasticization effect. For higher moisture uptake more than 1.4%, they relate the appearance of a second loss peak to the formation of colloidal, (i.e. weakly adsorbed moisture) and saturation of primary adsorption sites. Boinard et al. has evaluated the dielectric relaxation for an epoxy resin-carbon fibre composite over a frequency range from $10^{-1}$ to $10^9$ Hz as a function of exposure time. He attributed the change in dielectrics at the high frequency region (above 1 MHz) to free water molecules that cluster in the voids. Furthermore, he attributed the large increase of permittivity and loss at low frequency region (from 1 Hz to 1 KHz) to the presence of bonded water that acts on
two ways: produces ionic contribution by diluting mobile charges into adhesive layer and also plasticises epoxy matrix so a depression in dipolar conductivity is observed.

1.4 Objectives and Contribution

This study attempts to investigate the influence of water moisture uptake on the epoxy material by monitoring the change in electrical volume resistivity and the dielectric properties of the epoxy material for three different thickness samples. The aim is to try to characterize the type of water uptake, either a free or bonded water, taking place inside the epoxy material at given percentage of moisture uptake by analyzing measurements of volume resistivity and the spectra of dielectric permittivity over a wide range of frequencies.

This will facilitate better understanding of the behavior of moisture uptake inside the epoxy material. It will help in obtaining a macroscopic constitutive equation for electrical properties of epoxy under moisture ageing to achieve better prediction for the micro-mechanical damage in the future.
Chapter 2

Samples Making

Before the experimental tests can be conducted, the epoxy samples need to be manufactured from the raw materials into their final shape and dimensions that will make them adequate to be tested and measured by the available devices in order to fulfil the purpose of this study. This chapter describes all the details regarding how the epoxy samples were made and what type of procedures were followed to get the required dimensions and quality specimens.

2.1 Epoxy Material

The samples under this study were made from a commercially available epoxy system called EPOLAM 2063 that is supplied by Axson Technology Co. The resin is made from blinding the diglycidyl ether of bisphenol-A (DGEBA) and cycloaliphatic epoxy monomers. The blend resin was mixed with anhydride hardener at the last step with a mass ratio of (100:107).

This epoxy:hardener blinded mixture has a high glass transition temperature of (190 $^\circ$C) and a very low viscosity at 75 $^\circ$C, which allows it to be used in the manufacturing of composites using transfer molding technique or infusion techniques. For more details about the mechanical and chemical properties of EPOLAM 2063, please refer to the specification data sheet included at Appendix-A of this report.
2.2 Sample Mixing Procedure

In order to produce a neat epoxy thermoset sample, the resin alone is heated first for about 15 minutes at 60°C to facilitate good mixing with hardener. Then, heated resin is mixed with the anhydride hardener with a resin to hardener mass ratio of (100:107). After that, the mixture is stirred for 20 minutes at 80 °C to ensure homogeneous blending. Finally, a plastic dropper is used to inject an adequate amount of blinded mixture inside the stainless steel mold that is developed for this purpose and shown in Figures 2.1 and 2.2.

![Figure 2.1: Mold design, two vertical SS plates](image)

2.3 Mold Design and Preparation

The mold shown in Figures 2.1 and 2.2 consists of two 10 mm thick stainless steel plates that are coated internally with release agent and then bolted together including the u-spacer in between. The gaps between plates are carefully sealed from outside
Figure 2.2: Mold Design, U-spacer piece drawing

with a high temperature resistance Teflon tape in order to avoid leaks during curing. The mold is always kept at a vertical position inside the universal chamber during curing process at 180°C using a special support piece. This is to allow the release of air bubbles from the top side of the mold. In addition, it allows the excess amount of epoxy, that we place at the top groove of the mold, to drop down by gravity and fill the voids that are created on the surface of epoxy thin film plate by the release of air bubbles during curing process.

2.4 Curing and Post-Curing Procedure

To ensure full curing for the blinded mixture, it undergoes into two-steps of curing cycles as shown in (Fig 2.3 and 2.4). First, the curing process is done by keeping the mold inside the vacuum chamber at 80°C and 30 in Hg vacuum for 6 hours, and then cool it down to the ambient temperature as per Fig 2.3 below.

After removing the sample from the mold, it post-cured inside the universal oven
The curing cycle suggested by the supplier was modified and optimized to get the highest glass transition temperature. Thus, epoxy preparation is completed following the two-step curing cycle described here. First, the blend is kept at 80°C for 6 hours then cooled down to ambient. After unmoulding plates, they are heated up to 180°C and curing is completed after 8 hours. Finally, they are maintained in a desiccator at room temperature. Fig. 19 and 20 show the schematic graphs of curing and post-curing of epoxy.

**Figure 19: Schematic graph of curing cycle**

Sample dimensions are chosen in order to fit with equipment specifications. Note that for all samples, the ratio length over thickness is high enough so that transfer of water in the resin network is assumed to be only through the thickness. Thus, several samples are cut in the rectangular plates by mean of a diamond saw.

### 6 Description of Experiments

A description of experiments listed in the Table 3 is given here.

**Figure 20: Schematic graph of Post curing cycle**

6.1 Hygrothermal Strain Measurement

Vishay System 7000 (Fig. 21) was used to scan the strain during hygrothermal cycling. This is a high performance data acquisition instrument with measurement accuracy of 0.05% of full scale. The System 7000 Stress Analysis Data System acquires, stores, reduces and displays data from measurements made with electrical-resistance strain gages, strain-gage-based transducers, thermocouples, and high level transducers at rates of up to 2048 samples per second per channel.

**Figure 21: Vishay System 7000 scanner**

Unidirectional strain gauges (Fig. 22) with a grid resistance of 350 Ohms and a gauge factor of 2.065 at 24°C were used to monitor the strain developed in the samples.

**Figure 22: Unidirectional strain gauges**

### 2.5 Samples Dimensions and Numbering

The Struers Secotom-10 saw machine was used to cut all manufactured thin film plates into smaller samples as per the shape and dimensions specified in (Fig 2.5) below.

