



Norwegian University of  
Science and Technology

# Dielectric Spectroscopy of Bisphenol A Epoxy Resin Aged in Wet and Dry Conditions

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# Problem Description

The main objective with the work is to examine the effect of the combined action of high temperature and water on the long term performance of a Bisphenol A epoxy resin. This is characterized by measurements of dielectric response in frequency domain and glass transition temperature measurements by using Differential Scanning Calorimetry (DSC).

More specific, the master thesis includes:

Literature review of mechanical and electrical properties of epoxies subjected to humid environment.

Description of experimental setups, procedures and test sample materials.

Ageing of samples in wet and dry conditions.

Examine the effect of the ageing on the glass transition temperature ( $T_g$ ) of the epoxies and measure the impact on the complex permittivity.

Measurement of dielectric response in frequency domain of new and aged samples (dry and wet conditions).

To determine mechanical strength (stress-strain curve) of the epoxies.

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Deep Vaishampayan  
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## ABSTRACT

This thesis presents the laboratory test data on Bisphenol A epoxy insulation. This thesis work deals with electrical, mechanical and thermal analysis of Bisphenol A epoxy resin. The main aim of this thesis work was to examine if dry and wet aging changes the glass transition temperature ( $T_g$ ) of the epoxies and measure the impact on the complex permittivity under different ageing conditions namely dry and wet. During ageing the samples (epoxy discs and dog bones) were kept in water at 20°C, 45°C and 80°C both in dry and wet conditions for a period of one month. After the samples were removed from ageing they were conditioned in a vacuum oven for one week.

The effect of temperature and relative humidity on unaged epoxy i.e. dry characterization was determined by keeping the samples in climate chamber with 15%RH (Relative Humidity) and temperatures 20°C, 45°C and 80°C. The wet characterization was carried out with 90%RH and temperatures 20°C, 45°C and 80°C. The surface of these samples was painted with silver paint (electrodes). Two circular discs were used for dielectric response measurement and 2 rectangular pieces for water sorption measurement. The dielectric response was measured when equilibrium/saturation condition was achieved. The dielectric response was measured in the frequency range from 0.01 Hz to 1000 Hz at 200 volts (peak). The wet characterization showed  $\epsilon'$  increases with aging temperature. The dielectric loss  $\epsilon''$  was also increasing with the temperature. It can be deduced that the water uptake by the epoxy increases with increase in humidity and temperature. The dry characterization showed  $\epsilon'$  and  $\epsilon''$  has steady growth with aging temperature. Therefore it can be deduced that characterization done in dry condition didn't significantly affect the complex permittivity as compared with wet characterization.

The glass transition temperature ( $T_g$ ) of the samples were found using DSC (Differential Scanning Calorimetry) with a heating rate 20°C/min. The  $T_g$  was 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  $T_g$  of the epoxy polymer was studied.  $T_g$  was increasing with aging temperature, for both dry as well as wet samples. The increase in the value can be mainly attributed to post curing process of the epoxy.

The mechanical strength of the epoxy was studied by applying a tensile force to the dog bone shaped samples till breakdown and the stress versus strain curve was detected. This test was also performed on the dry aged sample before water absorption, then in sample which was kept under water at 20°C, 45°C and 80°C for absorption, and in sample which has undergone absorption and desorption at 20°C, 45°C and 80°C. The difference between the stress-strain curves was documented and discussed. The ageing temperature plays a significant role in reducing the value of stress and percentage strain at max. For dry aged epoxy, stress reduces around 14% from 20°C to 80°C. However for wet aged epoxy samples tensile strength reduces around 25%. For dry aged samples % strain reduces around 0,3 % and for wet aged samples it reduces around 0,5%.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS .....	1
ABSTRACT .....	2
1. INTRODUCTION .....	4
2. THEORY.....	5
2.1 Basis of epoxy insulation .....	5
2.2 Electrical properties of epoxy.....	6
2.3 Mechanical properties of epoxy.....	7
2.4 Fundamentals of glass transition temperature (T <sub>g</sub> ).....	8
2.5 Dielectric Response.....	10
2.6 Water Diffusion .....	11
2.7 Principles of Differential Scanning Calorimetry (DSC).....	12
3. PREPARATION OF EPOXY SAMPLES .....	15
3.1 Test samples .....	15
3.2 Ageing methods and preconditioning of samples.....	17
4. MEASUREMENT PROCEDURES .....	18
4.1 Water diffusion.....	18
4.2 Glass Transition Temperature (T <sub>g</sub> ).....	18
4.3 Dielectric Response.....	20
4.4 Mechanical testing (stress-strain curve).....	21
5. EXPERIMENTAL RESULTS AND DISCUSSION .....	22
5.1 Glass Transition Temperature (T <sub>g</sub> ).....	22
5.2 Dielectric Response.....	24
5.3 Mechanical Testing.....	27
6. CONCLUSIONS .....	30
7. FUTURE WORK.....	31
8. REFERENCES .....	32
9. APPENDICES .....	34
9.1 Theoretical Background.....	34
9.1.1 Mathematical Relations in the Frequency Domain .....	34
9.1.2 Expression of dielectric response in frequency domain.....	35
9.1.3 Insulation diagnostic using dielectric spectroscopy .....	36
9.2 Equipments used.....	38
9.2.1 Insulation Diagnostic Analyzer.....	38
9.2.2 Binder Vacuum Drying Oven .....	38
9.2.3 Vötsch Temperature & Climate Test Systems.....	39
9.2.4 Mettler Toledo Weighing Scale.....	39
9.2.5 Sample holder.....	40
9.2.6 Mettler Toledo DSC .....	40
9.2.7 Lloyd Instruments .....	41
9.3 List of figures .....	42
9.3.1 DSC curves.....	42
9.3.2 Stress-Strain Curves.....	44

## 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. [3]

The epoxy resins are distinguished among thermosetting resins, by their ease of handling, thermal stability, chemical resistivity and their outstanding mechanical and electrical properties. Epoxy is one of the most used materials for offshore oil and gas applications. Epoxy resins are widely used as matrices for structural composite materials, adhesives and organic coatings due to their good mechanical properties. As the epoxy materials used in sub sea oil and gas production experiences a very high variation in temperature as well as electric stress, it is necessary to study the effects of these factors in the properties of epoxy material.

Sensitivity of epoxy to humidity is indeed a serious matter of concern, when subjected to humid environments, these materials can absorb up to a few weight percent of water, leading to an overall degradation of the dielectric properties (lowering of resistivity, decrease in breakdown voltage, rise in dielectric constant and loss and affecting mechanical strength). Also the changes it may happen to its glass transition temperature and complex permittivity values. However, it is well known that these properties are strongly affected by moisture absorption, which causes plasticization, lowering glass transition temperature and diminishes their mechanical strength. [1]

In order to investigate the effects of the above mentioned issues it is important to study the aging phenomenon on the epoxy. However in the laboratory similar conditions which may occur in the service life are created and its effects on epoxy are studied. An attempt is made to study the effect of water on the dielectric properties of the material. The main aim of this thesis is to concentrate on the effect of water absorption and temperature on epoxy materials. Also to examine if wet ageing changes the glass transition temperature ( $T_g$ ) of the epoxies and measure the impact on the complex permittivity.

## 2. THEORY

### 2.1 Basis of epoxy insulation

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 in 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 coloring 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. The thermal conductivity increases when we add fillers.

The curing process is an exothermic chemical reaction, causing great heating in the inner parts of an object. Thus excessive internal mechanical stress may be “frozen” in during the curing process. This problem increases with the increasing size of the cast epoxy object, making it necessary to control the temperature of the curing process to facilitate stress relaxation.

At high temperature epoxy become soft, but does not melt. Above this “deflection temperature” both polar molecular groups and charge carriers move more freely. This causes a strong increase in both permittivity and dielectric loss.

Epoxy resins are extremely useful for their high mechanical strength, good adhesion to materials and metals (except polythene) and resistance to moisture. They are been used in high voltage switchgear, electrical machine insulation and in offshore oil & gas application. They are also finding application in low and high voltage transformer winding encapsulations as well as spacers for SF6 GIS installations. Glass-fiber-reinforced rods for overhead line polymeric insulators are another field of their application. [2]

The preparation of epoxy resins is performed normally by reaction of polyphenols, preferably diphenols of the type represented by 4,4'- dihydroxy diphenylmethane (Bisphenol A), with epichlorohydrin. This reaction yields the diglycidylether, or low molecular weight polymers, of Bisphenol A which have epoxide end-groups. [14]

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. [3]

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  $\approx 35^\circ$  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.

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. [3]

## 2.2 Electrical properties of epoxy

The electrical properties of the polymers to be measured are somewhat a function of whether the insulation is for magnet wire or for high voltage applications. For alternating current uses, the loss factor ( $\epsilon''$ ) and the dielectric constant or permittivity ( $\epsilon'$ ) are important electrical properties. These dimensionless quantities are constantly changing as a polymer cures. The relationship of the chemical nature of the polymer to its effect on these values is still uncertain and the values cannot be predicted, nor conversely can the chemical nature be evaluated from the  $\epsilon''$  values. Another value that is commonly determined is the dissipation factor (DF), loss tangent, or tan delta, which is the ratio  $\epsilon''/\epsilon'$ , sometimes expressed as a percent by multiplying the ratio by 100. These values express the response of the polymer to an external electrical field and can predict the possible failure of the insulation within an alternating current field.

If a cured epoxy polymer is subjected to dielectric measurements while its temperature is raised, a curve somewhat like Fig. 1 is obtained. The initial hump is caused by dipoles that are responding to the ac current. Once the polymer is warmed enough to allow ionic conduction, the movement of the ions is enough to contribute to heating, and the runaway thermal heating shown by the increasing second leg occurs. There are always enough ions in the polymer to cause this effect, so merely purifying the polymer to remove the ions is not enough to eliminate this condition. The only practical way is to cause the polymer to have a high enough  $T_g$  so that the runaway does not occur below the use temperature. Obviously the position of the curve in Fig. 1 is influenced by the frequency, so measurement and use frequency should be comparable. For high voltage applications, the tan delta commonly expressed as the percentage loss is expected to be less than 4% up to the operating temperature. The runaway temperature is the extrapolated point of the final curve back to the baseline. While the frequency of the measurement affects the position of the curve (the example is at 100 Hz), under controlled conditions, the temperature can give an indication of the insulation usefulness. [3]

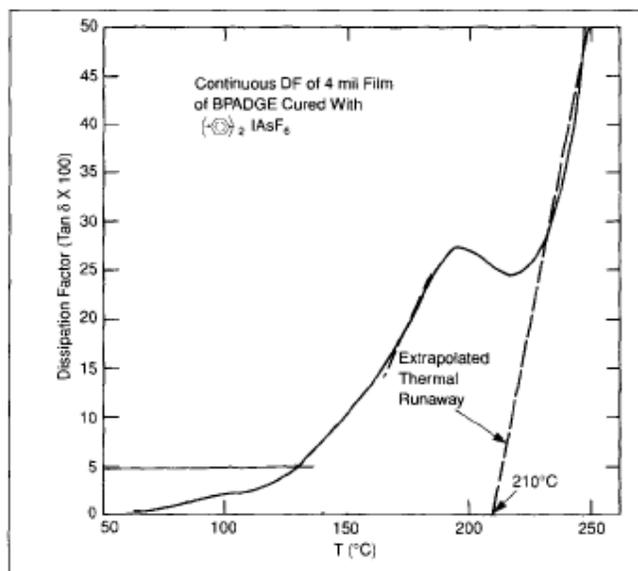


Fig.1: Plot of dissipation factor (as %) versus temperature for a typical cured epoxy polymer.

### 2.3 Mechanical properties of epoxy

The mechanical properties may be considered the most important of all the physical and chemical properties of high polymers for most applications. Thus everyone working with such materials needs at least elementary knowledge of their mechanical behaviour and how this behaviour can be modified by the numerous structural factors that can be varied in polymers. There are a great many structural factors that determine the nature of the mechanical behaviour of such materials. The following structural factors, in addition to the chemical composition, affect all of the major mechanical properties of polymers.

