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Water absorption and dielectric properties of Epoxy insulation

Saikat Swapan Dutta

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Supervisor: Erling Ildstad, ELKRAFT

Norwegian University of Science and Technology
Department of Electrical Power Engineering

Problem Description

This assignment is a part of an ongoing research project at NTNU/SINTEF Energy Research, which is sponsored by industry and the National Research Foundation (NFR). The main aim of this research project is to develop materials and design criteria facilitating development of power equipment for electrification of sub sea oil and gas production.

More specific the topics of this project assignment are to:

1. Review findings in the literature and:
i) Present the theoretical basis for diffusion and absorption of water in filled epoxy.
ii) Review of relevant literature with respect to the effect of water in epoxy related to its electrical and mechanical performance.

2. Perform experimental investigations to examine the effect of water in epoxy related to the following properties: Dielectric Breakdown Strength, Mechanical Strength, Dielectric Response, Glass transition Temperature. Also the effect of electrode materials on dielectric response is to be studied.

Assignment given: 14. January 2008
Supervisor: Erling Ildstad, ELKRAFT

Preface:

I would like to sincerely thank the following people. You have made my time at NTNU well spent. First and foremost I would like to thank Prof. Erling Ildstad, for being such a wonderful supervisor. I thank him for all his guidance, support, encouragement and supervision throughout the semester. I would also like to thank Dr. Sverre Hvidsten for his much helpful advice. I would also like to thank all my friends and colleagues for their support and understanding. Last but not the least I would like to thank my Family for their support which helped me a lot in completing my Masters Degree.

Abstract:

Characterization of Epoxy (diglycidyl ether of Bis-phenol A cured with Tri ethylene Tetra amine) without fillers was done. The Water absorption test at 95°C shows that at saturation the epoxy contains a water concentration of 2.089%. The diffusion coefficient of absorption is calculated as 0.021 cm^2/s. The diffusion coefficient of desorption is calculated as 0.0987 cm^2/s. The diffusion is almost 5 times faster than absorption. Also the material looses weight as the hydrothermal aging progresses. The water in the sample leads to chain scission which leads to the weight loss. The weight loss is more incase of absorption followed by desorption than only absorption. The chain scission leads to decrease in the mechanical strength by around 45%. The diffusion of water from the samples doesn't affect the mechanical strength of the materials. The glass transition temperature reduces by 20°C with water inside the sample. The diffusion of water out of the sample only increases by around 10°C. The Dielectric response of the material shows that after the water absorption the sample shows high losses at lower frequencies. Also the increase in the real part of the permittivity increases with low frequency. The rapid increase in the real art of the permittivity of the material at lower frequencies can be attributed to a polarization at the electrode due both to accumulation of the charge carriers and to chain migrations. The breakdown test of the samples shows that with water in the sample the breakdown strength of the material decreases by 10 KV, but the material regains its dielectric strength when the water is diffused out. This shows that the chain scission and weight loss of the samples has no or minimum effect on the dielectric strength of the sample.

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1 Introduction:

Epoxy resins have become an essential part of insulation materials since their commercial introduction over 60 years ago. The versatility, stability under adverse conditions, and ease of use has significantly improved the electrical equipment that relies on their insulating abilities. From the smallest computer to chip to the largest motors and generators, epoxy polymers serve their purpose and are required to do this for long period of time. The evolution in both equipments and materials have been used a close observation of the processes to ensure solutions to the inevitable problems.

Several conventions will be used in this paper to simplify discussions. Epoxy resins will refer to the uncured material, still containing epoxy rings intended for polymerization. The resin will frequently be compounded with other components to achieve the desired properties in the final polymer. Once the system is cured, the material becomes an “epoxy polymer”.

The conversion from resin to polymer is a chemical reaction that must be carried out every time in a proper fashion. Any change that can affect the rate of a chemical reaction can affect the final properties of the epoxy polymer.

2 Literature review:

2.1 General Epoxy Chemistry:

Epoxy resins are a family of thermoset polymers in which two components are mixed to eventually form a glassy product at room temperature which has reasonable electrical insulating properties. Many different curing agents are used to bring about cross-linking if this resin. The action of the curing agent or the “hardener” is to open and join into the epoxide rings. Cross-linking in cured epoxies can be very high and an extensive network of connections with high mechanical rigidity is produced.

To improve the physical and mechanical properties of the end product and also to control the cost, the epoxy resins are loaded with fiber-glass, fumed silica, and other

inorganic particulates fillers. Cast resin polymers are compounds that are formulated by mixing resin with hardener, filler, plasticizer, and colouring pigments. Here fillers may constitute 50% or more of the compound weight, during curing phase, epoxy may shrink by about 3%, which is reduced to less than 0.5% by adding mineral fillers.

Epoxy resin chemistry is based of the reaction if three membered rings of two carbons and an oxygen atom known as the oxirane group, commonly known as the epoxy group. This chemical reaction of the groups has been known for many years but only during the post World War II period sufficient raw materials containing the epoxy group were commercially available. Dow Chemicals, Ciba-Geigy and Shell Oil were early innovators in developing processes for the large scale production of materials containing this reactive group [1].

Insulation industry is not a large user of epoxy resin compared with other resin users in the chemical industry. Hence, the resins to be used for insulation must be available from the industry for other widespread uses, and electrical insulation must be "piggy-bagged" onto the larger uses. The largest quantity material made is the diglycidyl ether of Bis-phenol A, which is known by the acronym, BPADGE, and is made by the reaction of ephichlorohydrin with Bis-phenol A. The simple BPADGA (n=0) is a crystalline material (mp ≈ 35° C), which creates formulation problems. The displacement reaction is therefore carried out so there are additional reactions of the phenol with the epoxy group to form dimmers or oligomers. The resulting mixture then remains a viscous liquid, which is easier to handle in subsequent formulations using the epoxy resin. A range of molecular weight material is available from manufacturers, where the n in Fig. 1 can have a variety of values from 0.1 to 100.

There are numerous agents that react with epoxy resins to convert them to insulation polymers in the process called cure. The choice of system is dictated by the method of application, the cure process, and the properties wanted both in the uncured resin and in the final polymer. The polymer properties are affected by the curing agent as they are incorporated into the polymer. The common curing processes are:

Amine Cure: A common cure system is to use a multifunctional amine to react with the bis epoxy resins. The ring polymerizes by the amine which adds to the epoxy group to form an amino alcohol . The amine cures, the process can actually stop at this

stage, although some more additions can occur with the amine if secondary hydrogen is present. However, the usual process involves other amines reaction with other epoxy groups to form the final network of the crossed material.

In low molecular weight amines, the concentration of amine groups is high so that the heat of reaction becomes a serious problem, leading to runaway reaction and product charring. Also, the lower molecular weight amines tend to have toxic characteristics and their use is to be avoided. One of the ways to eliminate the low molecular weight amines is to use a polyamide. This is an oligomeric product of the reaction of amines with acids. While polyamides contain amide groups that can react through any hydrogen on the amide nitrogen, the reactant for the epoxies is generally the amines on the end of the amide chains. The reduction in concentration and the higher molecular weight solves the high reactivity and the toxicity problems, and the use of the amide chains provides an additional way to vary the physical properties of the end polymer.

Acid Cure: The cationic polymerization of the epoxy by an acid or cation proceeds by a different mechanism than the amine polymerization. The acid adds to the oxygen of the epoxy ring and opens to the carbonium ion intermediate. This intermediate can in turn add to another epoxy ring. This process is actually a chain addition reaction and results in many rings being polymerized with each acid or cation, in contrast with the previously mentioned amine case, where only one or two rings are polymerized with each amine group. Finally, the carbonium ion ether acquires a hydrogen atom or reacts further with another epoxy, continuing the polymerization.

The epoxy unit, when polymerized by a ring opening process, releases energy to the system. This is not an insignificant amount of heat. One who has mixed considerable amount of epoxy resin will know. The exotherm can be quite vigorous at its extreme. The heat release must be controlled, but since it is depended upon for many cures, it cannot be totally eliminated. However, the heat rise of the exotherm is important, especially in systems where it is difficult to provide enough heat for cure. For example, room temperature cure epoxies do not generally give satisfactory physical properties unless there is enough material present to create an exotherm, which provides enough heat to cure the resin.

Cure of epoxy resins is ended when all available epoxy groups have been opened and their energy released. The usual method of determining cure on a laboratory scale is with differential scanning calorimetry (DSC), which measures the residual heat in a given sample. The method is particularly valuable for determining when the bulk of the heat is released but becomes less sensitive as the end of the reaction is approached and the concentration of remaining epoxy group diminishes. Because most of the important physical and electrical properties are generated in the final stages of cure, it is very important to be able to follow this part of the cure system.

The glass transition temperature (Tg) is the temperature where the polymer undergoes a transition from the glassy, brittle and rigid state at the lower temperature to the rubbery or flexible state. At a high temperature, polymer can reach the melting point (Tm) where the rubbery polymer becomes liquid and begins to flow. In the case where the polymer is cross-linked, as with epoxies, there is no melting point and the polymer does not reach the point where it starts to flow. Molecular movement is severely limited below Tg, and cure effectively stops once the Tg is reached by the polymer, since the molecules cannot slide around anymore.

The presence of hydroxyl group in the polymer that results from the ring opening polymerization makes the polymer susceptible to water absorption. The water can cause the polymer to lose some strength which is present in the dry polymer. This is worse when the use temperature is near or above Tg, because the water effect causes a disastrous failure. It is knows that water can cause a 20° to 30°C drop in Tg of an epoxy[1]. This drop can cause the tensile strength of the epoxy to drop from 40% to 75% [1].

When more cross links are present the drop in Tg is lower. And the drop in tensile strength is less. There is some indication that the use of anhydrides for cure allows the epoxy polymer to have better properties when the polymer is used at temperatures slightly above Tg.