Samples shapes and dimensions have been decided based on the limitation on the instruments and devices that we are using to take measurements. For example, the
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<td>60 X 60 mm</td>
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<td>0.250 mm</td>
<td>(2x) Two samples were reused at all measuring points</td>
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<td></td>
<td></td>
<td>0.50 mm</td>
<td>(2x) Two samples were reused at all measuring points</td>
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<td></td>
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<td>(2x) Two samples were reused at all measuring points</td>
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<tr>
<td>20 X 10 mm</td>
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<td>0.250 mm</td>
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<td>0.50 mm</td>
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<td></td>
<td></td>
<td>1 mm</td>
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<td>72</td>
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Figure 2.5: Dimension and total number of samples for each test

Figure 2.6: Struers Socotom Saw Machine

device selected for measuring the volume resistivity, Keithley 6571B High Resistance Electrometer, has a test chamber fixture Model 8009 that is equipped with a 55 mm diameter circular electrode. In order to use this test fixture, the epoxy sample must
be large enough such that all the surfaces of the electrodes can make good contact with the epoxy sample. Therefore, the volume resistivity samples were specified to be in a square shape with (60 X 60 mm) size. The same volume resistivity samples were used for taking the gravimetric analysis mass measurements as per (Fig 2.5).

Likewise, the Agilent 4294A Precision Impedance Analyzer device that is used to measure the dielectric properties has a test fixture provided with two small conductive copper poles. A tiny gap between the copper poles allows only a small sample to be fitted in between as shown in (Fig 2.8). Therefore, the dielectric permittivity samples were made in a rectangular shape with (20 X10 mm) size as per the table in (Fig 2.5).

The reason behind having a huge number of samples for permittivity and loss factor dielectric measurements, as shown in (Fig 2.5), is actually due to the fact that the dielectric samples are needed to be double side coated by Silver paste in order to be conductive for the electric field that is applied by the Agilent Impedance Analyzer. In Addition, return the Silver plated samples back to the ageing chamber after taking
Figure 2.8: Agilent 4294A Precision Impedance Analyzer with dielectric test fixture measurement was avoided in order to prevent having two mass uptake ratios on the epoxy sample and on the Silver coating layer. Therefore, it was decided to produce large number of dielectric samples and place them all inside the ageing chamber to take them one by one during each cycle of measurement without retiring them back to the chamber.
Chapter 3

Experimental Campaign

This chapter describes all the details and procedures followed during the experimental campaigns to be able to measure the targeted data shown in Table 3.1 below at different moisture uptake percentage. More details about how the targeted data were measured using different laboratory devices and instruments are included in this chapter.

<table>
<thead>
<tr>
<th>No.</th>
<th>Experimental Test</th>
<th>Reference Name</th>
<th>Target Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gravimetric Analysis</td>
<td>GA</td>
<td>Mass uptake, (M)</td>
</tr>
<tr>
<td>2</td>
<td>Electrical Resistivity</td>
<td>EM</td>
<td>Volume resistivity, (ρ_V)</td>
</tr>
<tr>
<td>3</td>
<td>Dielectric Relaxation Spectroscopy</td>
<td>DRS</td>
<td>Equivalent Capacitor, (C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dielectric Loss Factor, (ε'')</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dielectric Dissipation Factor, (D)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dielectric Constant/Permittivity, (ε')</td>
</tr>
</tbody>
</table>

3.1 Experimental Methodology

During experimental campaign, the manufactured three thicknesses specimens of (0.250 mm, 0.500 mm and 1 mm) were subjected to two ageing processes: First, the Sorption process, which is wetting the samples by keeping them inside the Tenney Climatic Chamber at 50°C and 60% relative humidity for 64 hours; and Second, the
Desorption process, which is drying the samples by keeping them inside the Themo Lindberg Vacuum Chamber at 50 °C under 30 inches Hg of vacuum for another 64 hours.

The measurements were carried out every 8 hours during sorption and desorption processes, and the targeted data that are shown in Table 3.1 were collected for later analysis.

### 3.2 Samples Preparation before Experimental Campaign

Prior to the start of the ageing campaign, all the specimens mentioned in (Fig 2.5) were placed on some Teflon trays and initially dried inside the Themo Lindberg Vacuum Chamber for about 48 hours at 50 °C and 29 in Hg vacuum. This initial drying is to ensure removing all traces of moisture from the samples before the start of the real experiment. The initial values of mass, volume resistivity and dielectric properties including permittivity dielectric constant and loss factor are recorded and tagged as \((S_0)\) which represents the initial dry measurement values for the samples before they are subjected to any water moisture.

### 3.3 Gravimetric Measurements

Gravimetric analysis was conducted every ageing cycle (i.e.: every 8 hours) by taking each sample out of the climatic chamber or vacuum chamber to measure its mass using the OHAUS Balance device that is shown in (Fig 3.2). The mass uptake is then calculated by applying the following formula:

\[
M\% = \left(\frac{W - W_d}{W_d}\right) \times 100\% \tag{3.1}
\]
Where: \( W \) is the weight of epoxy specimen after sorption or desorption, and \( W_d \) is the initial weight of the specimen when it was dry. To ensure the removal of the excessive amount of water that is accumulated on the surface of the sample, all the specimens are wiped by a tissue and allowed to stand free at room temperature for 1 minute before measurement is started.

![Figure 3.1: OHAUS Balance for measuring mass of samples](image)

### 3.4 Volume Resistivity Measurements

Keithley 6517B High Resistance Electrometer (Fig 2.7) was used to measure the volume resistivity in (ohm.cm) on the epoxy samples after each cycle of ageing applying very small DC current of (20 nA) that is produced by the high resistance epoxy insulating materials when subjected to a very small voltage of (400 mVolt) by applying Ohms Law \( R = V/I \).