- Molecular weight
- Cross-linking and branching
- Crystallinity and crystal morphology
- Copolymerization (random, block and graft)
- Plasticization
- Molecular orientation
- Fillers
- Blending
- Phase separation and orientation ion blocks, grafts and blends

In addition to the structural and molecular factors listed above, the following environmental or external variables are important in determining mechanical behaviour:

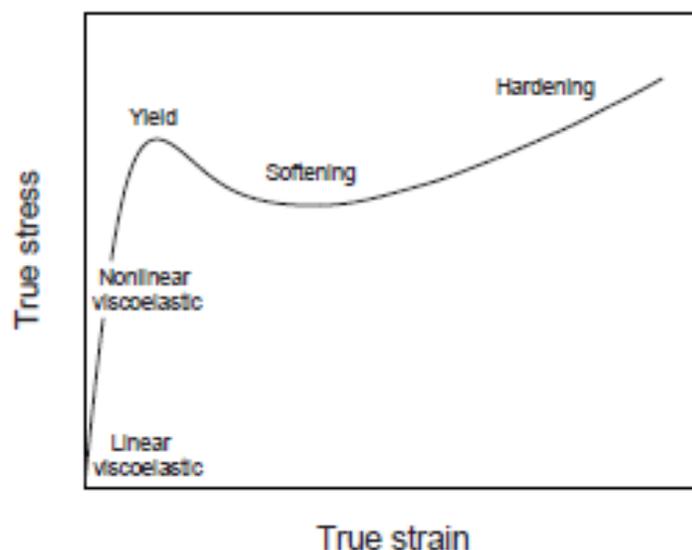
- Temperature
- Time, frequency, rate of stressing or straining
- Pressure
- Stress and strain amplitude
- Type of deformation (shear, tensile, biaxial, etc.)
- Heat treatment or thermal history
- Nature of surrounding atmosphere, especially moisture content

There is strong dependence on temperature and time of the properties of polymers compared to those of other materials such as metals. This strong dependence of properties on temperature and on how fast the material is deformed (time scale) is a result of viscoelastic nature of polymers. Viscoelasticity implies behaviour similar to both viscous

liquids in which the rate of deformation is proportional to the applied force and to purely elastic solids in which the deformation is proportional to the applied force. In viscous systems all the work done on the system is dissipated as heat, whereas in elastic systems all the work is stored as potential energy, as in a stretched spring. [15]

- o **Intrinsic deformation behaviour**

Intrinsic deformation is defined as the materials' true stress-strain response during homogeneous deformation. Since generally strain localization phenomena occur (like necking, shear banding, crazing and cracking), the measurement of the intrinsic materials' response requires a special experimental set-up, such as a video controlled tensile or an uniaxial compression test. Although details of the intrinsic response differ per material, a general representation of the intrinsic deformation of polymers can be recognized, see Fig. 2



**Fig. 2: Schematic representation of the intrinsic deformation behaviour of a polymer material.**

Initially we find a viscoelastic, time-dependent, response that is considered to be fully reversible. For small loads the material behaviour is linear viscoelastic, while with increasing load the behaviour becomes progressively nonlinear. At the yield point the deformation becomes irrecoverable<sup>1</sup> since stress-induced plastic flow sets in leading to a structural evolution which reduces the material's resistance to plastic flow: strain softening. Finally, with increasing deformation, molecules become oriented which gives rise to a subsequent increase of stress at large deformations: strain hardening. [16]

## 2.4 Fundamentals of glass transition temperature (T<sub>g</sub>)

Glass Transition is a method to characterize a property of a polymeric material. The glass transition is the temperature where the polymer goes from a hard, glass like state to a rubber like state. The best way to envision this type of transition is to put a rubber band (rubber like state, very flexible) into a container of liquid nitrogen. When removed the rubber band is solid and inflexible (glass state) and in fact the rubber band can be shattered. Upon standing and warming to room temperature the rubber band will again become flexible and rubbery (rubber like state).

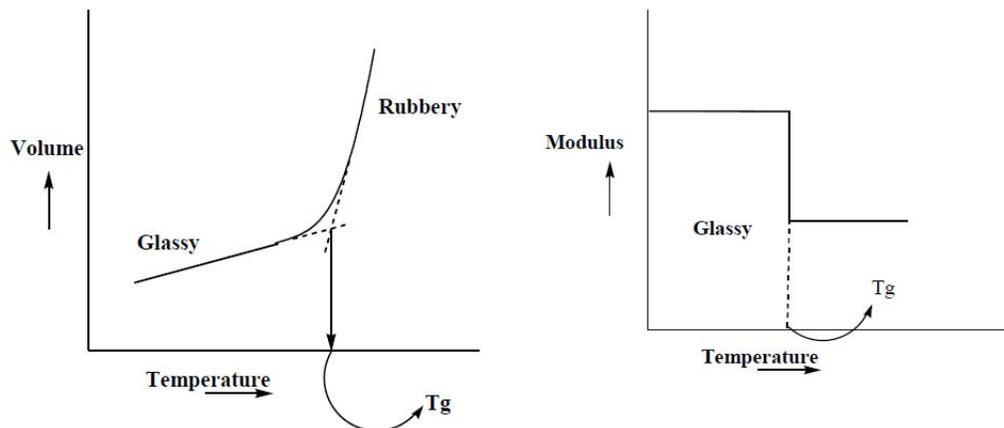
DSC defines the glass transition as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state. This is a second order endothermic transition

(requires heat to go through the transition) so in the DSC the transition appears as a step transition and not a peak such as might be seen with a melting transition. At low temperatures, all amorphous polymers are stiff and glassy, sometimes called as the Vitreous State, especially for inorganic polymers. On Warming, polymers soften in a characteristic temperature range known as the glass-rubber transition region.

The glass transition temperature ( $T_g$ ), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states.  $T_g$  constitutes the most important mechanical property for all polymers. In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured.

The following physical properties undergo a drastic change at the glass transition temperature of any polymer:

- a) hardness
- b) volume
- c) modulus (Young's module)
- d) percent elongation-to-break



**Fig.3: Volume Vs Temperature and Modulus Vs Temperature plots**

Young's Modulus  $E$  may be written as:

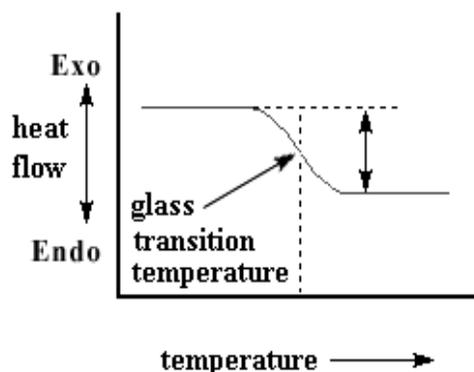
$$\sigma = E\varepsilon$$

$\sigma$  = Tensile stress;  $\varepsilon$  = Tensile strain

Young's modulus is a fundamental measure of the stiffness of the material. The higher its value, the more resistant the material is to being stretched.

Unit of  $E$ : dynes/cm<sup>2</sup> (10 dynes/cm<sup>2</sup> = 1 Pascal)

When we heat the polymer a little more after a certain temperature, the plot will shift downward suddenly,



**Fig. 4: Heat flow Vs Temperature plot**

This means heat is being absorbed by the sample and that we have an increase in its heat capacity. This happens because the polymer has just gone through the glass transition. Polymers have a higher heat capacity above the glass transition temperature than they do below it. Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a polymer's glass transition temperature. We usually just take the middle of the incline to be the T<sub>g</sub>. [8]

The glass transition temperature (T<sub>g</sub>) 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 (T<sub>m</sub>) 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 T<sub>g</sub>, and cure effectively stops once the T<sub>g</sub> 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 T<sub>g</sub>, because the water effect causes a disastrous failure. It is known that water can cause a 20° to 30°C drop in T<sub>g</sub> of an epoxy. This drop can cause the tensile strength of the epoxy to drop from 40% to 75%. When more cross links are present the drop in T<sub>g</sub> 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 T<sub>g</sub> [3].

## 2.5 Dielectric Response

Dielectric response is a method used for characterisation of dielectric materials as well as practical insulation systems. Classical methods of measuring dielectric response include (power frequency) capacitance-Tan  $\delta$  and insulation resistance. More recently extensions such as measurements of dielectric frequency response, polarisation and de-polarisation currents and return voltage have found increasing popularity. [6]

Dielectric response can be measured either in time or frequency domain. In time domain this is based on subjecting a DC voltage and measurement of currents as a function of time. In

frequency domain this is based on subjecting an AC voltage and measurement of capacitance and dielectric loss as a function of frequency. The mathematical relations and expression of dielectric response are presented in Appendix 9.1.1 and 9.1.2 respectively.

The basic idea behind a frequency domain measurement is to study the response of the dielectric material from a sinusoidal excitation of one arbitrary frequency. A frequency domain measurement is because of this, compare to a time domain measurement, a narrow-band measurement. The advantage with a narrow-band measurement is that the measurement equipment can be tuned into the measurement frequency and by this reduce the influence of noise. The drawback with this is that repeated measurements must be done in order to reveal the whole frequency spectrum of the dielectric material. Even though it is possible to filter away most of the noise in a narrow-band measurement it is preferable to chose the measurement frequency in such a way that known disturbances are avoided. For example it is better to measure at 47 Hz than 50 Hz if 50 Hz is the net frequency. It is also possible to study non-linearities in a dielectric material with a frequency domain measurement. This is done by looking at the fundamental measurement frequency and the higher harmonics. [10]

Dielectric spectroscopy analysis technique was used in this thesis to determine complex permittivity  $\varepsilon^*(f) = \varepsilon'(f) + j\varepsilon''(f)$ . The real and imaginary part of the permittivity was analyzed with respect to frequency. The measuring technique - insulation diagnostic using dielectric spectroscopy is stated in Appendix 9.1.3

The geometric capacitance ( $C_0$ ) of the epoxy disc was calculated by:

$$C_0 = \varepsilon_o \left\{ \frac{A}{d} \right\} \quad (1)$$

Where  $\varepsilon_o$  is the permittivity of free space =  $8.854 \times 10^{-12}$  F/m, **A** is the area of the effective electrode rested on the disc = 75mm and **d** is the thickness of the disc= 1mm

The value of calculated geometric capacitance (**C<sub>0</sub>**) = 3.91 pF

The actual real  $\varepsilon'$  and imaginary  $\varepsilon''$  values of complex permittivity are calculated by

$$\varepsilon' = \frac{c'}{C_0} \quad (2)$$

Where **c'**= real part of the capacitance value, **C<sub>0</sub>**= geometric capacitance of epoxy disc and  $\varepsilon'$  = real part of the complex permittivity

$$\varepsilon'' = \frac{c''}{C_0} \quad (3)$$

Where **c''**= imaginary part of the capacitance value, **C<sub>0</sub>**= geometric capacitance of epoxy disc and  $\varepsilon''$ = imaginary part of the complex permittivity

## **2.6 Water Diffusion**

Diffusion may be defined as the process by which matter is transported from one part of system to another by random molecular motions. [5]

The moisture diffusion in epoxy has been frequently represented by Fick's two laws which describe the diffusion of water or any other liquid through a solid material. Fick's First Law is used in steady state diffusion, i.e., when the concentration within the diffusion volume does

not change with respect to time. Fick's first law states that in the steady state condition, the flux of water  $J$  [ $\text{g}/\text{mm}^2$ ] through a solid is proportional to the gradient of the water concentration [ $\text{g}/\text{mm}^3$ ]. [4]

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. The water in epoxy is present in two states [19]:

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

Epoxy is hygroscopic in nature and absorbs water when exposed to humidity. The absorption and diffusion of water in polymeric materials such as epoxy systems is related to the free volume and the polymer–water affinity. The amount of free volume depends on the molecular packing and is affected by both the crosslink density (and therefore the extent of curing) and physical aging. The polymer–water affinity is significantly influenced by the presence of hydrogen-bonding sites within the polymer. Water can sometimes be absorbed without causing swelling; when this happens, it is suggested that it remains unbound to the polymer and is effectively accommodated within the free volume. On the other hand, bound water molecules that attach to the polymer through hydrogen bonds disrupt the inter-chain hydrogen bonds and induce swelling and plasticize the polymer. [14]

In this report moisture diffusion is not calculated, just it is introduced, as the main purpose was to know the water uptake in the epoxy and to find out whether epoxy sample has reached the equilibrium state. The figure shown below illustrates the saturation condition. Where in after 80% the curve straightens or is flat enough to conclude the equilibrium condition in the sample.