One of the uses of epoxy potting material is to conduct heat through the polymer. This heat can be as simple as the heat of reaction of the polymerization, a one-time problem during the curing cycle. It can also be important during the use of the system where heat much be conducted away from an active part to a heat sink. Most polymers conduct heat at about the same rate where the thermal conductivity (TC) is from .17 to

.22 watts/meter-degrees Kelvin (W/mK). This number can be increased by the addition of inorganic fillers. By mixing 30% to 40% by weight of these fillers the TC can be raised to .31 W/mK. Even higher value can be reached using glass fibers, or in the case of high voltage application, 50% or more mica can be used to reach value of .35-.4 W/mk [1] .

2.2 Water absorption in Epoxy

It has been long known that epoxy and epoxy composites easily absorb water when exposed to humid environments. This reduces the stable lifetime of the material. Experiments show that the water in epoxy is present in two states [7]:

- Evenly distributed water molecules between the polymer chain
- Condensed water in fractures and cavities.

In Epoxy with mineral fillers it has been seen that water destroys the bond at the interface between the filler and polymer. This creates additional cavities along the fibers that can be filled with water.

Although the sorption processes of liquids and vapour in glassy polymers follow complex water diffusion mechanisms in epoxy resin matrices, their behaviour has frequently been found to approximate to that corresponding to Fickian diffusion. The characteristics of Fickian diffusion have been described as under:

- The sorption curves are linear in the initial stages.

- Above the linear portion both absorption and desorption curves are concave to the abscissa. For absorption the linear region extends to over 60% or more of the region studied.

- When a series of reduced absorption curves are plotted for films of different thickness, the curves are super-imposable.

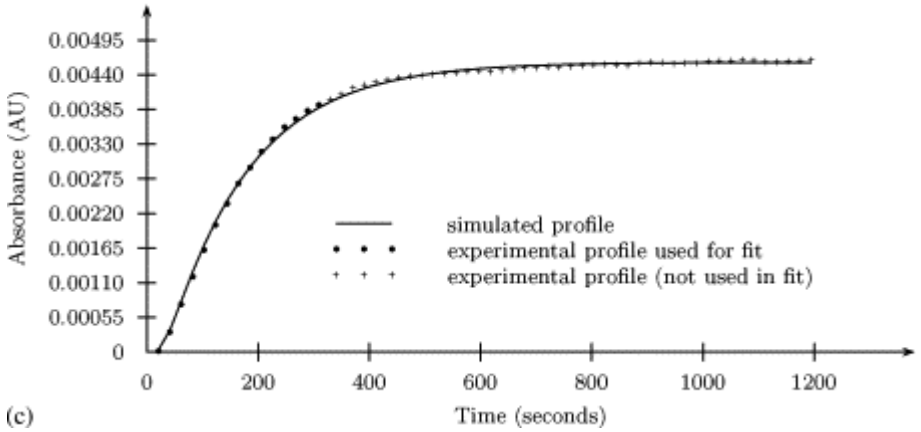

Figure 1: Water absorption in epoxy with mineral fillers. Sample thickness of 5.3 µm [7] .

3 Procedure Methods and Experimentation:

3.1 Work Outline:

The main aim of the project is characterization of unfilled epoxy polymer (bis-phenol A cured by amine). The raw material used for epoxy casting was RenLam© CY 219 (epoxy resin) and Ren© HY5160. These are procured from the company Huntsman. The work for this thesis includes making epoxy samples and then performing different tests on them for characterization. The casting was done using two different ways. In one way the resin and the hardener was mixed manually and then put in to a form then the mixture is vacuum cured at 60° C. In the other method the mixture of the resin and hardener was mixed in the machine and then put into the forms and then vacuum cured at 60° C. Both the samples were studied for dielectric response to find if there is any difference due to the way of mixing the resin and hardener before curing.

For the ease of mixing large quantity of epoxy resin and hardener, the materials for all samples casted were mixed in the machines. The samples were casted in different shapes for different kind of tests. The following are the shapes, in which the epoxy samples are casted,

- Disc (1mm thick X 10 mm diameter)
- Dog bone shaped (4 mm X 115 mm X 10 mm)
- Rogowski shaped (1mm think)

Figure 2: "Dog bone" shaped Epoxy sample

Figure 3: Disc epoxy samples

Figure 4 : Rogowski samples for breakdown.

To study the effect of electrode material on dielectric response one of the disc shaped sample was casted with one side with aluminum foil casted into it. The aluminum foil acts as the high voltage electrode. In the other sample the sides of the epoxy were painted with silver paint, which acted as the high voltage electrode.

The main characterization of the unfilled epoxy sample was done on the basis of water absorption at 95° C. The following are the tests performed on the sample;

- Dielectric response
- Glass Transition Temperature
- Mechanical Strength (stress – strain curve)
- Breakdown Strength.

Also the absorption and desorption coefficients for the material was found.

4 Casting of Epoxy samples:

For the casting of the epoxy samples RenLam© CY 219 and Ren© HY 5160 were used. RenLam© CY 219 is the epoxy resin and Ren© HY 5160 is the hardener. They are mixed with each other in the proportion 100 (RenLam© CY 219) **:** 50 (Ren© HY 5160) by weight. CY 219 is a diglycidyl ether of bis-phenol A, which is known by the Acronym, BPADGE. HY 5160 is hardener containing a multifunctional amine. The things that have to taken care of while mixing manually that the mixture should not contain any trapped air bubbles, as it is very easy if proper care is not taken to introduce air bubbles, in the resin and hardener mixture. Also the resin and the hardener are to be mixed thoroughly, else the polymerization is not proper and the physical, mechanical and electrical properties of the polymer are not to the level expected. While the mixture is put into the cast again care should be taken not to introduce any air bubble in the mixture. Though this is very hard and practically impossible hence the curing is done in a vacuum oven. The trapped air bubbles are released when the vacuum is turned on. Another important thing to take care of is that sufficient Teflon spay is to be added on the surface of the cast so that the cured epoxy can be easily removed. This is necessary as the thickness of some

samples are small (1mm) hence the samples may break while removing it from the cast if they are stuck to the cast. The figure below shows the pictures of the casted epoxy samples. One sample is casted with aluminum foil on one side. This is used as an electrode for measuring the dielectric response. The effect of electrode material is studied. On the other samples the electrode was silver paint. As shown in Fig 6. Due to the shrinkage problem the casting to epoxy with aluminum foil is difficult as the cured epoxy is not a flat disc it gets a bit curved and hence causes trouble while placing it in the arrangement for measuring the dielectric response. The other samples are made in Machine and applied silver paints on both sides as shown in the Fig 5. The samples were very good and flat. Hence the tests are carried on the samples with electrodes as silver paint. Also the samples were easy to cast with the machines than manually.

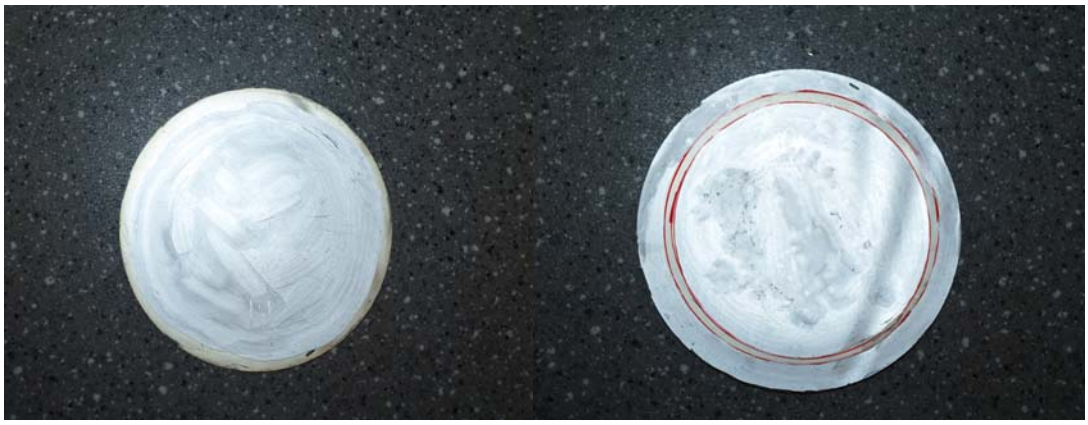

Figure 5: Epoxy samples casted in machine. With silver painted electrodes.

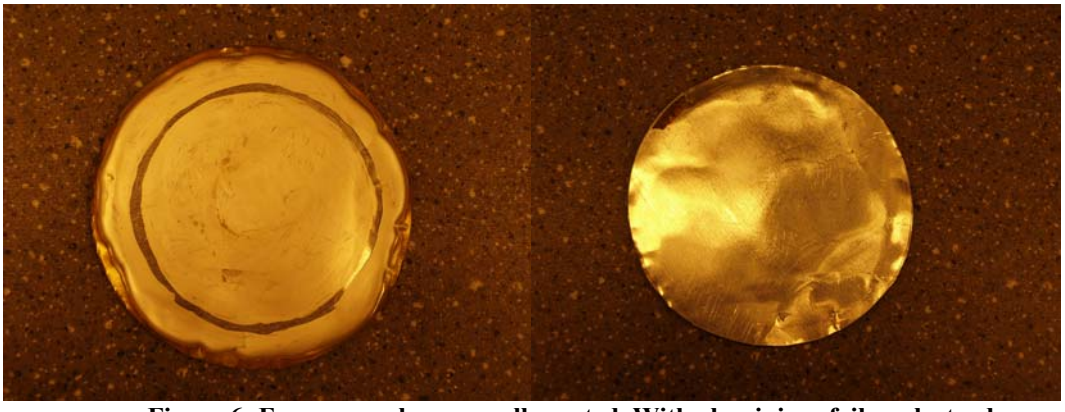

Figure 6: Epoxy samples manually casted. With aluminium foil as electrode.

5 Equipments Used

5.1 IDAX 206

The IDAX 206 is an insulation diagnostic system designed and manufactured by **"PAX Diagnostics"**. It employs the principle of dielectric spectroscopy as described in section 2.4, and balances out the capacitive current before measuring it.

The IDAX 206 is by designed intended for performing insulation diagnostic in the field, for instance on transformers, high voltage cables, bushings etc. It has two built in signal generators capable of generating sinusoidal voltage of 10V peak and 200V peak respectively. The frequency range is between 0.1 mHz to 1 kHz using the built in voltage sources. The voltage is measured by a voltmeter and the current is measured by electrometer acting as a current to voltage converter. The analogue signals are then converted to digital samples used in calculations.