Volume resistivity is defined as the electrical resistance through a cube of insulating material. When expressed in ohm-centimetres, it would be the electrical resistance through a one-centimetre cube of insulating material. Volume resistivity is measured
by applying voltage potential across the opposite sides of an insulator specimen and by measuring the resultant current throughout the specimen as shown in (Fig 3.2). The Keithley 6517B Electrometer can automatically perform the following formula and displays the volume resistivity directly:

\[
\rho_V = \frac{K_V}{\tau} R \tag{3.2}
\]

Where, \(\rho_V\) is volume resistivity, \(K_V\) is the effective area of the guarded electrode for the particular electrode arrangement employed, \(\tau\) is the average thickness of the sample, and \(R\) is the measured resistance in ohms \((V/I)\). More details about the procedure and setup for measuring the electric volume resistivity are available in Appendix-B.

![Diagram of volume resistivity measurement technique](image)

**Figure 3.2: Volume resistivity measurement technique**
3.5 Dielectric Properties Measurements

The dielectric spectroscopy measurement is the method to measure the materials dielectric properties as a function of frequency. The dielectric spectroscopy is based upon the interaction of the electric dipole moments within the sample and the applied field. It can provide the dielectric properties of the materials, such as relative permittivity, dielectric constant and loss factor. By testing the samples dielectric properties, the information about what happens to polymer’s structure can be provided. Dielectric spectroscopy measurement have been widely carried out by researchers to study the material structure. A schematic diagram for dielectric spectroscopy measurement is shown in (Fig 3.3).

![Schematic diagram for dielectric spectroscopy measurement](image)

Figure 3.3: Schematic diagram for dielectric spectroscopy measurement

Agilent 4294A Precision Impedance Analyzer with 16453A test fixture is used to perform the dielectric spectroscopy measurements as shown in (Fig 3.4). Both the Capacitance in series ($C_s$) and the Dissipation Factor ($D$) values of epoxy samples under moisture uptake were measured over a frequency range from 40 Hz to 110 MHz. The samples were cut into (20 X 10 mm) rectangular pieces with 0.250 mm, 0.50 mm, and 1 mm thicknesses. The applied voltage was set to 500 mVolt and the resulting Dielectric Constant ($\varepsilon'$) and Dielectric Loss Factor ($\varepsilon''$) are then calculated using equation (4.3) and (4.16) in section 4.1 and 4.2 respectively.
3.6 Samples Silver Coating

In order to increase the surface conductance, the (20 X 10 mm) thin film samples allocated for dielectric measurements are coated with Silver Paste before the dielectric properties can be measured. For getting results by Agilent 4294A Impedance Analyzer, both sides of (20 X 10 mm) samples need to be coated by Silver paste.

The CHEMAT KW-4A Spin Coater machine is used to coat the sample films as shown in (Fig 3.5). KW-4A spin coater machine is designed to coat the sample for SEM microscopy, but it can be also used for coating in case of the dielectric properties measurements.

Figure 3.5: CHEMAT KW-4A Spin Coater with a photo of Silver coated sample
Chapter 4

Principle of Dielectric Spectroscopy

4.1 Theory of Dielectric Response

Dielectric properties of the material is basically reflect the electric charge movement inside the material in response to an external electric field $E$. When an external electric field $E$ is applied to the dielectric material as shown in (Fig 4.1a), a current density $J$ inside the material will be induced as:

$$J = \sigma_s E + j\omega\varepsilon_0\varepsilon_r E \quad (4.1)$$

Where $\sigma_s$ is the DC conductivity, $\omega$ is the angular frequency of the applied field, $\varepsilon_0 = 8.8541878176e^{-12}$ F/m is the permittivity of vacuum and $(\varepsilon_r)$ is the complex relative permittivity that consists of two parts: the real part $(\varepsilon')$ which is called the Dielectric Constant, and the imaginary part $(\varepsilon'')$ that is called the Dielectric Loss Factor.

Therefore, the above equation can be rewritten in the following format:

$$J = \sigma_s E + j\omega\varepsilon_0(\varepsilon' - j\varepsilon'')E \quad (4.2)$$
Figure 4.1: (a) parallel plate capacitor formed when AC current applied to the plated thin film sample. (b) An equivalent circuit with Capacitance $C = \varepsilon_r \varepsilon_0 A/d$ and Conductance $G = \sigma A/d$

Considering the fact that the dielectric response of any material is always frequency dependent and the volume resistivity is the reciprocal of the DC conductivity. Thus, the above equation (4.2) can be extended as the following:

$$J = \frac{1}{\rho_V} E + j \omega \varepsilon_0 (\varepsilon'(\omega) - j \varepsilon''(\omega)) E$$ (4.3)

According to the diffusion-reaction model considered in El Yagoubi et al. [2] paper and described by the schematic shown in (Fig 4.2), at any point of mass uptake, the relation between the three species of water uptake (W, R and Y) is given by:

$$W + R \leftrightarrow Y$$ (4.4)

From both equations (4.3) and (4.4), we can conclude that at every point within the domain, the material can be characterised by three materials parameters: $\sigma_s$, $\varepsilon'$ and $\varepsilon''$ which are dependents on the type of water species (W, Y).
Figure 4.2: Three different species in El Yagoubi et al. diffusion-reaction scheme that coexist in the domain based on the height \( z \)

Therefore, equation (4.3) can be rewritten as:

\[
J = \sigma_s(W, Y)E + j\omega \varepsilon_0(\varepsilon'(\omega, W, Y) - j\varepsilon''(\omega, W, Y))E
\]  

(4.5)

Considering the case of measuring the volume resistivity by applying DC current on the specimen, the angular frequency in this case will equal zero (\( \omega = 0 \)).

Accordingly, equation (4.3) in this case will become:

\[
J = \sigma_s(W, Y)E
\]  

(4.6)

Since \( W \) and \( Y \) are dependent on \( z \), then we can write equation (4.6) in the form:

\[
J(z) = \sigma_s(W(z), Y(z))E(z)
\]  

(4.7)

In order to define an equivalent homogenous continuum to our original heterogeneous epoxy material, we can consider that the flux density \( J(z) \) is constant among the material since it will not change during the application of the DC current.