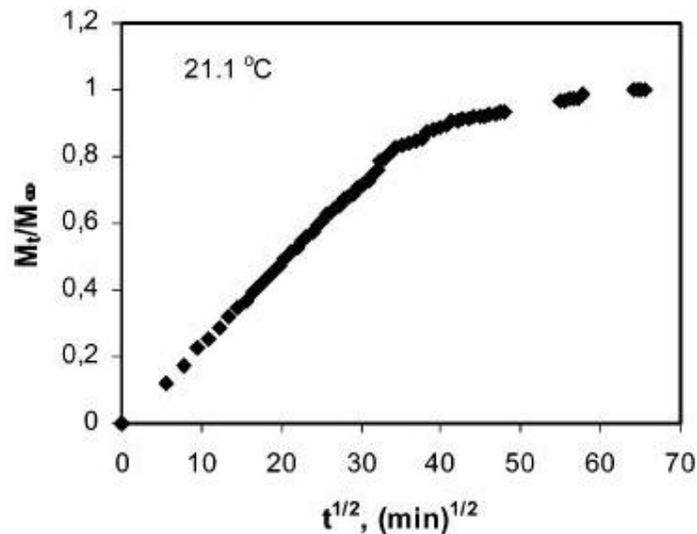
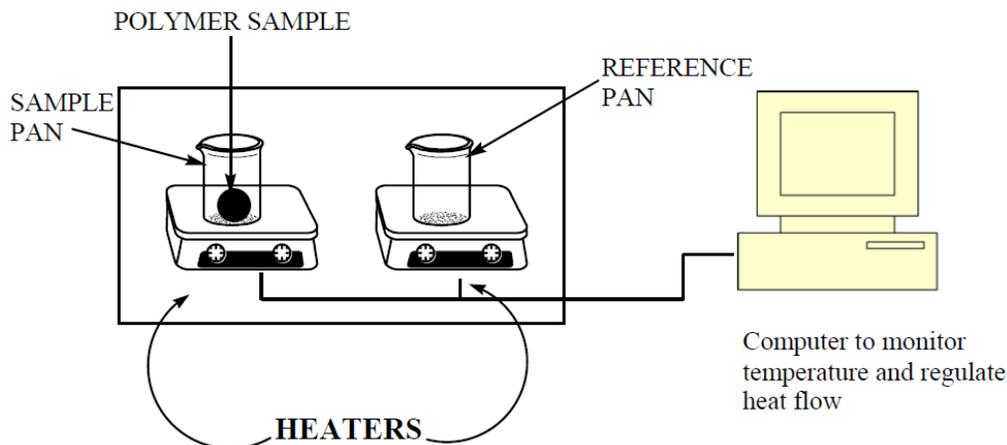


Fig. 5: Illustration of change of moisture content with square root of time. The initial rate of change is almost constant.

## 2.7 Principles of Differential Scanning Calorimetry (DSC)

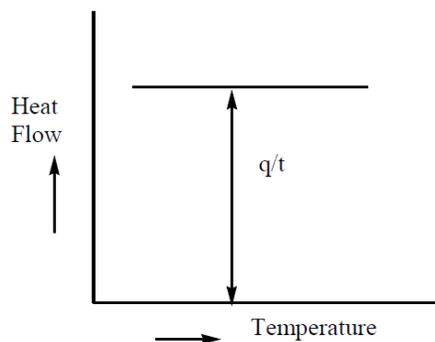
Differential scanning calorimetry is a technique that is used to study the thermal transition of a polymer. Thermal transitions are the changes that take place when a polymer is heated. The melting of a crystalline polymer and the glass transition ( $T_g$ ) are examples of thermal transitions.



**Fig. 6: DSC setup**

The device that is used to measure  $T_g$  and other thermal transitions (such as the melting and crystallization temperatures) is shown in the Figure. This device consists of two pans. In one pan, the polymer sample is loaded. The other pan is the reference pan and is normally left empty. These two pans are located on top of a heater. The computer assembly will turn on the heaters and the heating rates ( $q/t$ ) of the two pans are accurately controlled (about 10 C per minute). The computer programs the heating rate to stay exactly the same through out the experiment. It is also important to note that the two separate pans, with their heaters are heated at the same rate as each other.

The presence of polymer material in the sample pan results in an uptake of more heat in order to keep the temperature of the sample pan increasing at the same rate as the reference pan. This means that the heater underneath the sample pan will provide more heat energy than the heater under the reference pan. The DSC experiment is all about the measurement of how much heat that the sample pan heater has to put out as compared to the reference pan heater. In DSC experiments the data of temperature increase ( $T$ ) are plotted against the difference in heat output of the two heaters at a given temperature. Mathematically,



**Fig. 7: Heat flow Vs temperature plot**

The computer will provide plots of the difference in heat output of the two heaters against temperature. This means that the above plot is the heat absorbed by the polymer against temperature.

$$\text{Heat / time} = q/ t = \text{heat flow}$$

$$\text{Temperature increase/ time} = \Delta T/t = \text{heating rate}$$

When we divide the heat flow  $q/t$  by the rate of heating  $\Delta T/t$ . We obtain:

$$(q/t)/(\Delta T/t) = q/\Delta T = C_p = \text{Heat Capacity}$$

The amount of heat it takes to get a certain temperature increase in a material is called *heat capacity*, or  $C_p$ . Heat capacity is obtained by dividing the heat supplied by the temperature increase. Therefore DSC plot gives  $C_p$ . [10]

### DSC Measuring Principles

ISO 11357-1 [1] and DIN 51005 [2] identify two DSC methods for measuring the difference between thermal transitions in a specimen and those in a reference material:

- Heat-flux DSC
- Power-compensation DSC

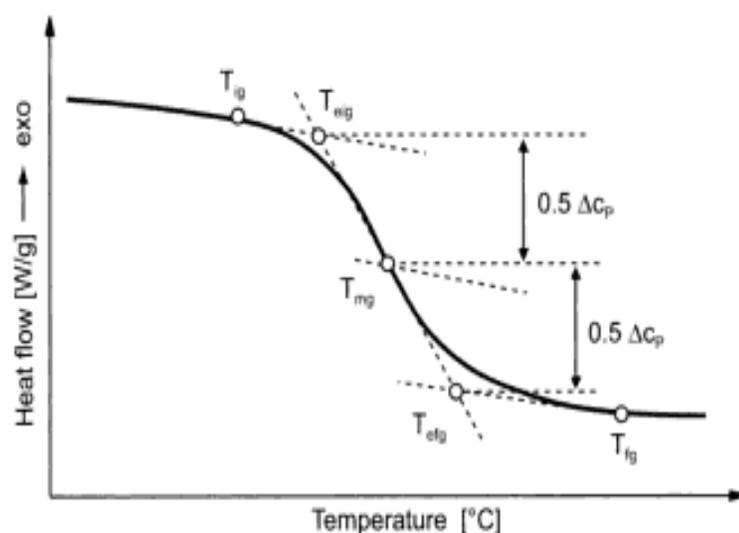
In **heat-flux DSC**, the test chamber consists of a furnace in which the specimen and reference material are heated or cooled together according to a controlled temperature program. The temperature of two points of measurement, which are located on a thermally conducting metal disc, is measured continuously. As long as the specimen and the reference material respond to the temperature program in the same way, the heat flux into both the specimen and the reference material remains constant. Thus, the temperature difference between the two points of measurement is also constant.

#### Advantages of **heat-flux DSC**

- Robustness.
- Easy handling.
- Straight forward measurement, even in the case of offgassing specimens.
- Heating curves have a stable baseline and permit glass transitions to be measured very clearly.

In **power –compensation DSC**, the test chamber consists of two small, separate furnaces that are controlled independently by a defined primary heating program. If an exothermic or endothermic reaction in the specimen leads to a temperature difference between the two furnaces, power (energy) is applied to or removed from the specimen furnace to compensate for the energy change in the specimen.

Power-compensation DSC can be used to measure very rapid reactions because the small furnaces have low time constants. As electrical compensation occurs very quickly, the temperature differences between specimen and reference material are very small. [9]



$T_{ig}$	<i>Onset temperature:</i>	<i>Temperature of first detectable deviation from the baseline</i>
$T_{eig}$	<i>Extrapolated onset temperature:</i>	<i>Intersection of the inflectional tangent with the extrapolated baseline for temperatures below the glass transition</i>
$T_{mg}$	<i>Midpoint temperature, glass transition temperature:</i>	<i>Temperature at which half of the change in specific heat capacity (<math>0.5\Delta c_p</math>) has occurred; the temperature at which a line connecting the extrapolated baselines before and after the glass transition intersects with the DSC curve</i>
$T_{eig}$	<i>Extrapolated end temperature:</i>	<i>Intersection of the inflectional tangent with the baseline extrapolated from temperatures above the glass transition</i>
$T_{fg}$	<i>End temperature:</i>	<i>Temperature of the last detectable deviation from the baseline</i>
$\Delta c_p$	<i>Change in specific heat capacity:</i>	<i>Step height of endothermic glass transition</i>

**Fig. 8: Characteristic temperatures of a glass transition, based on ISO 11357-1[1]**

### 3. PREPARATION OF EPOXY SAMPLES

#### 3.1 Test samples

The main aim of the project is characterization of unfilled epoxy polymer (Bisphenol-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.

Bisphenol A epoxy systems (i.e resin plus curing agent) have a variety of industrial uses including as adhesives, molding resins, surface coatings and reinforced plastics. Also used in electrical industry as insulators and encapsulating agents for power transformers, insulation of coil in rotating machines as well.

The work for this thesis includes fabrication of epoxy samples and then performing different tests on them for characterization.

The unfinished epoxy samples were made circular in shape with smoothing the edges. Disc samples were used for dielectric characterization. Figure 8 shows the disc samples with silver painted electrodes. The disc samples have dimensions 1mm thick X 94 mm diameter. The rectangular pieces were prepared for water sorption measurements having dimensions 10 mm X 30 mm.

The dog bone shape epoxy samples were used for mechanical (stress-strain) test. The dimensions of the dog bone were 4 mm X 115 mm X 10 mm.

Two disc samples were used for measuring of dielectric response at each setting of temperature and relative humidity, just to check uniformness in the readings. 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.

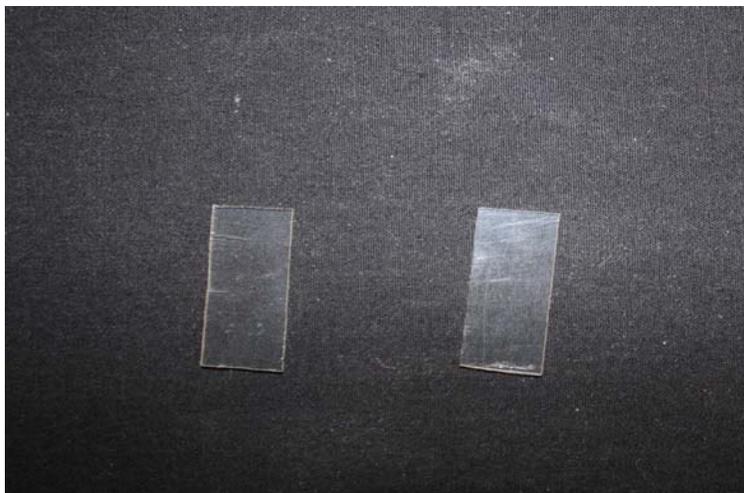
The samples were casted in different shapes for different kind of tests. The following are the shapes, in which the epoxy samples were casted. [11]



**Fig. 9: Epoxy disc sample (1mm thick X 94 mm diameter ) used for dielectric characterization.**



**Fig. 10: Dog bone shaped epoxy sample (4 mm X 115 mm X 10 mm) used for mechanical (stress-strain) measurements.**

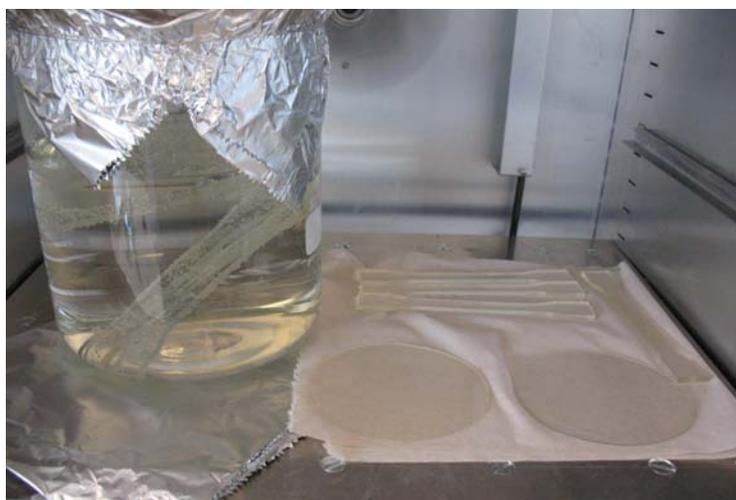


**Fig. 11: Rectangular shape epoxy sample (10 mm X 30 mm X 1 mm) used for water sorption measurements.**

### **3.2 Ageing methods and preconditioning of samples**

The epoxy samples (dog bone shaped and disc shaped) were immersed in tap water for one month. For wet aging the samples were kept in ovens with different settings viz. 20°C i.e. at room temperature, 45°C at T<sub>g</sub> and 80°C in a glass beaker containing tap water. For dry aging the samples were kept in the oven ovens with different settings viz. 20°C i.e. at room temperature, 45°C at T<sub>g</sub> and 80°C just besides the glass beaker as shown in fig.12

After removing the samples from the glass beaker the samples were conditioned in a vacuum oven for one week at room temperature. The glass transition temperature, dielectric response measurement and mechanical stress-strain measurements were carried out.