The system operates fully standalone, essentially containing a PC with a slimed down version of Windows Xp operating system for embedded systems and a hard drive for storing measurement data. Measurements are programmed using a specialized scripting language, and executed through instrument control software. The instrument is capable of calculating any of the parameters in different insulation models, and can also export the calculated values to text files for manual post-processing.

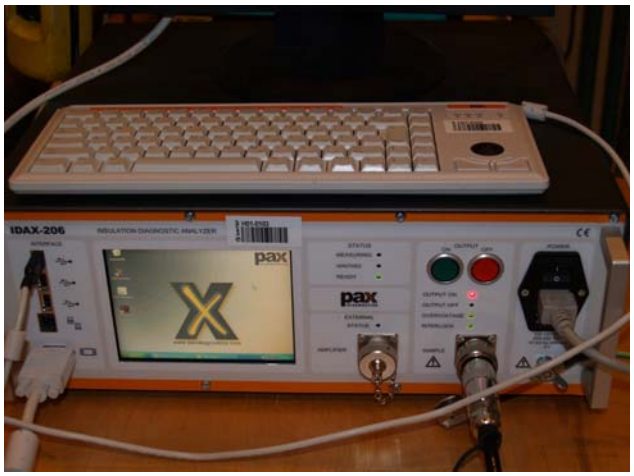

Figure 7: IDAX 206

5.2 Mettler Toledo AT250

The Mettler Toledo AT250 is a precision scale for measuring weights up to 200g with a resolution of 0.01 mg. It calibrates itself automatically when it detects a change in temperature or relative humidity. It is shown in Figure:8

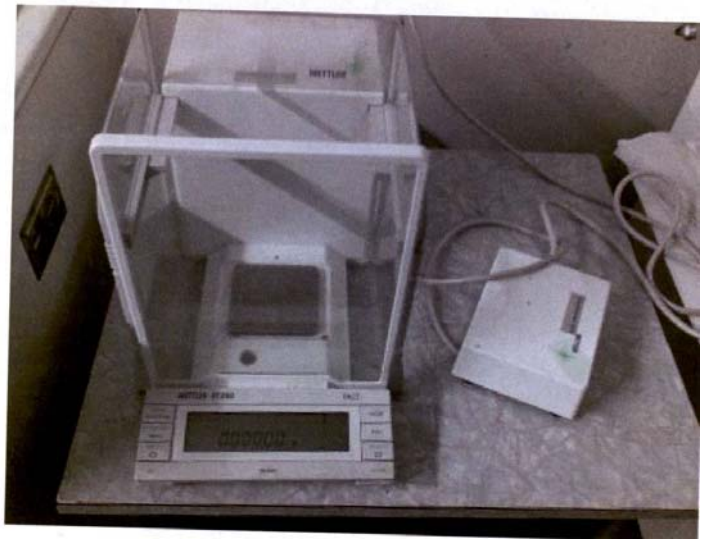

Figure 8: Mettler Toledo AT250

5.3 Mettler Toledo DSC822

Mettler Toledo DSC822 is Differential scanning calorimetry equipment. It can measure the Glass Transition temperature of the given polymer samples. It is shown in Fig 9.

Figure 9: DSC822

5.4 Lloyd Instruments LR 5K:

Lloyd Instruments LR 5K is the equipment for applying the tensile force on the dog bone shaped objects. This unit is connected with a computer which records all the data of the stress and the Extension during the test. This equipment can apply tensile force upto 5 Kilo Newton.

Figure 10: LR 5K

6 Tests Performed (Experimentation):

To characterize the epoxy material Different tests were performed. The following tests were performed:

To study the effect of electrode material two samples were taken. One of the samples was casted with aluminum foil casted on one side to be used as the high voltage electrode; where as in the other sample there was no metal foil casted, the surface of this sample was painted with silver paint. Both the samples were tested for Dielectric response for frequency range 1000 Hz to 0.01 Hz. The results were noted. The value of dielectric loss factor and permittivity (both real and imaginary part) were studied.

The samples were put in water at 95°C and the water absorption and desorption were studied. The graph of water content as a percentage of weight of the polymer versus time is plotted and the coefficient of absorption and desorption were found out.

Dielectric response test was done on the samples in three different stages, namely in Dry condition before the start of water absorption, after the samples are kept under water for absorption at 95°C (hydro thermal ageing) in wet condition and after the desorption is done. The results were documented and the effects of the water in the samples in the dielectric response were discussed. Also the effect of hydrothermal aging is on dielectric response is discussed.

The glass transition temperature (Tg) of the samples were found using DSC (Differential Scanning Calorimetry). The Tg is measured in the samples in dry condition before the water absorption process, then in samples after the water absorption process with moisture in the sample, and then in sample after the desorption. The effect of water on the Tg of the epoxy polymer is studied and the result is documented and discussed.

The mechanical strength of the epoxy polymer is studied. A destructive test has been performed. A tensile force is applied to the dog bone shaped samples till it breaks and the stress versus strain curve is plotted. This test is also done in dry sample before water absorption, then in sample which was kept under water at 95°C for absorption, and in sample which has undergone absorption and desorption at 95° C. The difference between the stress-strain curves is documented and discussed.

Breakdown testing is done in Rogowski shaped object to find the dielectric breakdown strength of the materials at different condition to study the effect of water in Dielectric breakdown strength of the material. The test is again performed on three type of samples, Dry samples (before water absorption), Wet samples (after water absorption at 95°C), and on samples after desorption. The breakdown strengths of the materials is documented and discussed.

7 Results and Discussion:

7.1 Effect of Electrode Material on Dielectric response:

The effect of electrode material on the dielectric response of the material was studied. On one sample the high voltage electrode is painted with silver paint. On the other sample the aluminum foil which is casted on to the sample is used as the high voltage electrode. The measuring electrodes of both the samples are silver painted. Fig 11.

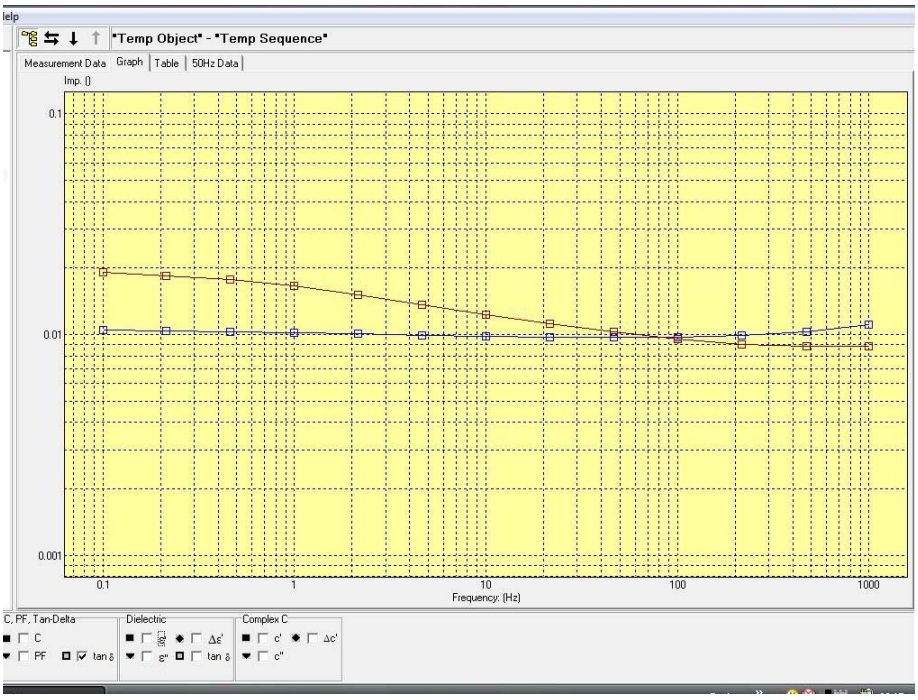

Figure 11: Dielectric losses for sample with two different types of electrodes

The dielectric response test was performed on both the samples. The frequency range used was from 1000 Hz to 0.1 Hz. The dielectric losses at high frequency for both the samples don't have much difference. But at lower frequencies the losses of the sample with silver paint is higher. As can be seen from the graph the dielectric response of the material is affected by the materials of the electrode used. The aluminum foil casted onto the sample and that is the fact that there is perfect connection between the electrode and the epoxy. As there the silver paint is applied on the sample there are some

gaps in the connection. As the surface of the epoxy is not uniform in the micro level, the silver painted electrodes has some interface with the epoxy. Hence there is an interfacial polarization. This polarization loss adds to the dielectric loss. At lower frequency this is clearly visible by the increased loss with the sample with silver paint. As interfacial polarization in a relaxation mechanism, at lower frequency it is dominant and at higher frequencies it is negligible. Also the Work function of Aluminum is lower than that of silver. An shrinkage of the epoxy was seen when the aluminium foil is casted into it. This skrinkage might crease voids on the contact between epoxy and the foil. This give rise to many problems like partial discharge. Also if water is absorbed my the sample it may condensate in to the voids giving rise to high losses and early breakdown.

7.2 Water absorption and desorption in Epoxy:

The samples as shown in Fig 2 are kept under water at 95°C in a heating cabinet. The weights of samples were measured from time to time and the weight gain was noted. The graph percentage weight gain with against time was plotted. It is seen that the absorption process here is following the Fick's law. A curve fitting was done. The equation used for fitting the curve is

$$Y = Cs(1-(e^{(K\times X^{0.75})}) \qquad 1$$

Where,

Cs = water concentration at saturation

K = how close to saturation the sample is.