By applying Reuss’s homogenisation approach, the macroscopic flux density can
be considered equal to the microscopic flux density and microscopic electric field can be written as:

$$J(z) = J_M$$  \hspace{1cm} (4.8)

$$E(z) = \frac{1}{\sigma_s(W(z), Y(z))} J_M$$  \hspace{1cm} (4.9)

By defining a macroscopic electric field $E_M$ equal to the average over all microscopic fields, we can get the following equation:

$$E_M = \langle E(z) \rangle = \frac{1}{H} \int_{-\frac{H}{2}}^{\frac{H}{2}} E(z) \, dz$$  \hspace{1cm} (4.10)

Substituting $E(z)$ from equation (4.9) into equation (4.10) gives:

$$E_M = \frac{1}{H} \int_{-\frac{H}{2}}^{\frac{H}{2}} \frac{1}{\sigma_s(W(z), Y(z))} d\frac{\rho}{dz} J_M$$  \hspace{1cm} (4.11)

by replacing the reciprocal of DC conductivity in equation (4.11) by volume resistivity, we obtain:

$$E_M = \frac{1}{H} \int_{-\frac{H}{2}}^{\frac{H}{2}} \rho_v(W(z), Y(z)) d\frac{\rho}{dz} J_M$$  \hspace{1cm} (4.12)

Since $J_M = \sum_M E_M$, then macroscopic field can also be written as:

$$E_M = \rho_v J_M$$  \hspace{1cm} (4.13)

By comparing equation (4.12) with (4.13), we can get the macroscopic volume resistivity in the following form:

$$\rho_M = \frac{1}{H} \int_{-\frac{H}{2}}^{\frac{H}{2}} \rho_v(W(z), Y(z)) \, dz$$  \hspace{1cm} (4.14)
4.2 Principle of Dielectric Polarization

The investigations about dielectric permittivity are based on the dielectric polarization inside the material when an external electric field is applied to the dielectric materials that contain some charged molecules called dipoles. When an alternating electric field is applied to a dielectric, the dipoles rotate to align themselves with the field. As time passes, the electric field reverses its direction, and the dipoles must rotate again to remain aligned with the correct polarity. As they rotate, energy is lost through the generation of heat (friction) as well as the acceleration and deceleration of the rotational motion of the dipoles. The degree to which the dipoles are out of phase with the incident electric field and the losses that result, determine how large the imaginary part of the permittivity is as a function of material and frequency. The larger the imaginary part, the more energy is being dissipated through motion, and the less energy is available to propagate past the dipoles. Thus, the imaginary part of the relative permittivity directly relates to the loss in the system.

![Unpolarized](image1)

![Polarized by an applied electric field](image2)

Figure 4.3: Polarization effect on material dipoles after applied electric field

The dielectric displacement, which is due to the response of dielectric materials under the external applied electric field, is known as the polarization. The polarization
Under the applied field can be written as:

\[ P = D - D_0 = (\varepsilon'' - 1)\varepsilon_0 E \]  

(4.15)

The direction of polarization changes as the applied field changes. There is a delay between the change of the field and the change of polarization direction. Such phase-lag is known as the phase angle (\(\delta\)). The dielectric loss tangent, which is called Dissipation Factor (D), can be defined as the ratio of energy losses, and given as:

\[ D = \tan\delta = \varepsilon''/\varepsilon' \]  

(4.16)

### 4.3 Indication of Dielectric Parameters

#### 4.3.1 Dielectric Constant

The dielectric constant measurement is one of the most popular methods of evaluating insulators such as rubber, plastics, and powders. It is used to determine the ability of an insulator to store electrical energy. The complex relative permittivity (\(\varepsilon_r\)) consists of a real part (\(\varepsilon'\)), which represents the storage capability and an imaginary part (\(\varepsilon''\)), which represents the loss.

Dielectric constant measurement can be performed easier and faster than chemical or physical analysis techniques which makes it an excellent material analysis tool. The dielectric constant is defined as the ratio of the capacitance of the material to the capacitance of the air.

\[ \varepsilon' = \frac{C_x}{C_0} \]  

(4.17)

Where: \(C_x\) is capacitance with a dielectric material and \(C_0\) is capacitance without material, or vacuum capacitance. The \(\varepsilon'\) value of dry air is 1.00053, which for most
measurement applications is usually close enough to the value of a vacuum, which is 1.0000. Thus if a material is to be used for insulating purposes only, it would be better to have a lower dielectric constant, or as close to air as possible. To the contrary, if a material is to be used in electrical applications for storage of electrical charge, the higher the dielectric constant the better. More charge is stored when a dielectric is present than if no dielectric (air) is present. The dielectric material increases the storage capacity of the plate capacitor, hence the dielectric constant of any solid or liquid would be greater than 1. (Fig 4.4) below is showing the dielectric constant values for some common plastic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Remarks</th>
<th>t/°C</th>
<th>Frequency</th>
<th>ε × r'</th>
<th>104 × tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plastics (miscellaneous)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline resin</td>
<td>unfilled</td>
<td>20</td>
<td>3 GHz</td>
<td>3.5</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>paper filled</td>
<td>20</td>
<td>1 MHz/1 GHz</td>
<td>5/4</td>
<td>600/300</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>20</td>
<td>1 MHz/1 GHz</td>
<td>3.5</td>
<td>300/400</td>
<td></td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>20</td>
<td>50 Hz/100 MHz</td>
<td>3.8/3.2</td>
<td>100/300</td>
<td></td>
</tr>
<tr>
<td>Ebonite</td>
<td>unfilled</td>
<td>20</td>
<td>1 kHz/1 GHz</td>
<td>3/2.7</td>
<td>90/30</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>filled (MgCO₃)</td>
<td>20</td>
<td>50 kHz/1 GHz</td>
<td>4.1/3.8</td>
<td>100/180</td>
</tr>
<tr>
<td>Melamine resin</td>
<td>20</td>
<td>3 GHz</td>
<td>4.7</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>fabric filled</td>
<td>20</td>
<td>1 MHz</td>
<td>5.5</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>paper filled</td>
<td>20</td>
<td>1 MHz/1 GHz</td>
<td>5</td>
<td>300/800</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>1 MHz/10 MHz</td>
<td>6</td>
<td>800/400</td>
<td></td>
</tr>
<tr>
<td>Urea resin</td>
<td>wood filled</td>
<td>20</td>
<td>1 MHz</td>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>paper filled</td>
<td>20</td>
<td>1 MHz</td>
<td>6</td>
<td>300</td>
</tr>
<tr>
<td>Vinyl acetate (poly-)</td>
<td>plasticized</td>
<td>20</td>
<td>1 MHz/10 MHz</td>
<td>4</td>
<td>500</td>
</tr>
<tr>
<td>Vinyl chloride (poly-)</td>
<td>plasticized</td>
<td>20</td>
<td>1 MHz/10 MHz</td>
<td>4</td>
<td>600</td>
</tr>
</tbody>
</table>