**Fig. 12: Epoxy samples wet aged in water and dry aged.**

## 4. MEASUREMENT PROCEDURES

### 4.1 Water diffusion

In this thesis the application of dielectric spectroscopy to analyze the effect of temperature and relative humidity is presented. Two circular discs and 2 rectangular epoxy pieces were selected.

The circular disc was used for dielectric response measurement and rectangular pieces for water sorption measurement with set temperature and relative humidity.

The procedure used for water sorption measurement is as follows:

- Two rectangular pieces of dimension 30mm x 10 mm x 1 mm were used in this experiment. See fig. 11
- Before being subjected to humidity, all the samples were dried in a vacuum oven at 50° C for approximately 7 days.
- The samples were then transferred to the climate chamber where in the temperature at 20°C, 45°C, 80°C and relative humidity at 90% were set.
- After regular intervals of time the weight gain of the samples were checked as a percentage of the original dry weight with the help of Mettler Toledo UMX 2 weighing scale.
- Water uptake was measured by weighing the samples with a precision balance (0.01 mg resolution)
- Prior to weighing, the samples were wiped off with absorbent paper in order to ensure no water remained on the surface.
- Also prior to weighing, the samples were passed through a de-ionizing unit to remove static charge on the sample as this can be a serious error source for some materials. The sample is put on the weight and after 15 seconds the weight is recorded. (15 seconds is the typical stabilization time for the balance)
- The total time from removal from climate chamber to the recorded value of mass increase (due to water sorption) should be approximately 1 minute.
- The above procedure is repeated until the equilibrium/saturation condition is achieved i.e. no further water uptake is recorded.

### 4.2 Glass Transition Temperature (Tg)

Differential scanning calorimetry (DSC) was used to investigate the glass-transition temperatures of epoxy materials i.e. the thermal analysis of Bisphenol A epoxy resin. The glass-transition temperature is determined as the mid-point of a temperature range over which the glass transition takes place. The glass transition temperatures of all epoxy samples were tested by a differential scanning calorimeter (Mettler Toledo HP DSC822). The glass-transition temperatures of the materials were measured as a heat flow measured as function of temperature. From the results of the glass-transition temperatures measured by DSC, the information about change in Tg might be estimated. **Heat-flux DSC** measuring

principle was used for this experiment. The test chamber consists of a furnace in which the specimen and reference material are heated or cooled together according to a controlled temperature program.

The steps involved in conducting a DSC experiment are as follows:

- Specimen preparation: The specimen and the reference were prepared by using 20 $\mu$ l container/pan. An empty pan is usually placed in the reference chamber.
- Specimen mass: The specimen is weighed on a weighing scale and its mass of 10 to 20mg is recommended for measurement of glass transitions.
- Pan: The pans and lids are made of aluminum. The specimen and (reference) empty pan are sealed with the aid of a press. The specimen and reference pans are placed into the test chamber/ furnace. To prevent the evaporating water from causing the pressure to build up, a small hole was punched in the lid of the pan. The cover of DSC-module is closed by placing it on top of the specimens.
- Purge Gas: To avoid the reactions with the environment, the chamber is purged with inert gas during experiment. Nitrogen gas and liquid nitrogen was used. Nitrogen gas and liquid flow is adjusted by opening main valve on the cylinders. The safety valve on pressure regulator is opened.  
The gas pressure was set to 5 bar on pressure regulator and gas flow to 55 ml/min.
- Temperature program: The temperature program was chosen to suit the material and specimen. The T<sub>g</sub> test was performed twice on each sample and the reading obtained on the second test was considered
- Starting temperature & End temperature: From the software program method was created for performing the glass transition test with T<sub>min</sub> -50<sup>o</sup>C to T<sub>max</sub>100<sup>o</sup>C with a total 35min duration time. The end temperature of T<sub>g</sub> should be approx. 50<sup>o</sup>C higher than that of transition, which was considered. The temperature and heat flux signal was constantly monitored.
- Heating & Cooling rate: The heating rate of 20<sup>o</sup>C/min was used for the experiment. The cooling rate should be same as heating rate, especially if the specimen is cooled to the starting temperature and then heated up again, which was maintained.
- 1<sup>st</sup> heating scan: Called as initial run, reveals the information about current specimen condition (thermal & mechanical history) i.e. processing influences, crystallinity and curing, service temperature.
- 2<sup>nd</sup> heating scan: 2<sup>nd</sup> run was used for determining characteristic properties of the material.
- Evaluation/Interpretation: After setting the temperature program, start the experiment by inserting the temperature and record the onset and midpoint temperatures. After completing the experiment, the transitions were evaluated and interpreted.

### 4.3 Dielectric Response

Dielectric spectroscopy analysis technique was used in this project to determine complex permittivity  $\epsilon^*(f) = \epsilon'(f) + j\epsilon''(f)$  i.e. electrical analysis of Bisphenol A epoxy resin. The real and imaginary part of the permittivity was analyzed with respect to frequency. The dielectric loss was also measured at different humidity's. For measurement of dielectric loss with respect to temperature was done on epoxy samples dry and wet aged. Two disc samples were used for each set of aging temperature and dielectric response was measured for both the discs.

The procedure used for dielectric response measurement is as follows:

- The dielectric response was measured before drying and after drying.
- Circular epoxy disc samples of diameter 94mm with thickness of 1 mm were used.
- The surfaces were painted with silver paint. This silver paint being highly conductive acts as an electrode.
- The dielectric loss at different frequency was measured with the help of IDAX-206 instrument.
- The samples were then transferred to the climate chamber where in the temperature at 20<sup>o</sup>C, 45<sup>o</sup>C, 80<sup>o</sup>C and relative humidity at 90% were set. At this temperature and relative humidity the complex permittivity was studied.
- For temperature at 20<sup>o</sup>C, 45<sup>o</sup>C, 80<sup>o</sup>C and relative humidity 15% the disc samples were just kept for 24 hours in the climate chamber for each temperature range and then dielectric characterization was carried out.
- The frequency at which the losses are measured was from 0.01 Hz to 1000 Hz with 4 measurement points per decade.
- The dielectric characterization was measured at 200 volts peak with ungrounded specimen test (UST) configuration. However for 80<sup>o</sup>C characterization temperature setting the IDAX setup/software gave errors in readings for 200 V therefore 10 Volts was used for 80<sup>o</sup>C temperature setting.
- The dielectric response was measured when equilibrium/saturation condition was achieved i.e. no further water uptake was recorded. The results were documented.

#### 4.4 Mechanical testing (stress-strain curve)

With respect to finding the characteristics of the epoxy, it is important to find the mechanical properties i.e. mechanical analysis of Bisphenol A epoxy resin. It's an important properties looked at in many industrial applications. The dog bone shaped samples were used for testing. All the tests were carried out at room temperature and 4 specimens were used at each experiment.

The procedure for stress-strain measurement is as follows:

- The Dog bone shaped epoxy samples of dimensions 4 mm X 115 mm X 10 mm were used.
- Lloyd Instruments LR 5K is the equipment for applying the tensile force on the dog bone.
- The sides of the dog bones were held in a jaw like structure.
- The apparatus is controlled from a computer program from which the command is given to the test sample.
- The sample is then subjected to force from one end until it gets broken in two pieces.
- Four dry and wet samples with temperature 20<sup>0</sup> C, 45<sup>0</sup> C and 80<sup>0</sup> C were tested and stress, strain and extension values were determined.
- The standard deviation and the mean values of tensile strength and % strain at maximum were found out and graphs were plotted.

## 5. EXPERIMENTAL RESULTS AND DISCUSSION

### 5.1 Glass Transition Temperature (T<sub>g</sub>)

The glass transition temperatures of the samples were measured using Differential Scanning Calorimetry (DSC) Fig.13, shows the curve obtained from the DSC for the reference sample which was kept at room temperature. The curves for dry and wet aged samples can be found in appendix 9.3.3. Table1 shows the glass transition temperature (T<sub>g</sub>) onset and midpoint values measured by DSC for dry and wet aged samples.

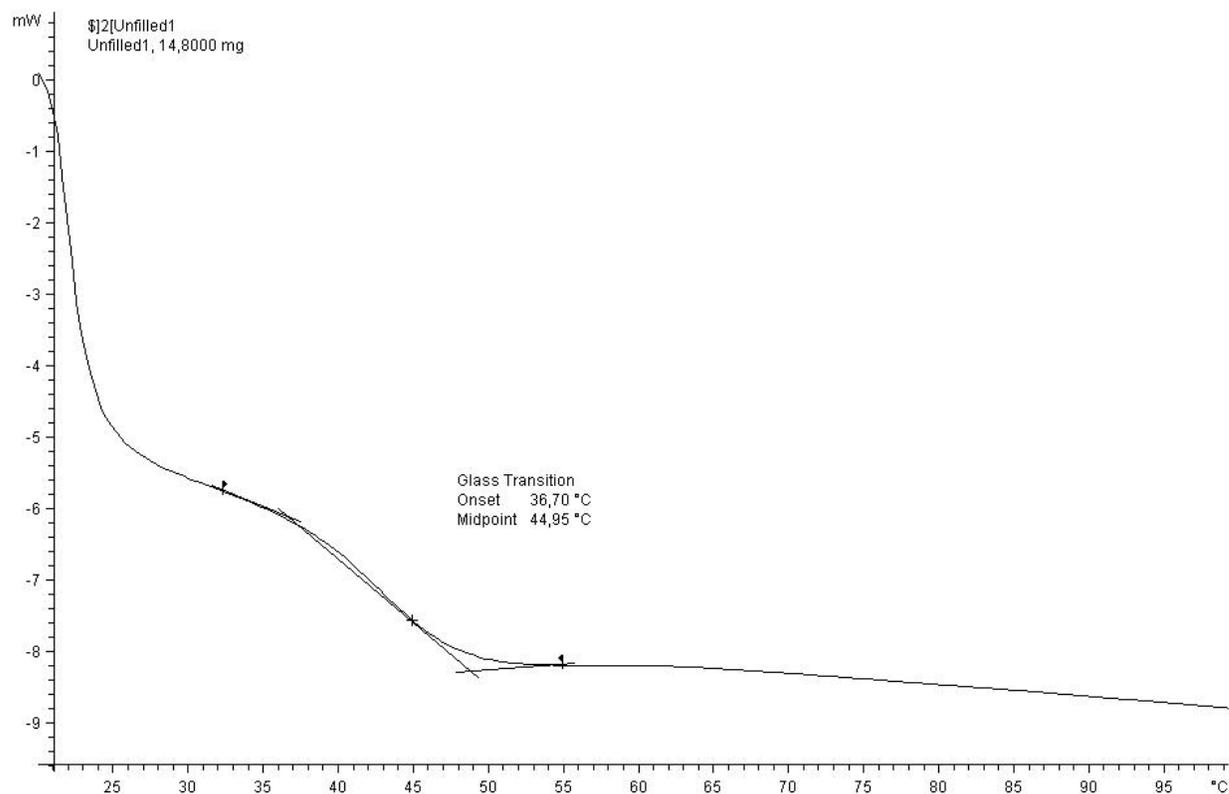
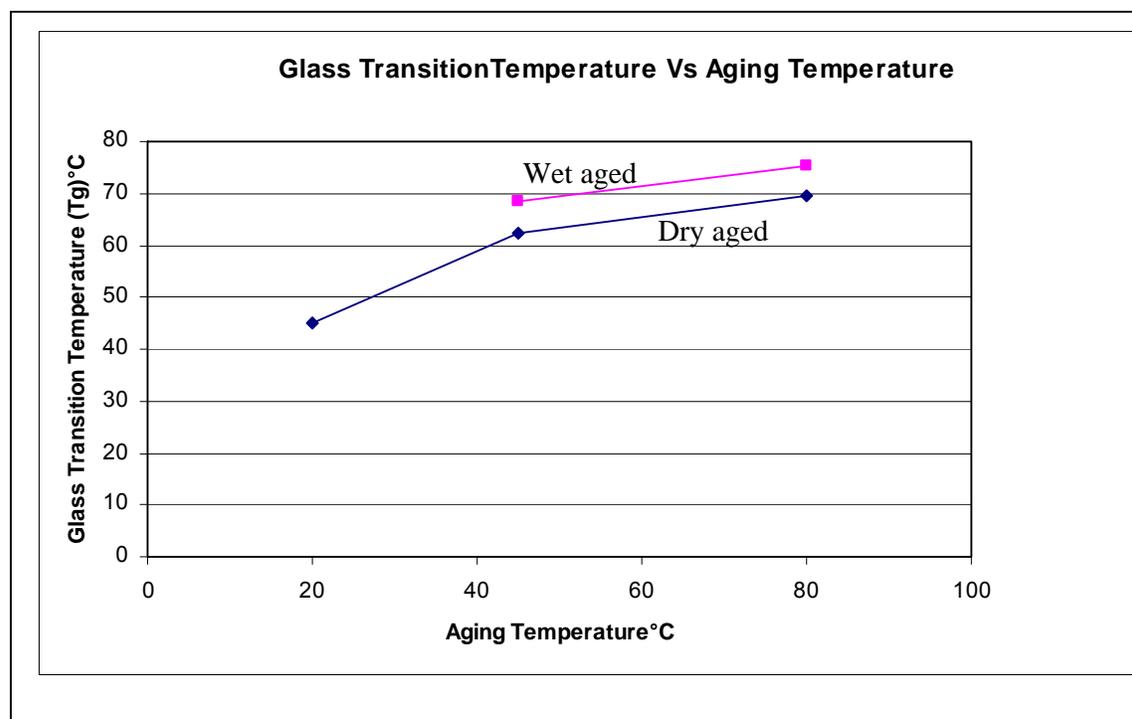