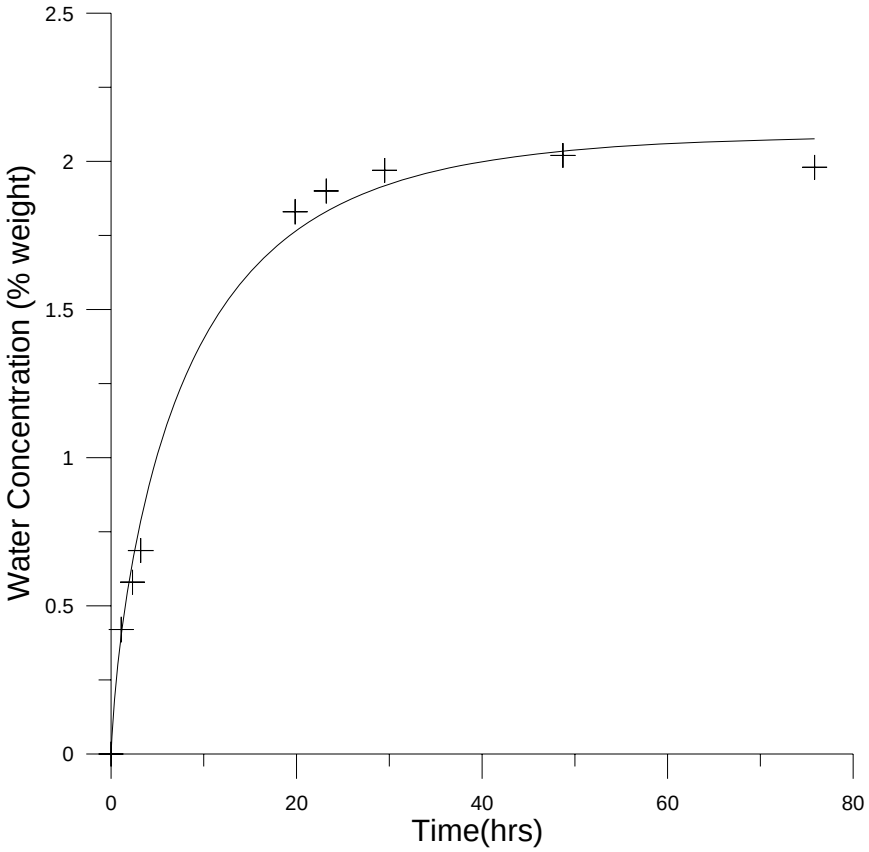

Figure 12: Water absorption Graph

The curve fitting is done in the software Grapher 4. Both the above parameters are adjusted to fit the graph so that the closest fitting is got to the points obtained experimentally. The Graph of water absorption is shown below.
The diffusion coefficient is calculated and is presented in Table 1.

Temperature	Absorption Coefficient (cm^2/s)	Saturation at Concentration (% of weight)
95°C	0.021	2.089

Table 1: Diffusion Coefficient

As can be seen from the absorption curve, initially, the resin gains weight linearly with time, the rate then decreases and the polymer starts loosing weight after around

75hours of aging. However, this absorption was not accompanied by any visible damage to the material.

From the absorption curve, it can be clearly seen that the residual weight change, ΔW, as a function of initial weight, W_0, increased initially, and was then followed by a reduction that led eventually to a weight loss. This behavior suggests irreversible trapping of water and degradation of the polymeric structure during hydrothermal aging. This result is in good agreement with Ref [14], where a commercial epoxy resin based on DGEBA was studied.

The absorption behavior shown in Fig 12 suggests the following scenario, in qualitative terms. Initially, the polymer absorbs water, of which a fraction reacts chemically, causing hydrolysis leading to chain scission. Schematically, we can write:

$$\sim A-B\sim +H_2O\rightarrow \sim A-OH+\sim B-H \qquad 2$$

where, A and B represent chemical groups in the epoxy main chain. In the early stages, chain scission leads to simply to the chemical addition of water that will be unable to leave upon drying. However, after the number of chemical reaction site has increased, the probability of a given inter crosslink chain being cut into two (or more) increases, thus facilitating separation and subsequent leaching of the detached segments from the network. This leads to a weight loss.

7.2.1 Desorption:

After the water absorption for a given period, the samples were surface dried and weight. Drying was continued, at the same temperature (95°C) as that of absorption , and the samples were periodically weighed until a good estimate of their final equilibrium weight after desorption could be obtained. This process normally took 1 to 2 weeks to finish.

Fig 13 below shows desorption of the epoxy samples at 95°C.

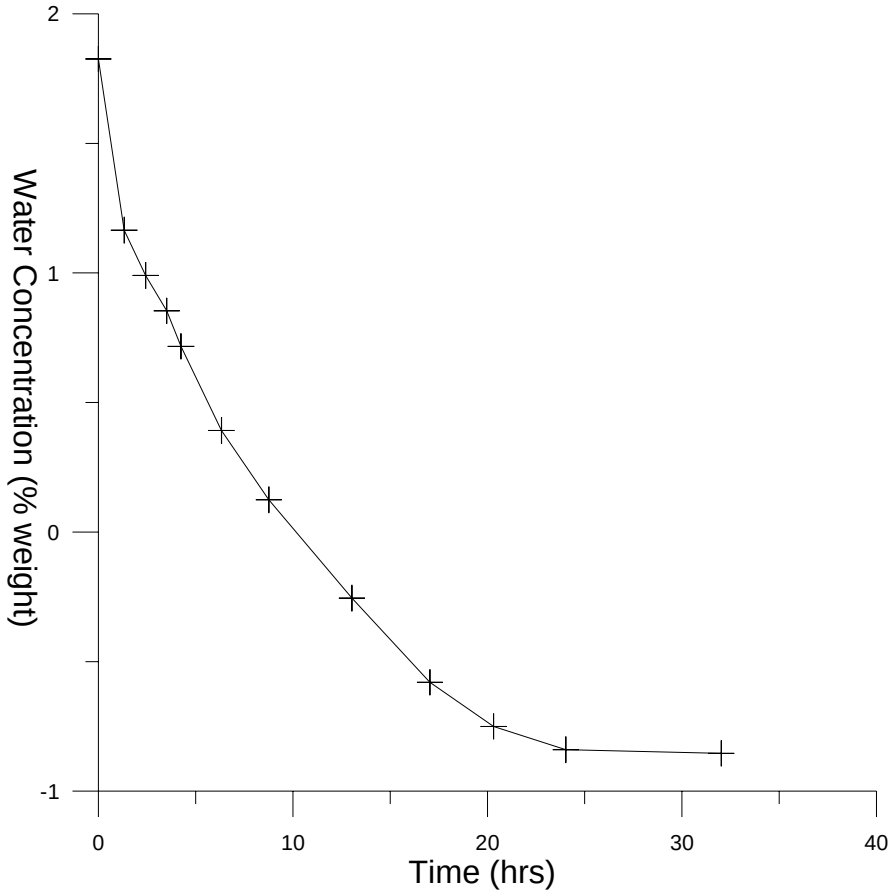

Figure 13: Desorption Graph

The coefficient of Diffusion is given in Table2. It can bee seen that the diffusion is around 5 times faster than absorption.

Temperature at which Desorption is done	Diffusion coefficient of Desorption (cm^2/s)
95°C	0.0987

Table 2: Desorption coefficient

It can be seen from the graph that the weight loss due to chain scission is more in case of absorption followed by desorption [1].

7.3 Glass transition temperature:

The glass transition temperatures of the samples were measured using Differential Scanning Calorimetry (DSC). Fig 14, Fig 15 and Fig 16 shows the curves obtained from the DSC for the dry sample, samples after water absorption and on samples after absorption followed by desorption. Table 3 shows the values of the measured Tg.