Figure 4.4: Values of dielectric constant and loss tangent for common plastic materials (*CRCHandbookofChemistryandPhysics*(1983))

### 4.3.2 Dissipation Factor

Dissipation Factor (D) is defined as the ratio of an insulating materials resistance to its capacitive reactance at a specified frequency. It measures the inefficiency or loss of the material, is always greater than 0, but usually much smaller than the dielectric constant. D measurements are an excellent means of quality control, which can
yield indication of contamination or change happens within the structure. Excessive moisture would increase the dissipation factor value telling us that something has changed as compared to the previously established values.

As mentioned previously, the dielectric loss tangent is also called the Dissipation Factor ($D$) and is defined as the ratio of energy losses, given as:

\[
D = \tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]  
(4.18)

Knowing the phase angle ($\delta$), both dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) can be calculated applying the following formulas:

\[
\varepsilon' = \varepsilon_r \cos(\delta)
\]  
(4.19)

\[
\varepsilon'' = \varepsilon_r \sin(\delta)
\]  
(4.20)

Where $\varepsilon_r$ is the relative permittivity that is given by the following equation:

\[
C = \frac{\varepsilon_r \varepsilon_0 A}{d}
\]  
(4.21)

Where $C$ is the Capacitance, $A$ is the sample surface area, and $d$ is sample thickness.
Chapter 5

Results and Discussion

Several experimental campaigns have been conducted under this study on the three thicknesses configurations: 0.250 mm, 0.500 mm and 1 mm. The mass uptake, volume resistivity and dielectric properties were measured over a redundant number of samples every 8 hours period of time involving sorption and desorption processes. Finally, different types of average curves were plotted against time, mass uptake, and frequency to evaluate the effect of various moisture uptake percentage on the volume resistivity and on the dielectric properties of the epoxy material. In this chapter, all types of curves will be shown including detailed analysis about each curve with an attempt to understand the correlations between different electrical properties and moisture uptake.

5.1 Mass Uptake Analysis

The evolution of the mass uptake ($M\%$ shown in equation 3.1) with respect to time in seconds is plotted for all the three thickness configurations in Figure (5.1) at (60% RH during sorption) and (30 inches of vacuum during desorption). In Figure (5.2a), the mass uptake is plotted versus $\sqrt{t}$ and also versus $\sqrt{t}/2H$ in Figure(5.2b), in order to scale the curves for checking the thickness dependence effect.

The curves in Fig (5.1) confirms the same fact reported by El Yagoubi et al. in
his paper [2] that we have a two-stage behaviour in mass uptake during sorption process (from zero to 230400 seconds): (1) the first linearly increased part (from zero to 0.0082 of mass uptake at 10800 seconds) which represents diffusion of water through the microstructure of the epoxy material, and (2) the second non-linear
largely increased part (from 0.0082 till 0.0138 of mass uptake at 230400 seconds) which represents reaction of water molecules with the hydrophilic groups inside epoxy’s chemical structure.

In Fig (5.2b) we can notice that the sorption curves of the three thickness are superimposed at the first linear portion of $\sqrt{t/2H}$ plot which confirms that the mass uptake is a thickness dependent process during the time of diffusion and it is a non-thickness dependent during the time of reaction as clearly shown in Fig(5.2a). The same results can be concluded when we consider the Desorption process (from 230400 to 432000 seconds) that is shown in Fig(5.3).

![Figure 5.3: Evolution of mass uptake vs. $\sqrt{t}$ and $\sqrt{t/2H}$ at desorption process only](image)

5.2 Volume Resistivity Analysis

After confirming that mass uptake has two-stage behaviour with respect to time, that is varying between diffusion and reaction processes, we have tried under this section to check if these two regimes has a unique or different effect on the electrical properties
of the material represented in volume resistivity. Therefore, the evolution of average volume resistivity with respect to time in seconds is plotted for all the three thickness configurations in Figure (5.4) to see if a special behaviour can be identified.

Figure 5.4: Evolution of average volume resistivity vs. time at sorption/desorption

Fig (5.4) shows that the variation of volume resistivity with respect to time follows two different regimes. At the beginning of sorption process (from zero to 10800 seconds), the resistivity is sharply decreases with time, while the variation is less marked (between 10800 and 230400 seconds). This kind of evolution is quite similar to the one reported by Gonon et al. in his paper [17] about epoxy composites. In addition, we have reflected the evolution of volume resistivity with respect to time during desorption process on the same Fig(5.4) which shows a reversible behaviour to the one in sorption part, i.e. sharp increase at the beginning of desorption (between 230400 and 246600 seconds) and a less increase at the rest period of desorption.