Fig. 13: DSC curve of reference epoxy

Ageing Temp °C	Glass Transition(T <sub>g</sub> )°C	
	Onset	Midpoint
20 Reference	36,70	44,95
45 Dry	53,47	62,19
45 Wet	57,12	68,47
80 Dry	59,01	69,41
80 Wet	65,55	75,2

Table1: Glass transition temperatures



**Fig. 14: Plot of Glass Transition temperature (Tg) Vs Aging temperature (Midpoint Values)**

The fig.14 shows Tg obtained at 20°C, 45°C and 80°C aging temperatures. After aging in water at different temperature settings, theoretically it was expected the Tg to decrease from the reference sample value of 45°C. As the role of absorbed water is to catalyze the breaking of the chain bonds; small amounts of water have large effect because water molecules migrate from one group to another, which lowers the Tg.

However from fig.14 it was observed that Tg was increasing with aging temperature, for both dry as well as wet samples. The increase in the value was caused due to post curing process of the epoxy. The glass transition temperature, Tg, was found to increase with increasing post-cure temperature and the size of the base line shift in the glass transition region on the DSC thermogram can serve as an indicator of the extent of cure. [20]

It was also observed that wet aged samples have higher Tg values than the dry samples.

DSC detects “extra” thermal absorptions/emissions from an epoxy (cured adhesive) as it is heated. Epoxy can undergo many thermal reactions when heated. Only one of these reactions is the glass transition, i.e., the temperature at which the polymer strands realign from a crystalline state to an elastic state. Many other energetic peaks do show up on DSC spectra including, additional chemical reactions, solids melting and amorphous reorganizations to a crystalline state. These other DSC peaks can interfere with the glass transition peak. Interfering peaks can hide the glass transition or combine with the glass transition to produce a peak between the two reactions.

For an epoxy, the endothermic glass transition is a large, energetic DSC peak. This peak will shift depending upon the cure cycle of the epoxy. [22]

It can also be hypothesized that DSC measurements are easy to misinterpret and should not be the sole decision criteria for movement on temperature. [9]

In order to get more accurate and precise results following points should be noted:

- Preparation work can greatly affect the results.
- Specimen preparation should be as gentle as possible.
- Large contact area promotes heat transfer.
- Different software algorithm yield different results.
- Curing of thermosets affects the results.

## 5.2 Dielectric Response

The dielectric response of the epoxy aged in dry and wet conditions were measured with an insulation diagnostic analyzer (IDAX-206, PAX Instruments). The dry characterization was determined by keeping the samples in climate chamber with 15%RH (Relative Humidity) and temperatures 20°C, 45°C and 80°C. The wet characterization was carried out with 90%RH and temperatures 20°C, 45°C and 80°C. The surface of these samples was painted with silver paint (electrodes). The Fig. 8 shows the picture of the samples prepared for testing. Two circular discs were used for dielectric response measurement and 2 rectangular pieces for water sorption measurement. The dielectric response was measured when equilibrium/saturation condition was achieved. The dielectric response was measured in the frequency range sweep varying logarithmically from 0.01 Hz to 1000 Hz at 200 volts (peak). The dielectric permittivity, capacitance and dielectric loss factor were calculated with the preinstalled software. Table 2,3,4&5 shows the calculated values from Eq. (3) (4) (5) respectively. For dry aged (15%RH) and wet aged (90%RH) samples the frequency range selected is 0.01 Hz and 1000Hz, just to figure out the observed changes the epoxy goes at the two extreme frequencies.

Characterization Temp°C	e' (80°C)		e'' (80°C)		e'(20°C)		e''(20°C)	
	dry	wet	Dry	wet	dry	wet	dry	wet
20	8,47E+00	8,24E+00	7,27E-01	5,08E-01	8,60E+00	8,23E+00	6,99E-01	6,82E-01
45	3,86E+01	5,01E+01	9,61E+01	8,74E+01	5,14E+01	4,12E+01	2,62E+02	5,44E+02
80	4,09+E02	2,16E+01	1,86E+05	6,04E+04	1,13E+03	1,54E+03	2,42E+05	3,23E+05

Table 2: Calculated values of e' and e'' aged at 90%RH for frequency 0,01Hz

Characterization Temp°C	e' (80°C)		e'' (80°C)		e'(20°C)		e''(20°C)	
	dry	wet	dry	wet	dry	wet	dry	wet
20	4,46E+00	4,66E+00	3,67E-02	6,57E-02	4,43E+00	4,57E+00	8,53E-02	6,68E-02
45	4,69E+00	4,61E+00	1,81E-01	1,86E-01	6,41E+00	5,50E+00	2,17E+00	1,11E+00
80	2,25E+01	1,08E+01	4,83E+02	7,52E+01	1,75E+01	1,61E+01	3,43E+03	3,17E+03

Table 3: Calculated values of e' and e'' aged at 15%RH for frequency 0,01Hz

Characterization Temp°C	e' (80°C)		e'' (80°C)		e'(20°C)		e''(20°C)	
	dry	wet	dry	wet	dry	wet	dry	wet
20	5,30E+00	5,06E+00	9,00E-02	1,46E-01	5,11E+00	4,87E+00	1,66E-01	1,22E-01
45	5,91E+00	5,43E+00	1,98E-01	9,41E-02	5,94E+00	5,98E+00	3,53E-01	3,29E-01
80	7,90E+00	7,27E+00	2,37E+00	1,18E+00	7,88E+00	8,24E+00	3,10E+00	3,77E+00

Table 4: Calculated values of e' and e'' aged at 90%RH for frequency 1000Hz

- Wet characterization influence on epoxy

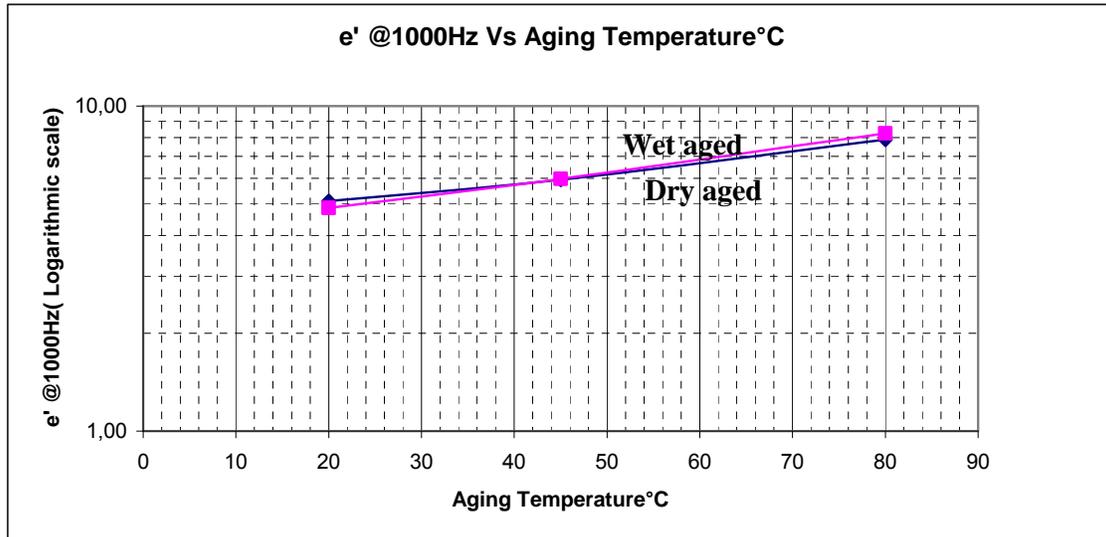


Fig. 15: Characterized in wet condition (90%RH) 20°C plot of e' Vs aging temperature

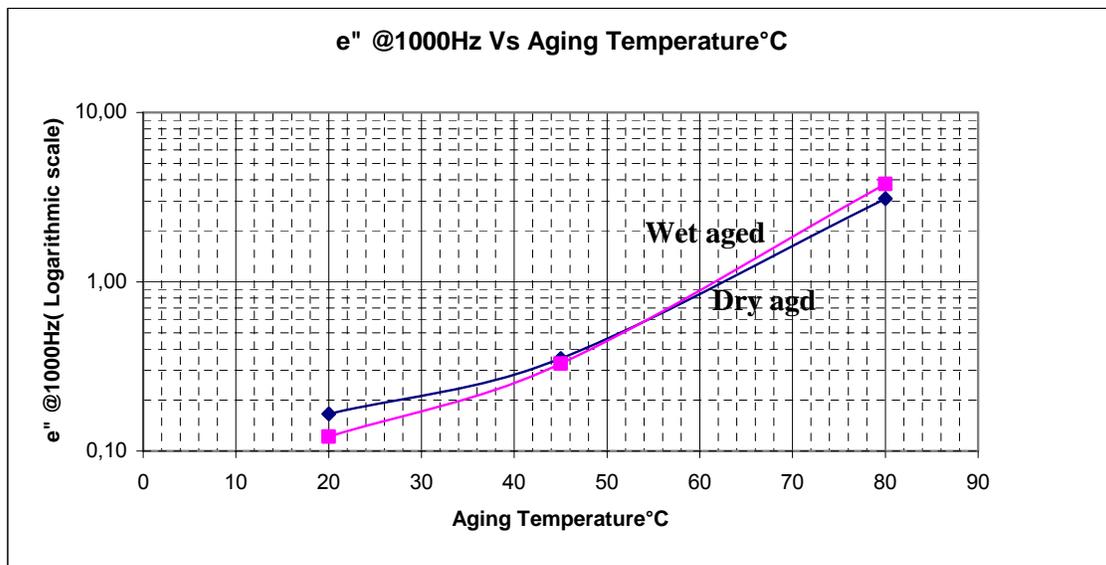


Fig. 16: Characterized in wet condition (90%RH) 20°C plot of e'' Vs aging temperature

For evaluation of the epoxy values at 1000Hz frequency are selected as the conductivity doesn't play a significant role on the complex permittivity. Dielectric constant  $\epsilon'$  is plotted on a logarithmic scale. Fig. 15 shows epoxy samples characterized in wet condition (90%RH). From fig. 15 it can be observed that epoxy samples aged at 90%RH and characterized at 20°C, the  $\epsilon'$  increases with aging temperature. The wet aged samples show higher values of dielectric constant  $\epsilon'$  i.e. the real part of the complex permittivity. The dielectric loss  $\epsilon''$  is also increasing with the temperature. It can be deduced that the water uptake by the epoxy increases with increase in humidity and temperature.

Due to epoxy's hydrophilicity, water diffuses into polymer, inducing stresses and then crazes and cracks. [17]

Initially, the polymer absorbs water, of which a fraction reacts chemically, causing hydrolysis leading to chain scission. The degradation of the resin was mainly caused by hydrolysis reactions. [18]

From fig. 16 shows the plot of  $\epsilon''$  Vs aging temperature. It is observed that wet aged epoxy has higher value than the dry aged epoxy.