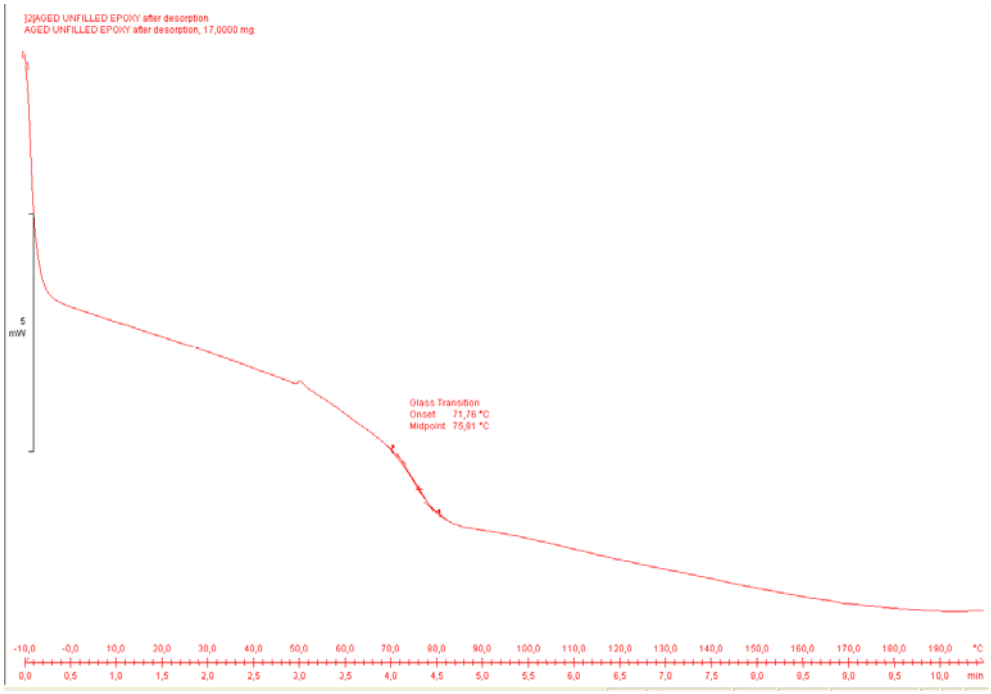

Figure 14: DSC of dry unaged sample

Figure 15: DSC of Wet aged sample

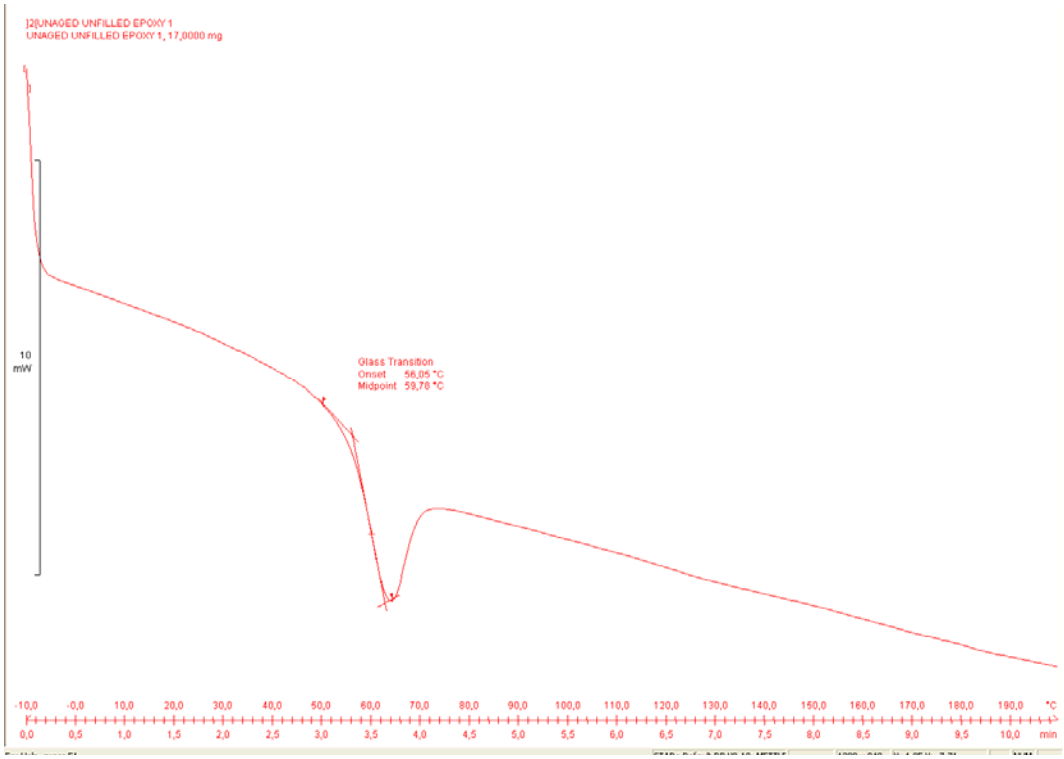

Figure 16: DSC of aged dried sample.

Samples	Onset Temperature	Midpoint Temperature
Unaged Dry sample	71.76°C	75.81°C
Aged wet sample	49.65°C	53.67°C
Aged sample (with water absorption followed by desorption)	56.05°C	59.78°C

Table 3: Glass transition Temperatures.

It can be observed that the Tg for the samples with water have reduced by approximately 20°C. With water concentration of around 2.0 % the Tg reduces by 20°C. The water in the sample can cause the polymer to lose some strength. This problem is even worse at high temperature and can lead to disastrous failure [1]. When the cross links are present, the Tg drop is lower and the drop in tensile strength is less. Knowing the Tg of the cured polymer is especially necessary where the polymer is used for its adhesion or cohesion properties. If the Tg is exceeded, the tensile strength and compressive strength of the polymer is drastically reduced, and even if the polymer is cross linked, the insulation can fail. There is some indication that the use of anhydrides for cure allows the epoxy to have better properties when the polymer is used at temperatures slightly above Tg [1].

In many systems, the insulation in use will be heated and the cure will continue to push the Tg to high temperature. If the stress damages the epoxy polymer as the Tg is exceeded, failure can occur. The practical solution to this problem is to ensure that the cure temperature exceeds the expected use temperature of the insulation.

7.4 Dielectric response:

Disc samples of dimension 10mm (diameter) X 1mm are used to study the dielectric response. The electrodes on the samples used are conduction silver paint. Fig 17 shows the picture of the samples prepared for testing. Three samples were tested. The first sample tested was a dry sample (un-aged). The dielectric response is shown in the Fig 17, blue curve.

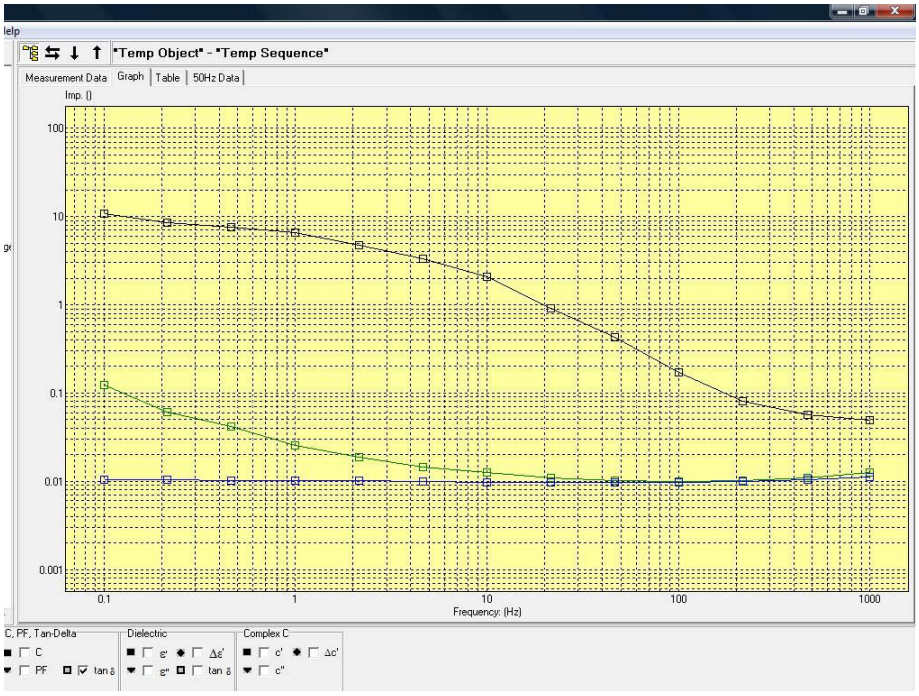

Figure 17: Dielectric response of unaged, wet aged and aged dried samples

The second sample tested is a sample that has undergone hydrothermal aging. The sample was put under water at 95°C and the weight gain was noted. The sample when near saturation with a water concentration of 2.089 %, it was removed from the water cooled down and dried superficially. The samples were cooled down so that no water is diffused out of the sample. The electrodes were pained with silver paint on both the sides of the sample. This sample is then tested with IDA 206 instrument for dielectric response. The frequency range used was 1000 Hz to 0.1 Hz. The Fig 17,black curve shows the

dielectric response of this sample. It can be seen that due to water in the sample the dielectric loss factor have increased considerably. Also there is a considerable increase in the real part of the permittivity of the material Fig 18 Green curve. At low frequency the dielectric loss factor increases rapidly this is due to the presence of water in the sample. This shows a conduction effect inside the sample due to the presence of water, which causes the high conductive current at low frequency. The rapid increase in the real art of the permittivity of the material at lower frequencies can be attributed to a polarization at the electrode due both to accumulation of the charge carriers and to chain migrations. The chain migration is high because the water causes a chain scission in the epoxy after absorption. With water present in the sample it's easy for the chain to migrate than in dry samples.

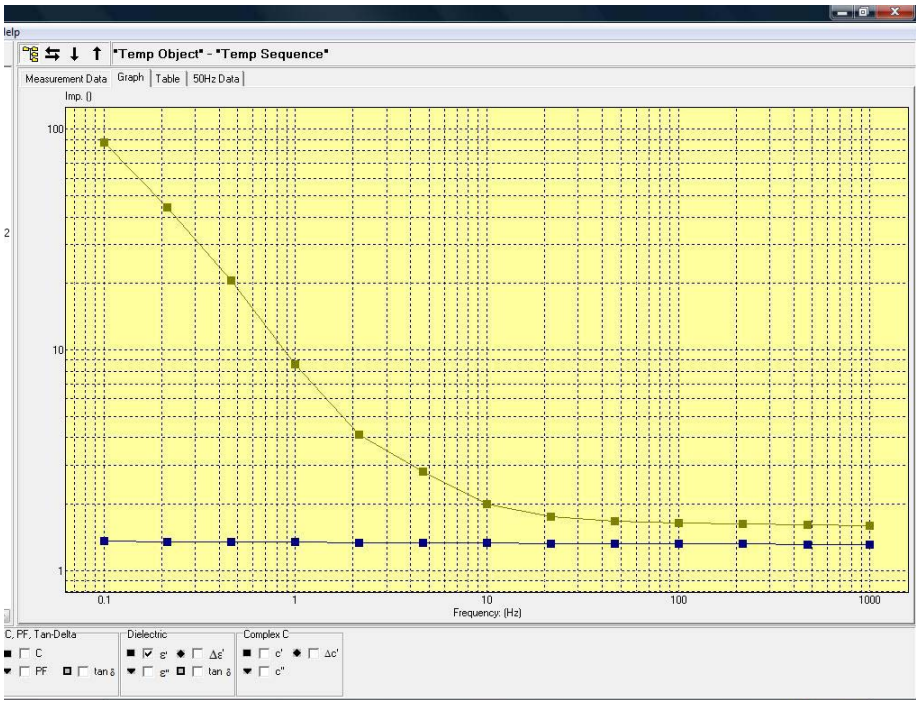

Figure 18: Relative permittivity of unaged and wet aged sample.

The third sample tested was kept under water at 95°C and then when reached saturation has been subject to desorption at same temperature. When the sample is dry then the samples is cooled down and then the electrodes were painted on to the sample. Silver paint is used for the electrodes. The Fig 17, Green curve shows the dielectric response. The below shown are the dielectric loss factor and the real part of the relative permittivity. It can be seen that after the absorption followed by desorption the dielectric

loss actually is quite close to the results already obtained. But in the lower frequency range a increase in the dielectric loss is observed.

7.5 Mechanical test:

With respect to finding the characteristics of the epoxy, it is important to find the mechanical properties as well. It's an important properties looked at in many industrial applications. The Dog bone shaped samples were used for testing. The Fig 2 shows the picture of the samples. The samples were then applied tensile force till breakage. The stress-strain curves were plotted. These Curves give the idea about the mechanical strength of the material.

Fig 19 shows the stress-strain curve of the unaged sample.