In Figure (5.5), the volume resistivity uptake was calculated using equation (5.1)
and plotted versus the mass uptake in a trial to figure out the type of relationship between volume resistivity and mass uptake during sorption and desorption processes.

\[ \rho V\% = \left( \frac{\rho_V - \rho_0}{\rho_0} \right) \times 100\% \]  \hspace{1cm} (5.1)

Figure 5.5: Evolution of volume resistivity uptake vs. mass uptake at sorption/desorption

Fig (5.5) shows that there is no direct relationship between volume resistivity and mass uptake. The three curves tell us that the relation is a complex relation as it doesn’t depend only on diffusion or reaction regimes. For instance, if we pick up any mass uptake point on one thickness curve, we will get more than one reading for volume resistivity including desorption process. This means that we were unable to return to the same point of volume resistivity even though we reversed the process of sorption to desorption. We can conclude from the above figure that the global mass uptake is not the right quantity to describe volume resistivity as it is clear
that we can get two different values for volume resistivity on the epoxy material although the material has gained the same amount of moisture uptake but by different ways of ageing. The results indicate that there was some change happened in the microstructure of the epoxy material under the effect of different ageing processes leads to the variation in the value of volume resistivity. Therefore, we decided to evaluate the effect of moisture uptake on another electrical property, that is the dielectric permittivity, as it will be explained in the next section of this report.

5.3 Dielectric Properties Analysis

In an attempt to further define the effect of moisture uptake on the dielectric properties of the epoxy material, both Capacitance (C) and Dissipation factor (D) were measured over a range of frequency (from 40 Hz to 110 MHz) on all samples at different levels of moisture uptake using Agilent 4294A Impedance Analyzer. Then, the dielectric properties: relative permittivity \( \varepsilon_r \), dielectric constant \( \varepsilon' \) and loss factor \( \varepsilon'' \) were calculated by applying equations (4.18), (4.19), (4.20) and (4.21).

5.3.1 Frequency-Dependent Dielectric Analysis

Figure (5.6) below represents the dielectric constant and dielectric loss factor data, respectively, for 0.250 mm thick sample as a function of frequency for sorption and desorption processes.

From Figures (5.6) (5.7) and (5.8), we can notice the following observations: First, there are common fluctuations at the beginning of all \( \varepsilon' \) and \( \varepsilon'' \) curves at the low frequency range area (from 100 Hz to 800 Hz). We anticipate the reason of this fluctuation due to the limitation in Agilent 4294A Impedance Analyzer, as it was running at a very low range of frequency that is so close to the devise limitation (i.e: 40 Hz), so a variation in the applied electrical field due to the low range of frequency
Figure 5.6: 0.250 mm thick sample evolution of dielectric constant $\varepsilon'$ and loss factor $\varepsilon''$ vs. log(freq) at both (a) sorption and (b) desorption.

Second, it can be seen that the real part of permittivity ($\varepsilon'$) decreases with the
frequency both for sorption and desorption for all thicknesses of tested samples. This global decrease is observed at all moisture concentrations. However, in all moisture concentrations, the slope of dielectric constant decrease, is higher at higher frequencies than at lower frequencies. This decrease of $\varepsilon'$ at mid-range of frequency (above $10^3$ Hz) was also reported for epoxy nano-composites and other types of polymers in Ilona et al. [18], Boinard et al. [16] and Reid et al. [15] papers. It was mainly attributed to the reduction in polarization caused by less orientation of dipolar groups in polymer. It also indicates the existence of two types of water molecules within the polymer’s microstructure (i.e. bonded and free water). Thus, at low frequency, both free and bonded water dipoles could rotate easily to align themselves with the direction of the electric field and as a result, permittivity-real part decrease will be less. At mid-frequency, as the speed of the oscillating current increases, part of the bounded water dipoles will be unable to rotate quickly to align with the electrical field, so as a result, permittivity-real part decrease will be higher in this case.

Third, the frequency variation of dielectric loss factor ($\varepsilon''$) is flattering and shows close values at different mass uptakes in both sorption and desorption with no evident for the existence of any relaxation peaks, which is different than what was reported by Boinard et al. [16] and Grave et al. [1] in their papers where some peaks appeared above (10 KHz) and they were attributed to the relaxation of the hydroxyl groups in epoxy material. The reasons for having no peaks in our case could be due to the fact that our epoxy system that we are using (i.e: EPOLAM 2063) is made by mixing monomers with anhydride hardener that has less number of hydroxyl groups compared to the amine and amide hardeners that were used in the case of Boinard and Grave studies.
Figure 5.7: 0.50 mm thick sample evolution of dielectric constant $\varepsilon'$ and loss factor $\varepsilon''$ vs. log(freq) at both (a) sorption and (b) desorption.
Figure 5.8: 1 mm thick sample evolution of dielectric constant $\varepsilon'$ and loss factor $\varepsilon''$ vs. log(freq) at both (a) sorption and (b) desorption
5.3.2 Time-Dependent Dielectric Analysis

Several testing campaigns were conducted to identify the revolution of complex relative permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) with respect to time. However, for clarity, results from only the last two tests (Test 5 and Test 6) are shown in the three Figures below, since the data from these last two tests are comparable with each other as the same period between measurements (every 8 hours) was maintained in both of them. The only difference between (Test 5) and (Test 6) is that (Test 6) has more data points at the first 8 hour’s step of sorption and the first 8 hour’s step of desorption also.

The evolution of relative permittivity with respect to time at various levels of mass uptake are plotted for three different frequencies (200 Hz, 1 KHz and 1 MHz in Figures (5.9), (5.10) and (5.11) respectively.

![Figure 5.9: Evolution of relative permittivity $\varepsilon_r$ vs. time at 200 Hz for both (a) Test 5 and (b) Test 6](image)

Although there is a slight difference between the results in Test 5 and Test 6 due to the unavoidable variation in the process followed to manufacture the samples of each style of thickness configuration. However, the general trend of the curves looks the same. From the three figures above, we can notice that the global trend is
an initial rapid increase in relative permittivity at the first stage of diffusion in all thickness configurations, after which the profile decreases slightly till become constant in some cases before the beginning of desorption at 230400 seconds. Then, the trend
is reversed during desorption, as relative permittivity rapidly decreases at the initial stage of desorption and then primarily increases till the end of desorption with an attempt for recovering the original value.