Regarding the dielectric constant  $\epsilon'$  and the loss factor  $\epsilon''$ , the general tendency is to observe an increase in those quantities under the influence of humidity. This can be explained by the hypothesis that increase in  $\epsilon$  could be related to damage which increases segmental mobility (breaking of bonds, increase in free volume, plasticisation). It has also been invoked that water increases the total dipole strength of the segments where it is absorbed. Water could also increase ionic conduction.

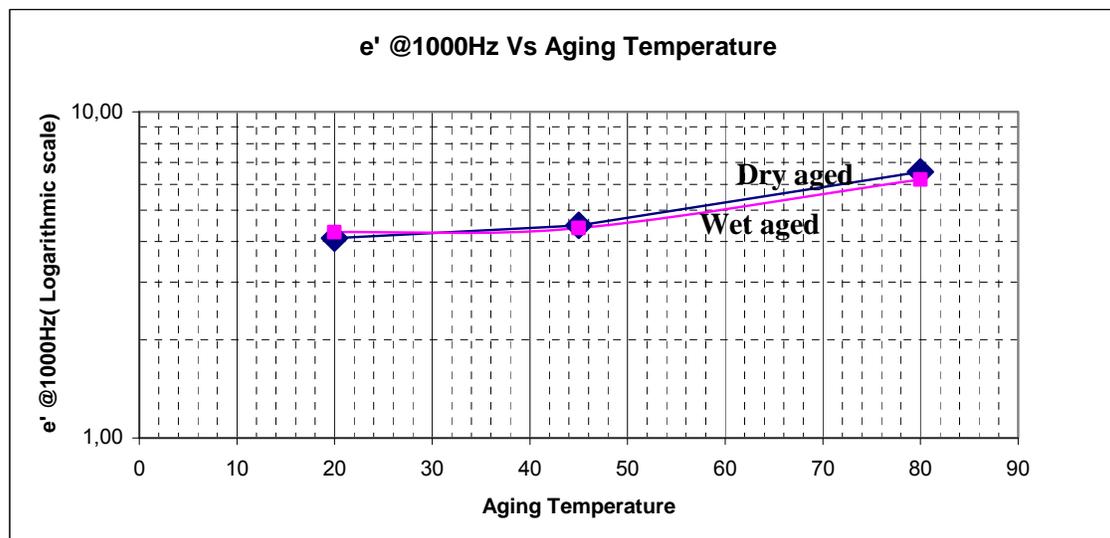
As an indicative order of magnitude, in epoxy it was observed that  $\epsilon'$  increases by about 10% for temperature from 20 to 80°C, while  $\epsilon''$  increases linearly with temperature from 20 to 80°C.

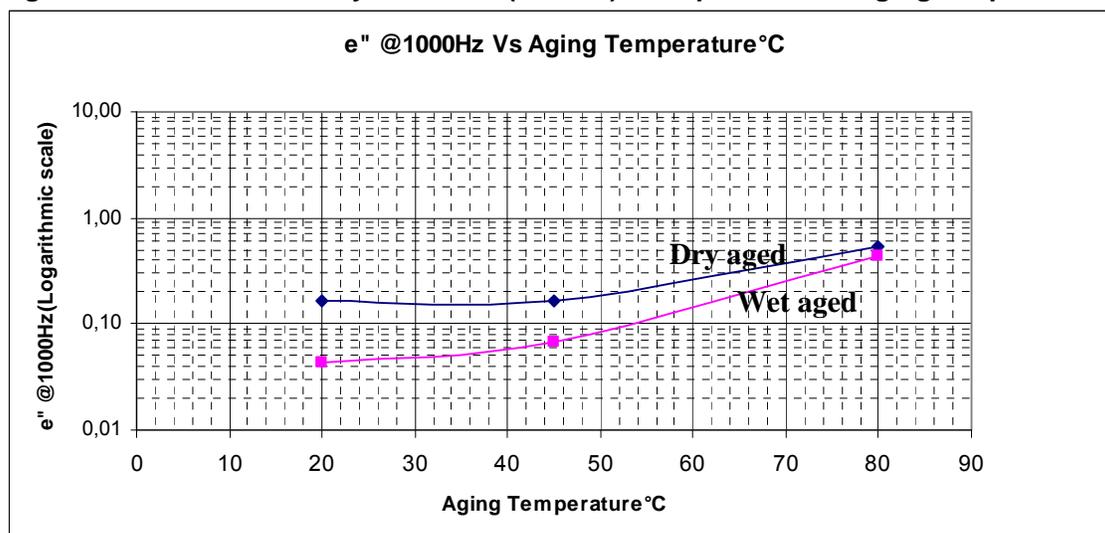
However the combined action of temperature and absorbed water creates structural damage in the epoxy, such as microcavities or cracks. Mechanisms which lead to such damage are not well known, but it is thought that upon thermal activation water breaks interchain bonds, reacts with additives and curing agents. [18]

o Dry characterization influence on epoxy

Characterization Temp°C	e' (80°C)		e'' (80°C)		e'(20°C)		e''(20°C)	
	dry	wet	dry	wet	dry	wet	dry	wet
Aging Temp°C								
20	4,23E+00	4,42E+00	3,93E-02	5,23E-02	4,10E+00	4,27E+00	1,67E-01	4,25E-02
45	4,31E+00	4,34E+00	3,97E-02	3,42E-02	4,49E+00	4,41E+00	1,66E-01	6,79E-02
80	5,49E+00	5,06E+00	2,71E-01	1,19E-01	6,55E+00	6,20E+00	5,31E-01	4,39E-01

Table 5: Calculated values of e' and e'' aged at 15%RH for frequency 1000Hz



**Fig. 17: Characterized in dry condition (15%RH) 20°C plot of  $\epsilon'$  Vs aging temperature****Fig. 18: Characterized in dry condition (15%RH) 20°C plot of  $\epsilon''$  Vs aging temperature**

Dielectric properties  $\epsilon'$  and  $\epsilon''$  of epoxy samples characterized in dry condition (15%RH) are shown in fig. 17 and 18 as a function of aging temperature. From fig. 17 it is observed that the dielectric constant  $\epsilon'$  is uniform for 20 and 45°C however increasing slightly for 80°C. From the graph it can also be observed that dry and wet aged values are nearly same and the aging effect is not much dominant. However for higher temperature dry and wet aged values seemed to be increasing.

The values of  $\epsilon'$  and  $\epsilon''$  have steady growth in characterization in dry condition. Therefore it can be deduced that characterization done in dry condition didn't significantly affect the complex permittivity as compared with wet characterization.

The fig. 18 shows different characteristics as compared to fig. 16. The result was quite surprising as it was expected to observe similar pattern to fig. 17 i.e. either, dry and wet aged lines overlapping each other or  $\epsilon''$  higher for wet aged than dry aged. In this case it can be noted that degradation process in the epoxy is not mainly related to polymer hydrolysis. Degradation perhaps could be related to oxidation. Also the shift in the values may be due to noise in the set up, because during the characterization testing time taken by set up for 80°C was longer than for 20 and 45°C.

### 5.3 Mechanical Testing

The mechanical properties of the Bisphenol-A epoxy were evaluated after the samples were dry and wet aged (immersed in water) at 20°C, 45°C, 80°C in the heating oven for one month respectively and then conditioned in vacuum oven for a week. Four dry and wet samples of dog bone shape of dimensions 4 mm X 115 mm X 10 mm were used for stress-strain test. The samples were then applied tensile force till breakage. The stress-strain curves were obtained from the Nexygen V4.0 software. The curves for 45°C, 80°C dry and wet aged samples can be found in appendix 9.3.2. These Curves give the idea about the mechanical strength of the epoxy material.

Fig. 19 shows the stress-strain curve of 4 parallel reference sample conditioned at room temperature (20°C).

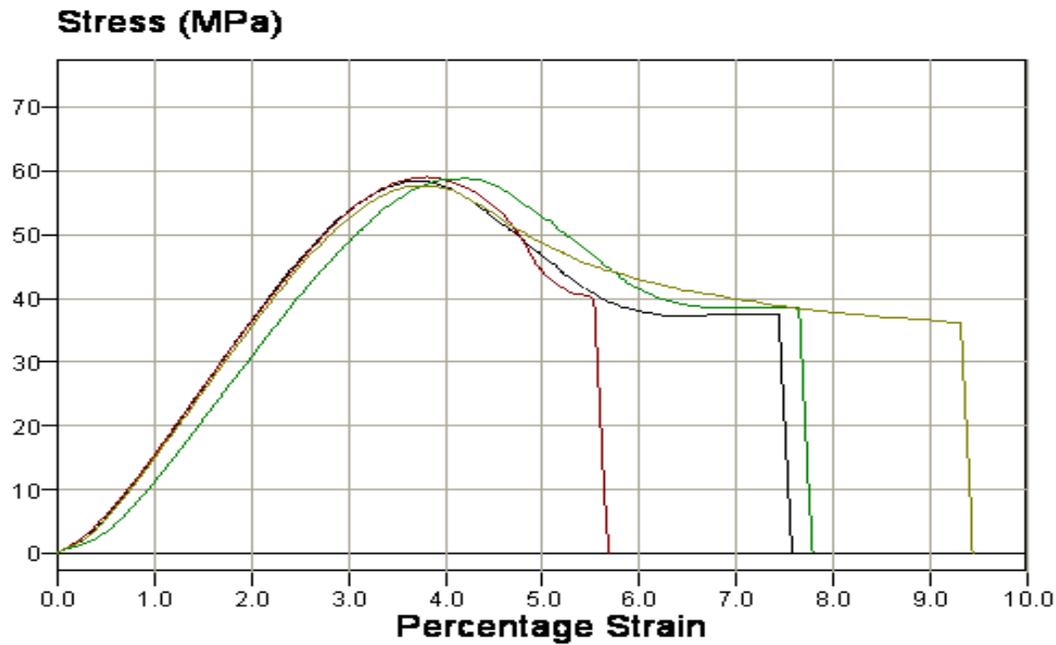


Fig. 19: Stress-Strain curve of a reference sample (4 Parallels)

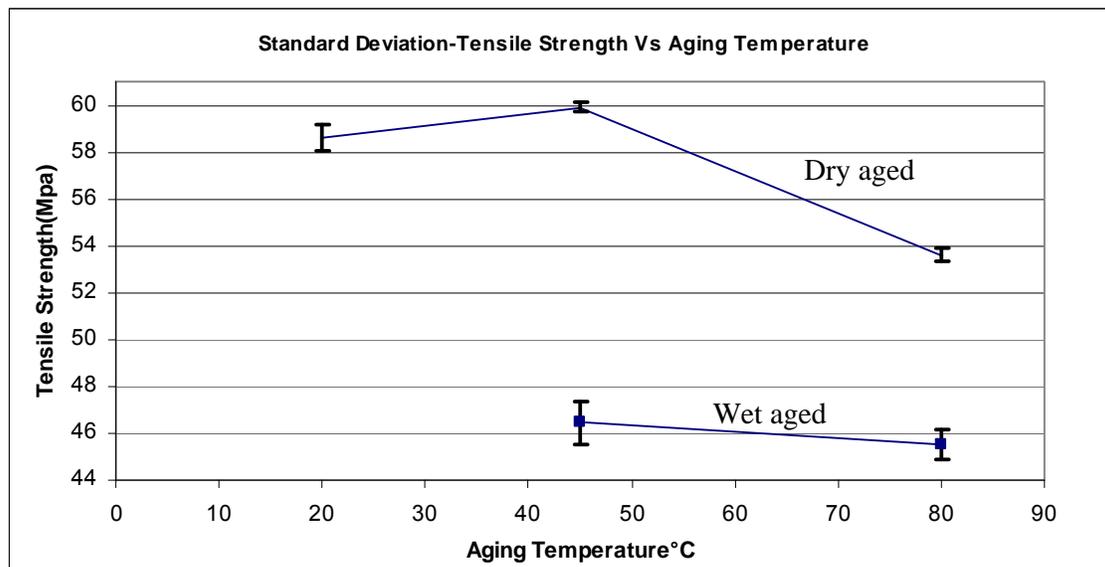
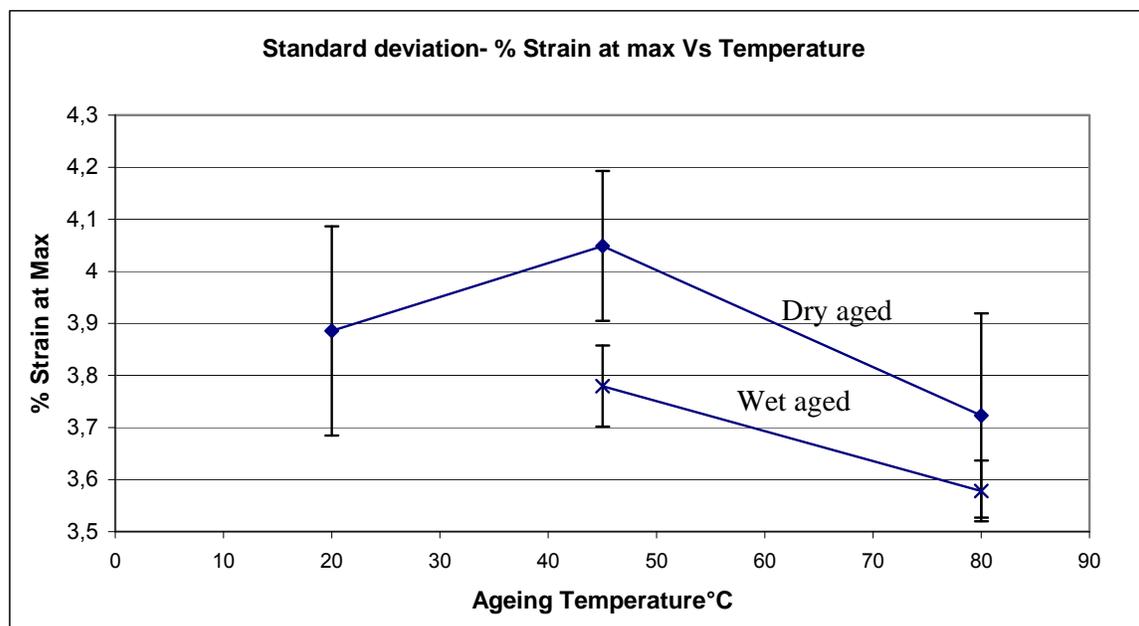