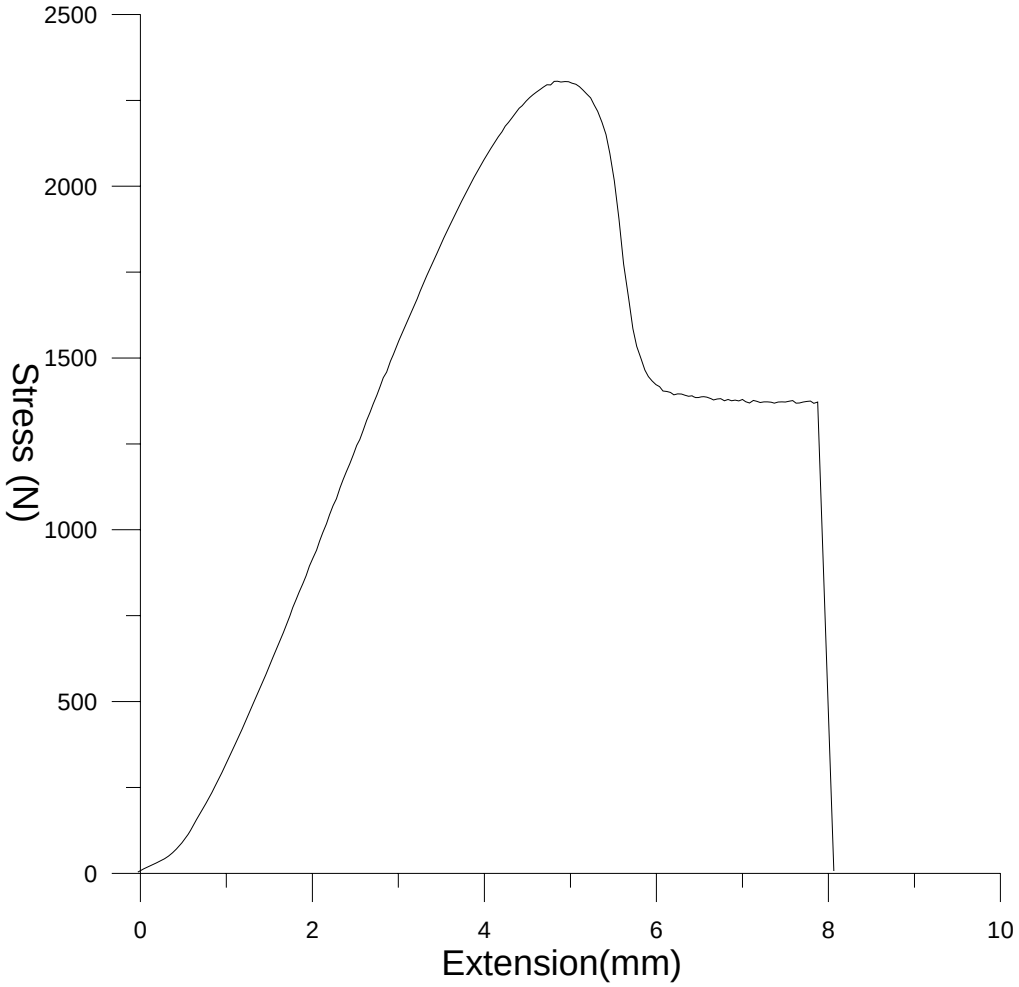

Figure 19: Stress – Strain Curve for Unaged sample

For the second set of test dog bone samples are immersed in water. Till they reach saturation around 2.089% of water concentration. The samples are then cooled down and dried superficially and then again tensile force is applied on them till break. The stress strain curve is plotted from the test. Fig 20 shows the stress-strain curve of the samples after they have undergone water absorption at 95°C. By comparing with Fig 19 it can be seen that the after the water absorption the material has much lower Yield stress. The Yield stress almost reduces by 50%. But the material can take much more strain before it breaks. The elongation at break is much larger with water in the sample. The water results in chain scission which in turn makes the sample less rigid. But the material suffers a permanent deformation after yield point. The stress at yield point is also reduced drastically.

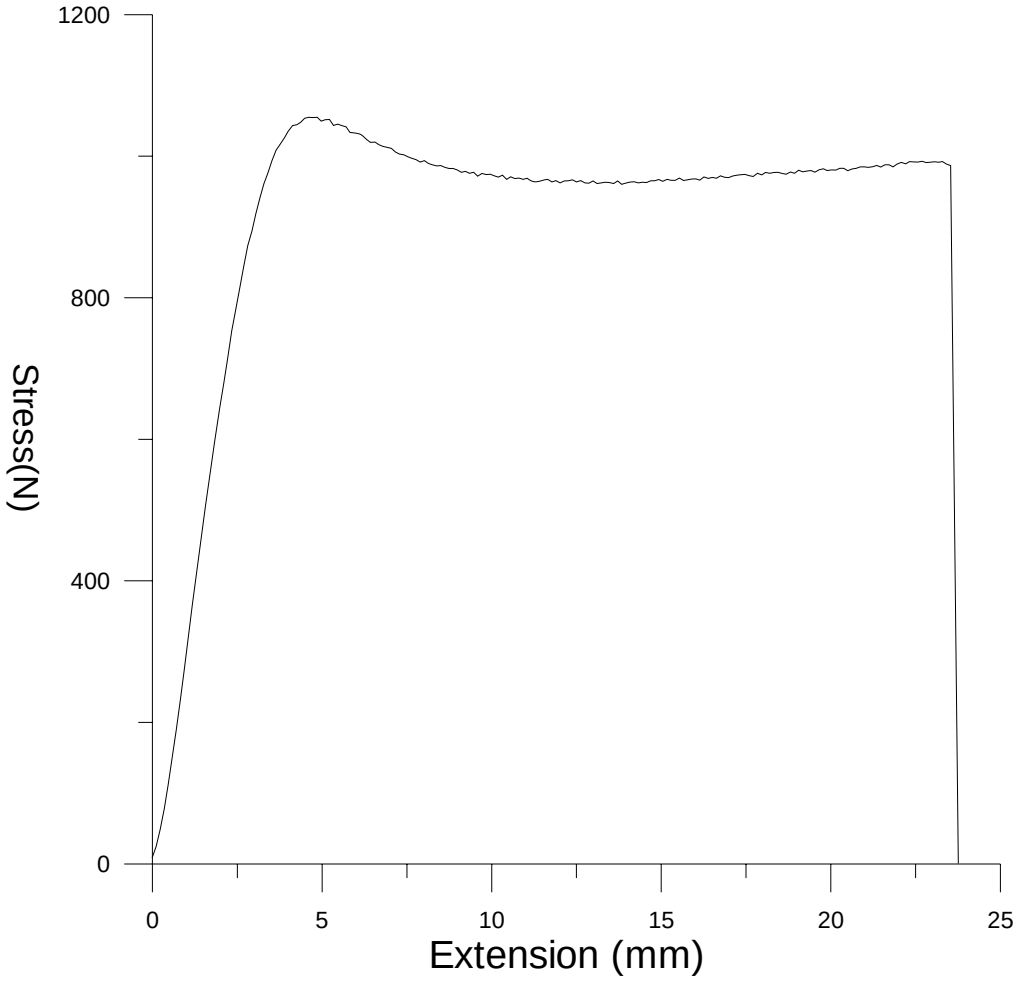

Figure 20: Stress – Strain curve for wet aged sample

For the third set of tests dog bone shaped samples were subjected to water absorption followed by desorption at 95°C. After the desorption process the samples are cooled down and then they were subjected to mechanical tensile force till break. The Stress-Strain curve is plotted for the samples. Fig21 shows the Stress-Strain curve. While comparing it with Fig 19 and Fig 20, we can see that even after desorption the material doesn't gain back the mechanical strength. That proves that the water present in the epoxy doesn't only acts as a flexibilizer, it results in chain scission causing permanent and irreversible damage to the cross linking in the materials. Due to this the material looses strength.