Figure 5.12: Schematic illustrating interpretation of global trend of relative permittivity vs. time

In Fig (5.12), we propose a schematic to illustrate our interpretation for this global trend of relative permittivity versus time based on equation (4.21) that implies direct proportional relationship between relative permittivity ($\varepsilon_r$) and capacitance ($C$). The initial rapid increase in permittivity from point 1 to 2 in Fig(5.12) could be attributed to the diffusion of free water molecules through the micro-voids of epoxy material. This diffusion of free water will rapidly increase the material capacitance and relative permittivity values since the air, which was filling the micro-voids, is replaced by...
water that has higher permittivity value compared to air as per the below table from CRC Handbook of Chemistry and Physics.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Permittivity, $\varepsilon_r$</th>
<th>Material</th>
<th>Relative Permittivity, $\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1</td>
<td>Dry soil</td>
<td>2.5–3.5</td>
</tr>
<tr>
<td>Air (at sea level)</td>
<td>1.0006</td>
<td>Plexiglass</td>
<td>3.4</td>
</tr>
<tr>
<td>Styrofoam</td>
<td>1.03</td>
<td>Glass</td>
<td>4.5–10</td>
</tr>
<tr>
<td>Teflon</td>
<td>2.1</td>
<td>Quartz</td>
<td>3.8–5</td>
</tr>
<tr>
<td>Petroleum oil</td>
<td>2.1</td>
<td>Bakelite</td>
<td>5</td>
</tr>
<tr>
<td>Wood (dry)</td>
<td>1.5–4</td>
<td>Porcelain</td>
<td>5.7</td>
</tr>
<tr>
<td>Paraffin</td>
<td>2.2</td>
<td>Formica</td>
<td>6</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2.25</td>
<td>Miča</td>
<td>5.4–6</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2.6</td>
<td>Ammonia</td>
<td>22</td>
</tr>
<tr>
<td>Paper</td>
<td>2–4</td>
<td>Seawater</td>
<td>72–80</td>
</tr>
<tr>
<td>Rubber</td>
<td>2.2–4.1</td>
<td>Distilled water</td>
<td>81</td>
</tr>
</tbody>
</table>

These are low-frequency values at room temperature (20° C).

Figure 5.13: Values of relative permittivity of common materials

The decrease in relative permittivity from point 2 to 3 in Fig(5.12) can be explained by the tendency of some part of free water to create hydrogen bonds with the hydroxyl groups in epoxy under the continues effect of moisture uptake increase, that will lead to a decrease in the capacitance and relative permittivity values due to the fact that the initial value of permittivity during diffusion has been changed to include the permittivity of bounded water during reaction also.

When desorption process took place (from point 3 to 4 in Fig(5.12)), what happens is that when drying started, the first molecules to depart from the material are the free water molecules since they are having little interactions with their surrounding leading to a rapid decrease in relative permittivity. After this, the only left bounded water molecules will need more time of drying to break their hydrogen bonds and recover back the original values of permittivity which will lead to an increase in relative permittivity till the end of desorption process.
Chapter 6

Conclusion

6.1 Concluding Remarks and future work

The mass uptake analysis has confirmed the result that moisture absorption has two-stage behaviour that can be characterized as: diffusion, which is a thickness dependent process, and reaction, which is a non-thickness dependent process. Further analysis for the relation between volume resistivity and mass uptake has shown that it is a reversible process but also a complex relation that we cannot depend on to quantitatively characterize the type of water content exist within the epoxy material. The frequency domain dielectric analysis has been able to show various dipolar activities at a medium range of frequency, as well as the time domain analysis of relative permittivity which has indicated the existence of two types of water molecules in the epoxy material that undergo two ageing conditions. However, these results could be regarded with more positives if the diffusion-reaction model proposed by El Yagoubi J. [10] is used to identify the correlation between the volume resistivity and the two types of water contents (free water $W$ and bounded water $Y$) which is an investigation that currently under study and hopefully it will form the basis of a future publication.
REFERENCES


APPENDICES
DESCRIPTION
Production of composite structures by RTM process.

PROPERTIES
- Low viscosity
- Long gel time
- Good behaviour in damp environment
- Good mechanical properties

PHYSICAL PROPERTIES

<table>
<thead>
<tr>
<th>Composition</th>
<th>RESIN</th>
<th>HARDENER</th>
<th>MIXED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix ratio by weight</td>
<td>100</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>Mix ratio by volume at 25°C</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Aspect</td>
<td>liquid</td>
<td>liquid</td>
<td>liquid</td>
</tr>
<tr>
<td>Colour</td>
<td>amber</td>
<td>amber</td>
<td>amber</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- at 25°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- at 75°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- at 100°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity at 25°C</td>
<td>1.12</td>
<td>1.20</td>
<td>1.16</td>
</tr>
<tr>
<td>Specific gravity of cured product at 23°C</td>
<td>ISO 1675 : 1985</td>
<td>ISO 2781 : 1996</td>
<td>1.20</td>
</tr>
<tr>
<td>Pot life at 100°C on 70 g (min)</td>
<td>250</td>
<td>50</td>
<td>1.16</td>
</tr>
</tbody>
</table>

MECHANICAL PROPERTIES at 23°C (1)

<table>
<thead>
<tr>
<th></th>
<th>23°C</th>
<th>150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural modulus</td>
<td>ISO 178 :2001</td>
<td>MPa</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>ISO 178 :2001</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>ISO 527 :1993</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>ISO 527 :1993</td>
<td>MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>ISO 527 :1993</td>
<td>%</td>
</tr>
<tr>
<td>Interlaminar shear</td>
<td>ISO 1410 :2003</td>
<td>MPa</td>
</tr>
</tbody>
</table>

PROCESSING CONDITIONS
- Before injection, make sure that mould and reinforcements are moisture free.
- During the injection, the mixing temperature has to be between 45°C and 80°C.
- Make the injection in a mould at a temperature between 60°C and 80°C.
- Before demoulding, dry the parts for 6 hr minimum at 80°C.
- Follow the steaming specifications indicated on the graph below (in case of strains during the steaming cycle, a holding structure is recommended.)