Fig. 20: Mean values of tensile strength

For statistical analysis the standard deviation is calculated from the mean values. The reason behind calculating the standard deviation is to get a wider significance of the data and also to determine spread of the distribution. The fig. 20 shows tensile strength Vs ageing temperature graph. From the graph it can be observed that the tensile strength reduces with aging temperature. Ultimately the yield strength of the epoxy also reduces. The tensile strength is higher for dry aged samples as compared to wet aged samples. For dry aged epoxy it reduces around 14% from 20°C to 80°C. However for wet aged epoxy samples tensile strength reduces around 25%. The elongation at the 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.



**Fig. 21: Mean values of % strain at max**

The fig. 21 shows the % strain at max Vs ageing temperature. The strain derived from measuring the deformation of the sample, i.e. elongation, compression, or distortion also tends to decrease with ageing temperature. The standard deviation from mean values for dry aged samples is quite high as compared to wet aged samples. For dry aged samples % strain reduces around 0,3 %. For wet aged samples it reduces around 0,5%. The ageing temperature plays a significant role in reducing the value of strain. The dry samples have slightly higher values than the wet aged samples. Moreover 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 loses strength. Thus it can be deduced that there is strong dependence on temperature, time and moisture content on the mechanical properties of epoxy.

## 6. CONCLUSIONS

The effect of the combined action of high temperature and water on the long term performance of a Bisphenol A epoxy resin was investigated. The mechanical, electrical and thermal analysis led to the following conclusions which I believe could be applied to epoxy insulation.

For the glass transition temperature ( $T_g$ ), theoretically it was expected that the value of  $T_g$  to decrease from the reference sample value of 45°C. As the role of absorbed water is to catalyze the breaking of the chain bonds; small amounts of water have large effect because water molecules migrate from one group to another, which lowers the  $T_g$ .

However it was observed that  $T_g$  was increasing with aging temperature for both dry as well as wet samples. It was also observed that wet aged samples have higher  $T_g$  values than the dry samples. Thus it can be deduced that the increase in the value is caused due to post curing process of the epoxy.

The results of dielectric response characterized in wet condition (90%RH) at 20°C, the wet aged samples show higher values of dielectric constant  $\epsilon'$  compared to dry aged. The dielectric loss  $\epsilon''$  was also increasing with the temperature. Initially, the polymer absorbs water, of which a fraction reacts chemically, causing hydrolysis leading to chain scission. The degradation of the resin is mainly caused by hydrolysis reactions. This is evident from the theory that the conductivity of the material increases as the temperature increases giving higher losses in the samples. It can be concluded that the water uptake by the epoxy increases with increase in humidity and temperature, thus resulting increase in permittivity.

Dielectric losses occur due to the inertia of the bound charges when they are accelerated in the driving field. Normally the dielectric loss factor depends upon the ionic conductivity. The loss factor can also be dominated by dipole orientation with a significant contribution of ionic conductivity.

For epoxy characterized in dry condition (90%RH) at 20°C it was observed that the  $\epsilon'$  values for dry and wet aged values are nearly same and the aging effect is not much dominant. However for higher temperature dry and wet aged values seemed to be increasing. Therefore it can be concluded that characterization done in dry condition doesn't significantly affect the complex permittivity as compared with wet characterization.

The dielectric  $\epsilon''$  showed a quite surprising result as it was expected to observe similar pattern i.e. either, dry and wet aged lines overlapping each other or  $\epsilon''$  higher for wet aged than dry aged. In this case it can be deduced that degradation process in the epoxy is not mainly related to polymer hydrolysis. Degradation perhaps could be related to oxidation. The shift in the values could also be due to noise in the set up.

The Mechanical test shows that the tensile strength of the material reduces with aging temperature. For dry aged epoxy it reduces around 14% from 20°C to 80°C. However for wet aged epoxy samples tensile strength reduces around 25%. Ultimately the yield strength of the epoxy also reduces. It can be concluded that the water in the sample has caused chain scission in the material and hence the mechanical strength is permanently reduced, 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.

For dry aged samples % strain reduces around 0,3 % and for wet aged samples it reduces around 0,5%. The ageing temperature plays a significant role in reducing the value of strain. The dry samples have slightly higher values than the wet aged samples. Moreover 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 loses strength. Thus it can be deduced that there is strong dependence on temperature, time and moisture content on the properties of epoxy.

## 7. FUTURE WORK

For a development scenario analysis following future work is recommended.

As DSC is the oldest and least expensive thermal analysis technique. It may give misleading values. It would be interesting to measure T<sub>g</sub> by dynamic mechanical analysis (DMA) which is considered one of the most accurate techniques for glass transition temperature measurement. In addition to glass transition temperature, dynamic mechanical analysis also provides the capability to measure many other material properties, such as the coefficient of thermal expansion or viscoelastic properties.

It would be interesting to study the effects of ageing for a longer duration instead of one month, in order to determine long term aging effects.

Dielectric characterization of an aged and unaged epoxy filled with inorganic/organic hybrid nanoparticles may also give some interesting results.

The A.C breakdown test can also be performed on aged and unaged epoxy. The most important parameters to observe will be the variations in dielectric strength with respect to temperature and humidity.

As it is said despite with numerous research work, the basic interactions of water with epoxy and the associated modification of the material properties, are not clearly understood. The above recommendations may help in better understanding and analyzing the influence humidity and temperature on the insulation properties.

Since this analysis has been done in relatively quick time a more comprehensive **SWOT** analysis (**S**trength, **W**eaknesses, **O**pportunities, **T**hreats) could be done if required to compare the results with the analysis done here.

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## 9. APPENDICES

### 9.1 Theoretical Background

#### 9.1.1 Mathematical Relations in the Frequency Domain

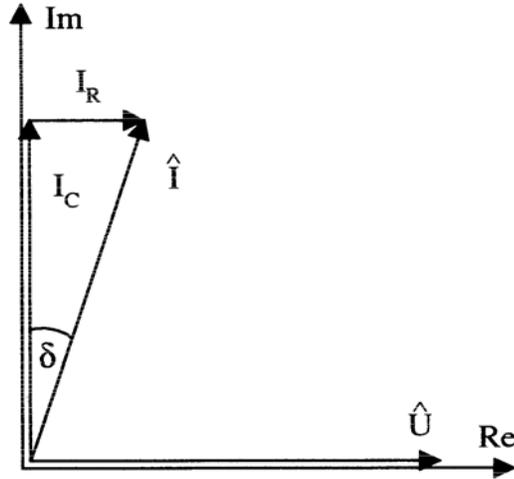
The current that flows through the insulation during the application of a sinusoidal AC voltage can be split into a capacitive and a resistive part;

$$\hat{I} = I(\omega) = jI_C + I_R \quad (1)$$

$$I(\omega) = \omega C_o U_o(\omega) \left[ j(\varepsilon_r + \Delta\varepsilon_r(\omega)) + \left( \frac{\sigma}{\omega\varepsilon_o} + \chi''(\omega) \right) \right] \quad (2)$$

Where  $\omega=2\pi f$  and  $f$  is the applied frequency,  $U_o$  is the applied voltage,  $C_o$  is the capacitance of the cable,  $\varepsilon_r$  is the permittivity,  $\Delta\varepsilon_r$  is the change in capacitance, and  $\chi''(\omega)$  is the dielectric susceptibility that corresponds to the response function  $f(t)$  in the time domain (a measure of the polarisation in the material).

The current that flows through the epoxy has one component that is in phase with the applied voltage, and one part that is phase shifted by  $90^\circ$ . This is illustrated in Fig. 21. The amplitude of the resistive part of the current is much less than that of the capacitive current. [21]



**Fig.21: Phase diagram of the applied voltage and current in the insulation.**

The **complex permittivity** can be expressed as;

$$\varepsilon''(\omega) = \frac{\sigma}{\omega\varepsilon_o} + \chi''(\omega) \quad (3)$$

$$\varepsilon'(\omega) = \varepsilon_r + \Delta\varepsilon_r(\omega) \quad (4)$$

$$\tan \delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{\varepsilon''(\omega)}{\varepsilon_r + \Delta\varepsilon_r(\omega)} \approx \frac{\varepsilon''(\omega)}{\varepsilon_r} \quad (5)$$

### 9.1.2 Expression of 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  $\mathbf{J}(t)$  through a dielectric material with an electric field  $\mathbf{E}(t)$  in time domain can be expressed as:

$$J(t) = \sigma E(t) + \varepsilon_0 \frac{\partial}{\partial t} \left\{ (1 + \chi_e) E(t) + \int_0^t f(\tau) E(t - \tau) d\tau \right\} (A / m^2) \quad (6)$$

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

$$\nabla \times H = \sigma E + \frac{\partial D}{\partial t} (A / m^2) \quad (7)$$

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

$$\nabla \times H = \sigma \hat{E}(\omega) + i\omega \hat{D}(\omega) .. (A / m^2) \quad (8)$$

The electric polarization in time domain is expressed as

$$P(t) = \varepsilon_0 \chi_e E(t) + \Delta P(t) = \varepsilon_0 \chi_e E(t) + \varepsilon_0 \int_0^\infty f(\tau) E(t - \tau) d\tau .. (C / m^2) \quad (9)$$

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

$$\hat{P}(\omega) = \varepsilon_0 \chi_e \hat{E}(\omega) + \varepsilon_0 \hat{f}(\omega) \hat{E}(\omega) = \varepsilon_0 (\chi_e + \hat{f}(\omega)) \hat{E}(\omega) .. (C / m^2) \quad (10)$$

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

$$\hat{\chi}(\omega) = \hat{\chi}'(\omega) - i \hat{\chi}''(\omega) = \hat{f}(\omega) = \int_0^\infty f(t) e^{-i\omega t} dt \quad (11)$$

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:

$$\begin{aligned} \hat{J}(\omega) &= \sigma \hat{E}(\omega) + i\omega \hat{D}(\omega) = \left\{ \sigma + i\omega \varepsilon_0 (1 + \chi_e + \hat{\chi}'(\omega) - i \hat{\chi}''(\omega)) \right\} \hat{E}(\omega) \\ &= i\omega \varepsilon_0 \left\{ 1 + \chi_e + \hat{\chi}'(\omega) - i \left( \frac{\sigma}{\omega \varepsilon_0} + \hat{\chi}''(\omega) \right) \right\} \hat{E}(\omega) .. (A / m^2) \end{aligned} \quad (12)$$

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  $90^\circ$  before the driving harmonic electric field  $E(\omega)$ . The part of the current which is in phase with driving field is 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 polarization 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  $90^\circ$  before the driving field, displacement current, is associated with the capacitance of the material.