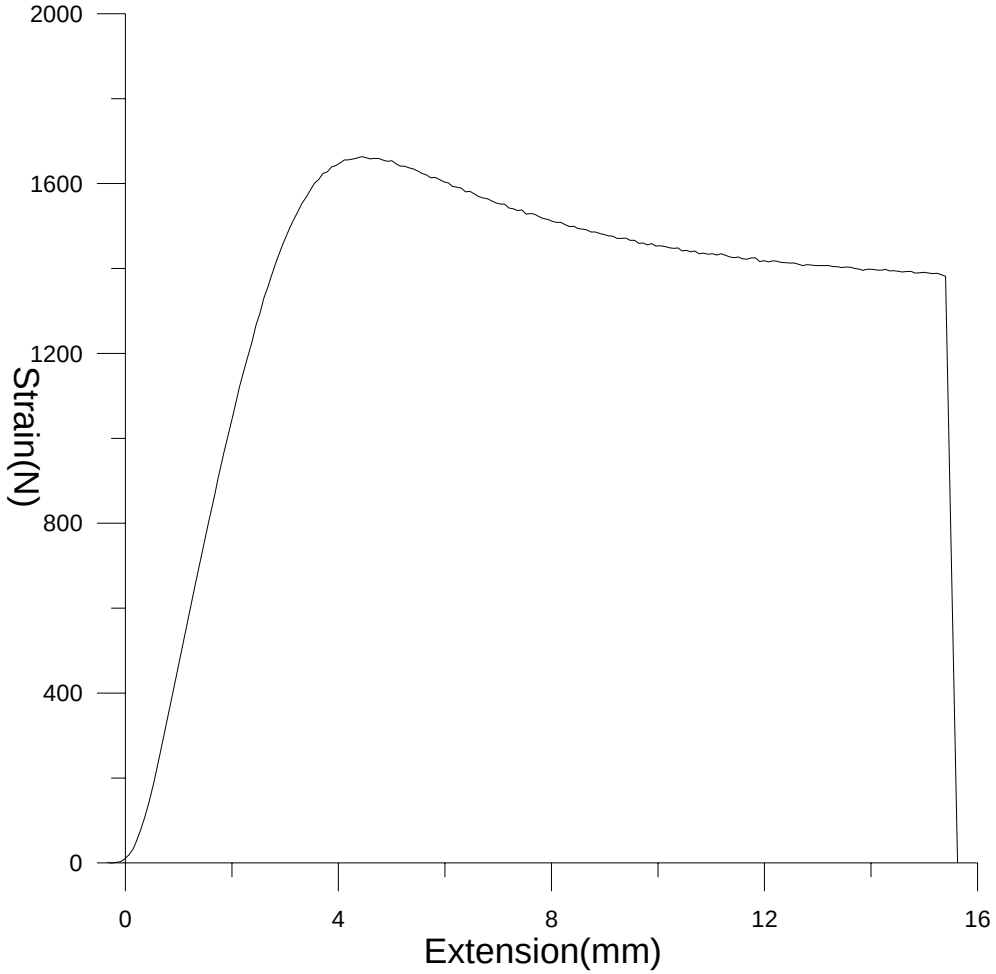

Figure 21: Stress – Strain Curve for the Aged dried samples

Sample Reference	Stiffness (N/m)	Young's Modulus (MPa)	Tensile Strength (MPa)
Dry sample 1	635055.1498	1825.783556	57.3426342
Dry sample 2	585805.87	1684.191876	55.00903548
Dry sample 3	656198.6968	1886.571253	57.69517294
Aged wet Sample 1	404038.9939	1161.612108	26.38791279
Aged wet Sample 2	399761.2448	1149.313579	26.04797695
Aged wet Sample 3	284783.2527	818.7518515	21.29674607
Test Sample aged dried 1	500984.3778	1440.330086	38.0221676
Test Sample aged dried 2	551794.613	1586.409512	39.27350708
Test Sample aged dried 3	615122.0248	1768.475821	41.6396404

Table 4: Mechanical test data of Unaged, aged wet and aged dried samples.

7.6 Electrical Breakdown Strength:

Electrical breakdown strength of the epoxy material was studied for this epoxy type. For this test Rogowski shaped materials were used. Fig 22 shows the samples. The Break down test was performed on three sets of samples. Each set consist of 3 samples. First set of samples were test for breakdown. These samples were not subjected to any kind of aging. The break down strength of the samples was given in Table 5.

Samples	Breakdown Strength.
C1	54 KV
C2	31.6 KV
C3	45.1 KV

Table 5: Breakdown strength of Unaged samples

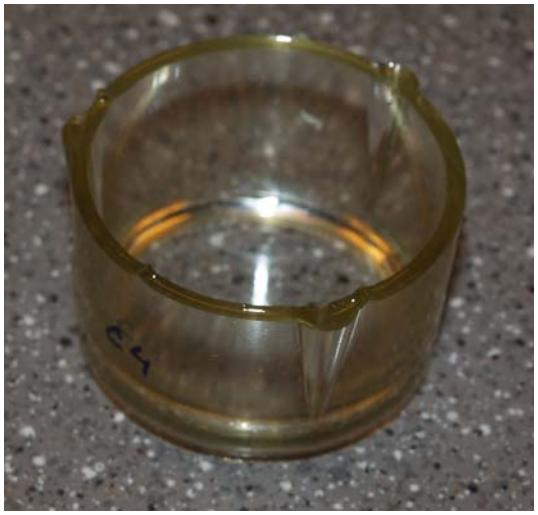

Figure 22: Unaged sample for breakdown.

The second set of samples was subjected to water absorption at 95°C. They were tested for electrical breakdown strength when the water concentration in the samples was 2.0 % of the weight of the samples. The Breakdown strength of the samples is shown in Table 6. Comparing the results of Table5 and Table 6 it can be seen that with water in the samples reduces the breakdown strength of the material. This can be concluded from the fact that water inside the samples helps in conducting the charges across the epoxy which leads to early breakdown of the material.

Samples	Breakdown Strength.
C4	29.5 KV
C5	37.0 KV
C6	29.7 KV

Table 6: Breakdown Strength of Aged wet sample

Figure 23: Aged wet sample for breakdown.

The third set of samples were subjected to water absorption at 95°C followed by desorption at the same temperature. The breakdown strength of these materials was then tested. Table9 shows the results of this test. The results shows that the epoxy regains their breakdown strength after the water is diffused out and the small weight loss after desorption don't affect the breakdown strength of the epoxy.

Samples	Breakdown Strength.
C7	50.3 KV
C8	44.0 KV
C9	50.7 KV

Table 7: Breakdown Strength of aged dried samples

Figure 24: Aged dried sample for breakdown.

8 Conclusion:

From the results of the water absorption tests it can be deduced that as the water absorption follows Fick's rule. It is even evident from the weight of the samples, that it starts decreasing after the water concentration in the sample have reached the saturation i.e. 2.089 %. From Desorption test it can be deduced that the desorption is approximately 5 times faster than the absorption. Water absorption causes the glass transmission to reduce by approx 20°C (from 75° C to 53°C). Even after all the water is diffused out the glass transition temperature of the sample increases just by around 7° to 8° C.

The results of Dielectric response suggest that after aging the losses of the material increases. Also during wet condition the increase in real part of permittivity at lower frequencies is of considerable interest. The rapid increase in the real art of the permittivity of the material at lower frequencies can be attributed to a polarization at the electrode due both to accumulation of the charge carriers and to chain migrations. The rapid rise of losses at lower frequencies gives the idea that there is a conduction current present due to the presence of water in the sample.

The Mechanical test shows that the Tensile strength of the material reduces by 50% when a water concentration of 2.089 % is present in the epoxy material. Also when the samples are dried the tensile strength doesn't regain the original value, hence suggesting that the water in the sample has caused chain scission in the material and hence the mechanical strength is permanently reduced.

The Breakdown strength test suggests that the breakdown strength of the material decreases when water is absorbed. But the dielectric strength is regained when the water is diffused out of the sample. So the chain scission for the short testing time is not affecting the breakdown strength of the material. This can be inferred from the test. For understanding the actual behavior of the breakdown strength further tests are needed.

9 Appendix:

9.1 Appendix A:

9.1.1 Background theory:

9.1.1.1 Water Diffusion in Polymers:

Water or any other fluid diffusion in a solid material is described by Fick's Two laws. Fick's first law states that in the steady state condition, the flux of water J [g/mm^2] through a solid is proportional to the gradient of the water concentration [g/mm^3].

$$J = -D \frac{\partial \phi}{\partial x}, \qquad 3$$

ϕ = Water concentration in the material

D = Diffusion coefficient or Diffusivity of the material [mm^2/s], relating to the speed at which the water concentration changes in side the material.

Fick's Second law is given by,

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \qquad 4$$

Lets consider a rectangular object as shown in Fig 25 . It has an initial concentration as ϕ_i. The object is exposed to moisture, giving a water concentration on the surface of ϕ_a . The boundary conditions are as under:

$\phi = \phi_i$, for $0 < x < h$.

$\phi = \phi_a$, for x > 0.

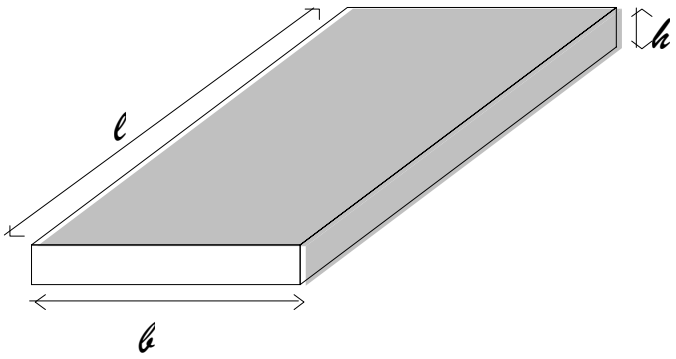

Figure 25: Geometry of Rectangular test specimen

Applying Fick's second law following solution can be found.

$$\frac{\phi - \phi_i}{\phi_m - \phi_i} = 1 - \frac{4}{\pi}\sum_{j=0}^{\infty}\frac{1}{2j+1}\sin\frac{(2j+1)\pi x}{h}\exp\left[-\frac{(2j+1)^2\pi^2 D_x t}{h^2}\right], \qquad 5$$

where ϕ_m is the water concentration when the object is fully saturated and D_x is the diffusivity normal to the surface. By integrating Eq. (3) over the object's full thickness the total water content can be obtained, giving the relation

$$G \equiv \frac{m - m_i}{m_m - m_i} = 1 - \frac{8}{\pi^2}\sum_{j=1}^{\infty}\frac{\exp-\left[(2j+1)^2\pi^2\left(\frac{D_x t}{h^2}\right)\right]}{(2j+1)^2} \qquad 6$$

where,

m = weight of the moisture at any given time,

m_i = initial weight of moisture on the object,

m_m = weight of moisture at full saturation.

G = measure of how close to full saturation the object is, It is dimension less.

The value of G can be approximated by the equation

$$G = 1 - \exp\left[-7.3\left(\frac{D_x t}{s^2} \right)^{0.75} \right] \qquad 7$$

The value of the parameter s is dependent on the fact if the object is exposed to moisture on either sides or a single side. It exposed on both sides, s = h. If exposed on only one side then s = 2h.

For Practical purposes, the percentage moisture content is the most interesting quantity. Usually defined as the weight gain of the material, give by the formula below,

$$M = M(t) \equiv \frac{W - W_d}{W_d}.100, \qquad 8$$

Where, W = weight of the sample at any given time.

W_d = weight of the dry material.

By putting $W = W_d + m$, and rearranging the terms we get

$$M = G(M_m - M_i) + M_i, \qquad 9$$

Where, M_i = initial moisture content

M_m = moisture content at full saturation.

The diffusivity can be estimated by plotting the water uptake versus time t and using numerical tool (Grapher 4) to fit to Eq.* to the experimental data. Also the diffusivity can be calculated by plotting water uptake versus $\sqrt{t}$ and D can be calculated by the following equation.