Figure A.1: EPOLAM 2063 Data Sheet
B Appendix B

B.1 Procedure to Measure Volume Resistivity

The Model 6517B can make surface resistivity measurements from 10E3 to 10E17 ohms and volume resistivity measurements from 10E3 to 10E18 ohm-cm. Typical resistivity test fixtures (such as the Keithley Instruments Model 8009) use circular electrodes. In order to use these test fixtures, the insulator sample must be large enough such that all the surfaces of the electrodes make contact with the sample. When using the Model 8009 test fixture, you do not have to make any calculations. For volume resistivity, you only need to know the thickness (in mm.) of the sample. The Model 6517B will automatically perform the calculation and display the reading.

To ensure proper operation, always enable zero check (ZeroCheck displayed) before changing functions (V, I, R, or Q).

The following steps summarize the basic steps to measure resistivity:

- Enable zero check by pressing Z-CHK

- Select and configure the desired resistivity measurement type from the MEAS-TYPE (RESISTIVITY) option of the ohms configuration menu (see Ohms configuration for more information).

- Select the V-source adjustment mode. With AUTO V-source selected, the instrument will automatically select the optimum V-source value (40V or 400V) for the measurement range.

- Connect the sample to be measured to the Model 6517B.
• Select the ohms function by pressing R.

• If the manual V-source adjustment mode is selected, use the cursor and the VOLT-AGE SOURCE adjust keys to set the voltage level. The V-source range can be changed from the RANGE item of the CONFIGURE V-SOURCE menu. Note that you will not be able to adjust the V-source if AUTO V-source is selected.

• Use the manual RANGE keys ( and ) to select the ohms measurement range, or select AUTO range. Note that with AUTO range selected, the instrument will not go the 2T, 20T and 200T ranges.

• Disable zero check by again pressing Z-CHK.

• Press OPER to place the V-source in operate and after an appropriate electrification period (bias time), note the resistivity reading. Typically, an electrification period of 60 seconds is used. A flashing VOLTAGE SOURCE OPERATE LED indicates that the V-source has gone into current limit. The programmed voltage is not being applied to the load. In this situation, try using a lower voltage for the measurement.

• Place the V-source in standby by again pressing OPER and enable zero check.
C Appendix C

C.1 Procedure to Measure Dielectric Properties

This chapter explains how to set up the measurement conditions for the Agilent 4294A Precision Impedance Analyzer, including the measurement signal and sweep.

C.1.1 Selecting Trace (Active Trace)

The Agilent 4294A can display the measurement results of one sweep measurement in two traces (waveforms) on the screen. These traces are called trace A and trace B. The settings using the key operations can be specified for trace A and trace B independently. Before making settings, be sure to check and select the active traces applying the following steps:

- [Format]
- [Display] - DEF TRACE [ ] (except for DATA MEMORY)
- [Display] - OFFSET
- [Display] - more 1/2 - TITLE
- [Scale Ref]
- Keys in the MARKER block

C.1.2 Selecting Sweep Parameter

- Press the [Sweep] key
• Press the PARAMETER [ ] key
• Select the desired sweep parameter
• Select [Frequency] from the list

C.1.3 Selecting Linear, Log, or List Sweep

• Press the [Sweep] key to display the sweep menu.
• Press the TYPE [ ] key to display the sweep type menu.
• Select the sweep type [LOG]

C.1.4 Setting Sweep Range

Sweep range can be set by specifying either start and stop values or center and span values.

• Press the [Start] key. This will display the current setting for sweep start value in the parameter settings area located in the upper-left part of the screen.
• Use the keys or the rotary knob in the ENTRY block in one of the following ways to specify a value for the sweep start.
• Enter the desired value with the numeric keys ([0] to [9], [,], and [-]) and then press one of the unit keys ([G/n], [M/m], [k/m], or [x1])
• Turn the rotary knob until the desired value is set
• Press the step keys to set the desired value
• Press the [Stop] key

C.1.5 Setting Number of Points (NOP)

• Press [Sweep] to display the sweep menu.
- Press the NUMBER OF POINTS key. This will display the current setting for number of points in the parameter settings area in the upper-left part of the screen.

- Use keys or the rotary knob in the ENTRY block in one of the following ways to specify a value for the number of points.

- Enter the desired value with the numeric keys ([0] to [9]) and then press the [x1] key

- or Turn the rotary knob until the desired value is set

- Press the step keys to set the desired value

C.1.6 Selecting Sweep Trigger/Measurement Point Trigger

You can select whether the event to be triggered (the trigger event) is a single sweep or a measurement at a single point.

- Press the [Trigger] key to display the trigger menu.

- Press the SOURCE[ ] key to display the trigger source menu.

- Press the EVENT[ ] key to select the event to be triggered (pressing the key toggles the selection).

- Press the SINGLE key once to select single sweep.

C.1.7 Specifying Sweep Times and Stopping Sweep

You can specify the number of times sweeping is actually executed upon occurrence of a trigger. After sweeping is repeated the specified times, the sweeping is stopped and no further sweeping is executed by any trigger that may follow. You can also set the sweeping to unlimited times (continuous sweep).
Stopping sweep

Pressing the HOLD key immediately stops sweeping, regardless of which sweeping state (single, specified times, or continuous) is selected. No further sweeping can be triggered after it is stopped.

C.1.8 Selecting the Graph Axis Format

The Agilent 4294A displays measurement results in a Cartesian-coordinate graph whose horizontal and vertical axes indicate the sweep and measurement parameter values, respectively. Use the following procedure to select the vertical axis format for a Cartesian-coordinate graph:

- Activate the trace for which you want to set the axis format. Trace [A] or [B]
- Press the [Format] key to display the Format menu.
- Select the desired vertical axis format by pressing [LIN] or [LOG]
- The horizontal axis format is automatically determined based on the selected sweep type.