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \qquad 10$$

If diffusion through the side surface can be neglected then $D_x \approx D$. If the diffusion through the side surface can't be neglected then D_x can be calculated by the following equation.

$$D_x = D\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \qquad 11$$

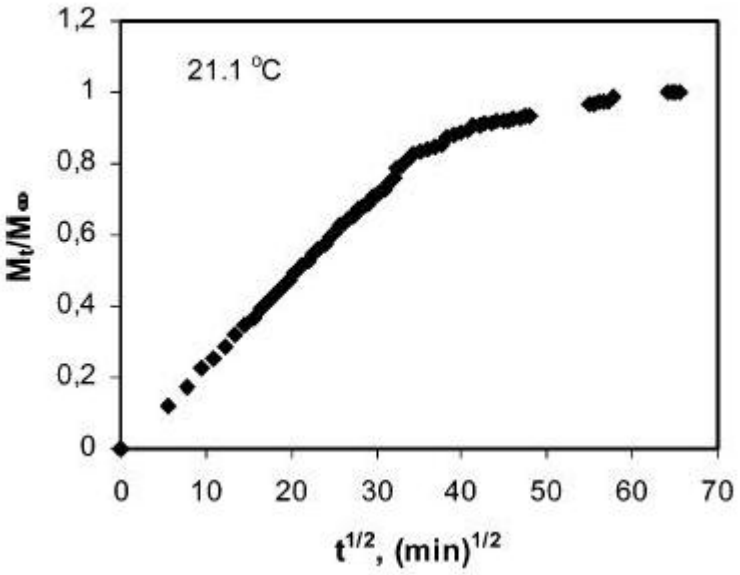

Figure 26: Illustration of change of moisture content with square root of time. The initial rate of change is almost constant.

9.1.1.2 Insulation Diagnostics Using Impedance Spectroscopy

In this method the different parameters of the Insulation under test is determined by calculating the impedance of the material. This is done in following project with the help of and Equipment from **PAX Diagnostic** called **IDAX-206**. The impedance of the sample is measured by applying a voltage across the sample. This voltage will generate current through the sample. By accurately measuring the voltage and the current, the impedance can be calculated.

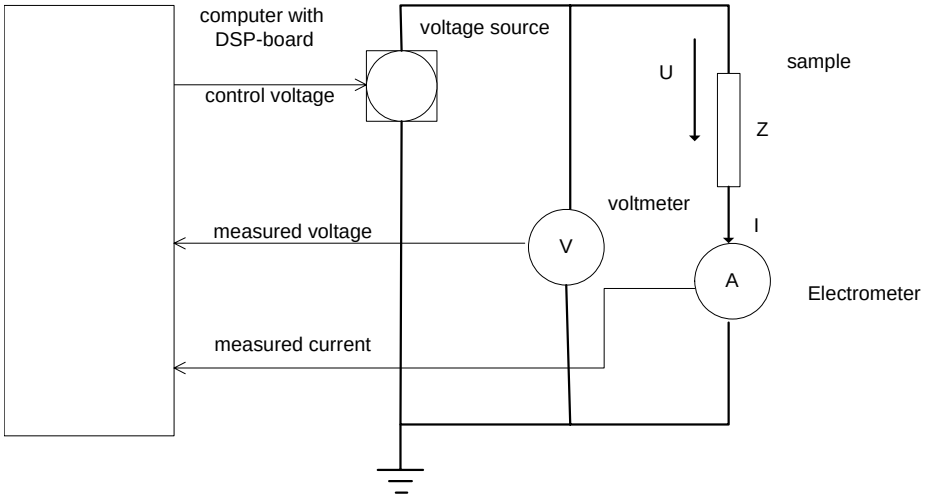

Figure 27: Measurement of electrical Impedance

The impedance is calculated using ohm's law:

$Z = U/I$

where Z, U and I are complex entities.

The voltage generated by the voltage source. The voltage is measured by means of a voltmeter and the current is measured by an ammeter or electrometer which acts as a

current to voltage converter. The analogue signals are then converted to digital samples of the signal that are used in subsequent calculations.

Insulation diagnostic is based on material characterization and therefore material models are often used. To be able to define material parameters from measured impedance Z the geometry of the sample, described in terms of the geometric capacitance C_0, has to be defined. In the picture bellow a vacuum capacitor of defined geometry is shown. Since no material is between the electrodes the capacitance of a) is the geometrical capacitance.

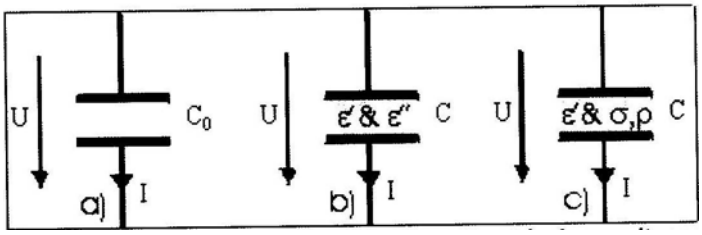

Figure 28: Material parameter models based on a geometrical capacitance C_0 and material parameter.

In picture above b) and c) a material is inserted between the electrodes and it will influence the current, I, flowing in the circuit. The influence of the material can be described by different parameters using either a dielectric model or a conductive model. In the dielectric model the "material capacitance", the permittivity is a complex function describing both the capacitance and the loss, whereas in the conductive model the capacitance is described by a permittivity and the loss by a conductivity (or resistivity). The dielectric and resistive models are derived as follows:

$$Z = \frac{1}{j\omega C}$$

$$C = C_0(\varepsilon' - j\varepsilon'')$$

Dielectric:

$$\varepsilon' = \mathrm{Re}\left\{\frac{1}{j\omega C_0 Z}\right\}$$

$\Delta\varepsilon' = \varepsilon' + k$ (k is an arbitrary constant)

$$\varepsilon'' = -\mathrm{Im}\left\{\frac{1}{j\omega C_0 Z}\right\}$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Resistive:

$$\varepsilon' = \mathrm{Re}\left\{\frac{1}{j\omega C_0 Z}\right\}$$

$$\rho = \frac{C_0}{\varepsilon_0 \,\mathrm{Re}\left\{\frac{1}{Z}\right\}}$$

$$\sigma = \frac{1}{\rho}$$

9.1.1.3 Dielectric Response in Frequency Domain

We assume here that the dielectric material is linear, homogeneous and isotropic. The material will then follow the Ampere's Law.

The current density **J(t)** through a dielectric material with an electric field **E(t)** in time domain can be expressed as:

$$J(t) = \sigma E(t) + \varepsilon_0 \frac{\partial}{\partial t}\left\{(1+\chi_e)E(t) + \int_0^t f(\tau)E(t-\tau)d\tau\right\}(A/m^2) \quad (12)$$

The Ampere's Law in time domain can be written as :

$$\nabla \times H = \sigma E + \frac{\partial D}{\partial t}(A/m^2) \quad (13)$$

If now only time-harmonic electric fields are considered the Fourier transform is applicable. The Fourier transformed Ampere's Law can be written as

$$\nabla \times H = \sigma \hat{E}(\omega) + i\omega \hat{D}(\omega)..(A/m^2) \quad (14)$$

The electric polarization in time domain is expressed as

$$P(t) = \varepsilon_0 \chi_e E(t) + \Delta P(t) = \varepsilon_0 \chi_e E(t) + \varepsilon_0 \int_0^\infty f(\tau)E(t-\tau)d\tau..(C/m^2) \quad (15)$$

If the separation of electric polarization in rapid and slow processes is done, the Fourier transformed electric polarization can be expressed as

$$\hat{P}(\omega) = \varepsilon_0 \chi_e \hat{E}(\omega) + \varepsilon_0 \hat{f}(\omega)\hat{E}(\omega) = \varepsilon_0 \left(\chi_e + \hat{f}(\omega)\right)\hat{E}(\omega)..(C/m^2) \quad (16)$$

Now the dimensionless frequency- dependent electric susceptibility $\chi(\omega)$ can be defined as

$$\hat{\chi}(\omega) = \hat{\chi}'(\omega) - i\hat{\chi}''(\omega) = \hat{f}(\omega) = \int_0^\infty f(t)e^{-i\omega t}dt \quad (17)$$

Now the total current density, $J(\omega)$ of a dielectric material under harmonic excitation, $E(\omega)$ can be expressed according to Ampere's law as:

$$\begin{aligned}\hat{J}(\omega) &= \sigma\hat{E}(\omega) + i\omega\hat{D}(\omega) = \left\{\sigma + i\omega\varepsilon_0\left(1+\chi_e+\hat{\chi}'(\omega)-i\hat{\chi}''(\omega)\right)\right\}\hat{E}(\omega) \\ &= i\omega\varepsilon_0\left\{1+\chi_e+\hat{\chi}'(\omega)-i\left(\frac{\sigma}{\omega\varepsilon_0}+\hat{\chi}''(\omega)\right)\right\}\hat{E}(\omega)..\left(A/m^2\right)\end{aligned} \tag{18}$$

From this expression it is seen that there is one part of the current $J(\omega)$ which is in phase and one part which is 90^0 before the driving harmonic electric field $E(\omega)$. The part of the current which is in phase with driving field in associated with the energy losses in the dielectric material. Two types of energy losses are seen in the material. The first type, which is due to the conduction (free charge) in the material, gives rise to ohmic losses. The second type, which is due to electric polarisation in the material, gives rise to what is called dielectric losses. Dielectric losses occur due to the inertia of the bound charges when they are accelerated in the driving field. The part of the current which is 90^0 before the driving field, displacement current, is associated with the capacitance of the material.

In many situations it is more convenient to talk about the complex permittivity which is defined as follows:

$$\hat{J}(\omega) = i\omega\varepsilon_0\left\{\hat{\varepsilon}'(\omega)-i\hat{\varepsilon}''(\omega)\right\}\hat{E}(\omega) \Rightarrow \begin{aligned}\hat{\varepsilon}'(\omega) &= 1+\chi_e+\hat{\chi}'(\omega) \\ \hat{\varepsilon}''(\omega) &= \frac{\sigma}{\varepsilon_0\omega}+\hat{\chi}''(\omega)\end{aligned} \tag{19}$$

It is seen from the equation above that the conductivity σ, the relative permittivity ε_r and the electric susceptibility $\chi(\omega)$ characterises the behaviour of the dielectric material under harmonic excitation. This equation shows that it is possible in frequency domain to make measurements which characterise the material.

9.2 Appendix B: List of Figures

9.3 Appendix C: List of Tables

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