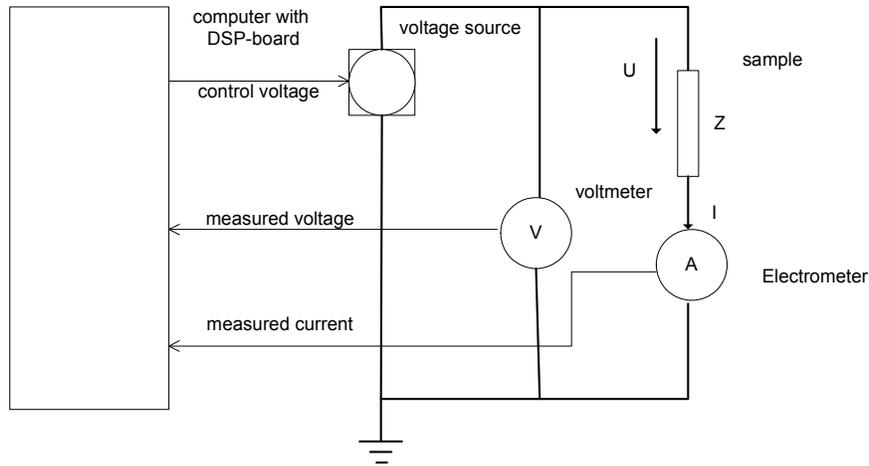
In many situations it is more convenient to talk about the complex permittivity which is defined as follows:

$$\hat{J}(\omega) = i\omega\epsilon_0 \{ \hat{\epsilon}'(\omega) - i\hat{\epsilon}''(\omega) \} \hat{E}(\omega) \Rightarrow \hat{\epsilon}''(\omega) = \frac{\sigma}{\epsilon_0\omega} + \hat{\chi}''(\omega) \quad (13)$$

It is seen from the equation above that the conductivity  $\sigma$ , the relative permittivity  $\epsilon_r$  and the electric susceptibility  $\chi(\omega)$  characterizes the behavior of the dielectric material under harmonic excitation. This equation shows that it is possible in frequency domain to make measurements which characterize the material. [10]

### 9.1.3 Insulation diagnostic using dielectric 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 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.



**Fig. 22: Measurement of electrical Impedance**

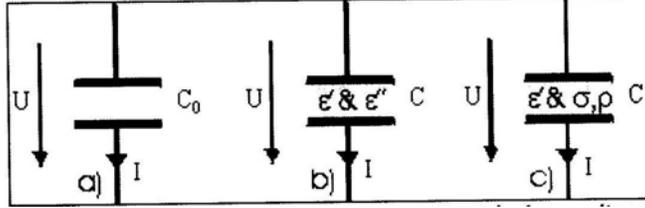
The impedance is calculated using ohm's law:

$$Z = U/I$$

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 geometrical capacitance  $C_0$ , has to be defined. In the picture below a vacuum capacitor of defined geometry is shown. Since no material is between the electrodes the capacitance of a) is the geometrical capacitance.



**Fig. 23: 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: [12]

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

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

**Dielectric:**

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

$$\Delta\varepsilon' = \varepsilon' + k \quad (k \text{ is an arbitrary constant})$$

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

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

**Resistive:**

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

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

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

## 9.2 Equipments used

### 9.2.1 Insulation Diagnostic Analyzer

The IDAX 206 is an insulation diagnostic system designed and manufactured by “**PAX Diagnostics**”. It employs the principle of dielectric spectroscopy and balances out the capacitive current before measuring it.

The IDAX 206 is by design 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 0.01 Hz 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 slimmed 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.



Fig. 24: PAX Insulation Diagnostic Analyzer

### 9.2.2 Binder Vacuum Drying Oven

The Binder drying oven-VD 23 is suitable for drying and heat treatment of solid or pulverized charging material, using the supply of heat under vacuum.

Vacuum drying is used for special drying problems, for which conventional methods cannot offer a solution due to physical limitation.

In the experiment it was used for conditioning of epoxy samples at room temperature. It is shown in Fig. 25



Fig. 25: Binder Vacuum Drying Oven

### 9.2.3 Vötsch Temperature & Climate Test Systems

The Vötsch industrietechnik climate chamber VC<sup>3</sup> 4034 is a humidity and temperature chamber wherein the required humidity and temperature can be set. In the experiment it was set for 20°C, 45°C and 80°C with relative humidity of 15% and 90%. It is shown in Fig. 26

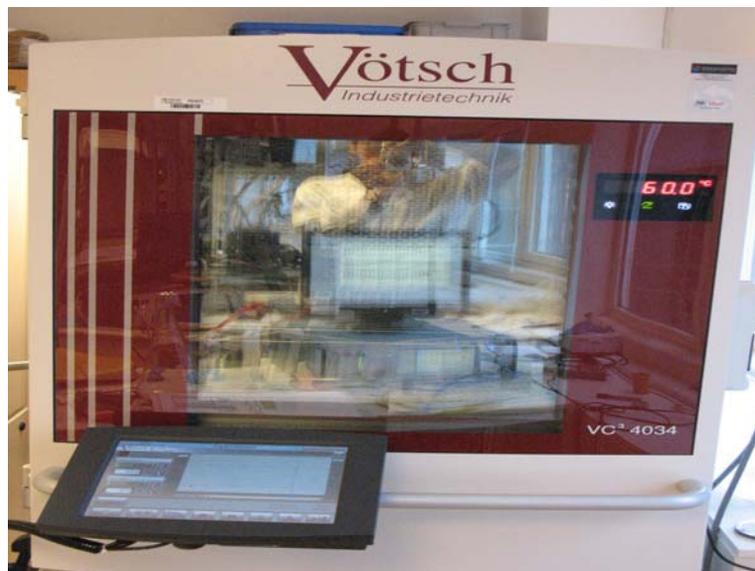


Fig. 26: Vötsch Industrietechnik Climate Chamber

### 9.2.4 Mettler Toledo Weighing Scale

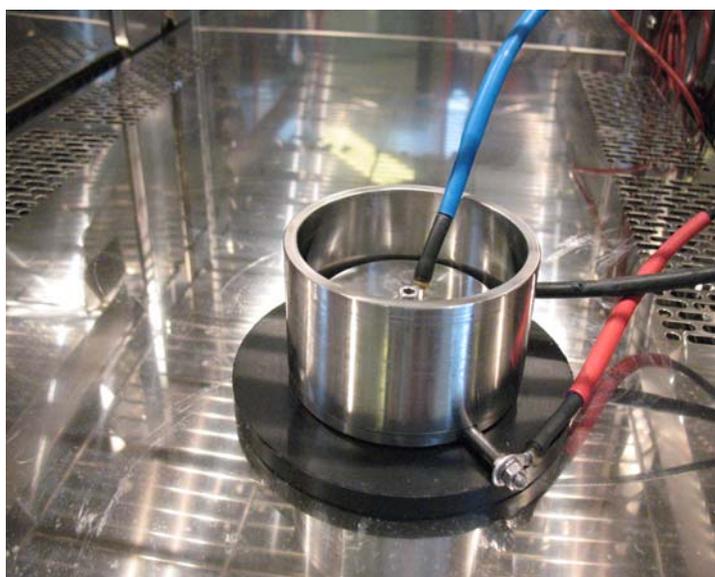
The Mettler Toledo UMX2 is a precision scale for measuring weighs up to 2.1g with a resolution of 0.01mg. It calibrates itself automatically when it detects a change in temperature or relative humidity. It is shown in Fig. 27



**Fig. 27: Mettler Toledo Weighing Scale**

### 9.2.5 Sample holder

The sample holder for carrying out dielectric response measurement was locally fabricated from the NTNU workshop. The M.S sample holder consisted of three parts. The top part which rested on the test object (epoxy disc) served as a positive electrode. The base plate acted as a negative electrode and a cylindrical cell which acted as a shielding/grounding the epoxy. It is shown in Fig. 28



**Fig. 28: Test cell**

### 9.2.6 Mettler Toledo DSC

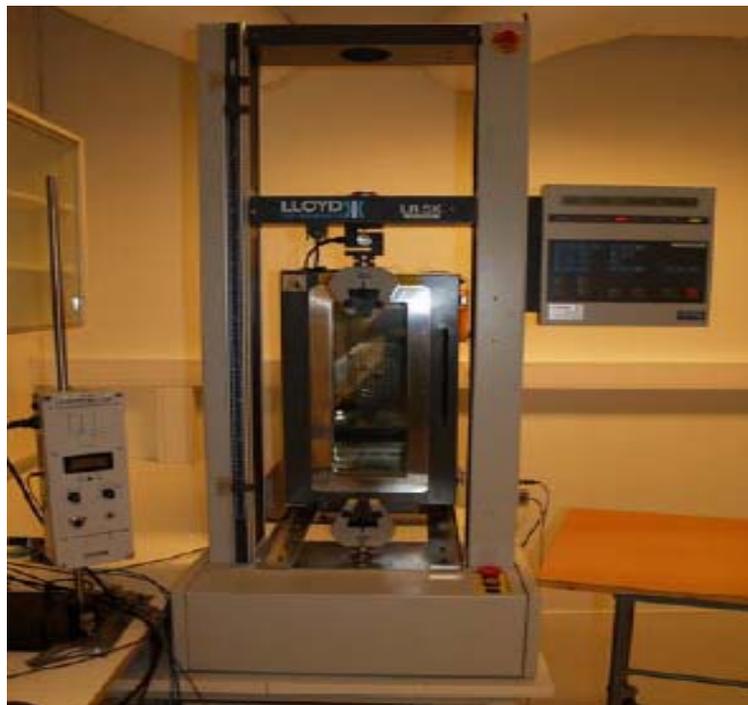
Mettler Toledo HP DSC822 is differential scanning calorimetry (DSC) equipment. It can measure the Glass Transition temperature ( $T_g$ ) of the given polymer samples. The setup is operated and controlled by a software program.



**Fig. 29: DSC module**

### 9.2.7 Lloyd Instruments

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, strain and the extension during the test. This equipment can apply tensile force up to 5 Kilo Newton.



**Fig. 30: Stress-Strain (Mechanical Test) setup**

### 9.3 List of figures

#### 9.3.1 DSC curves

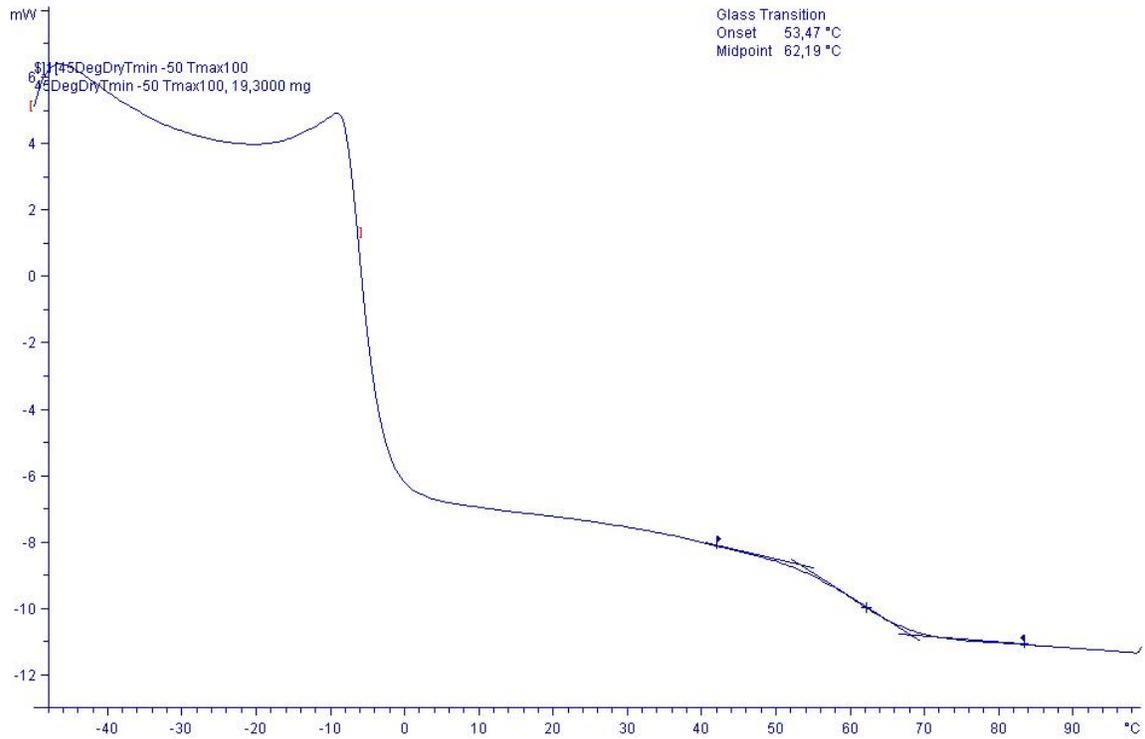


Fig. 31: Glass Transition (Tg) curve dry aged at 45°C

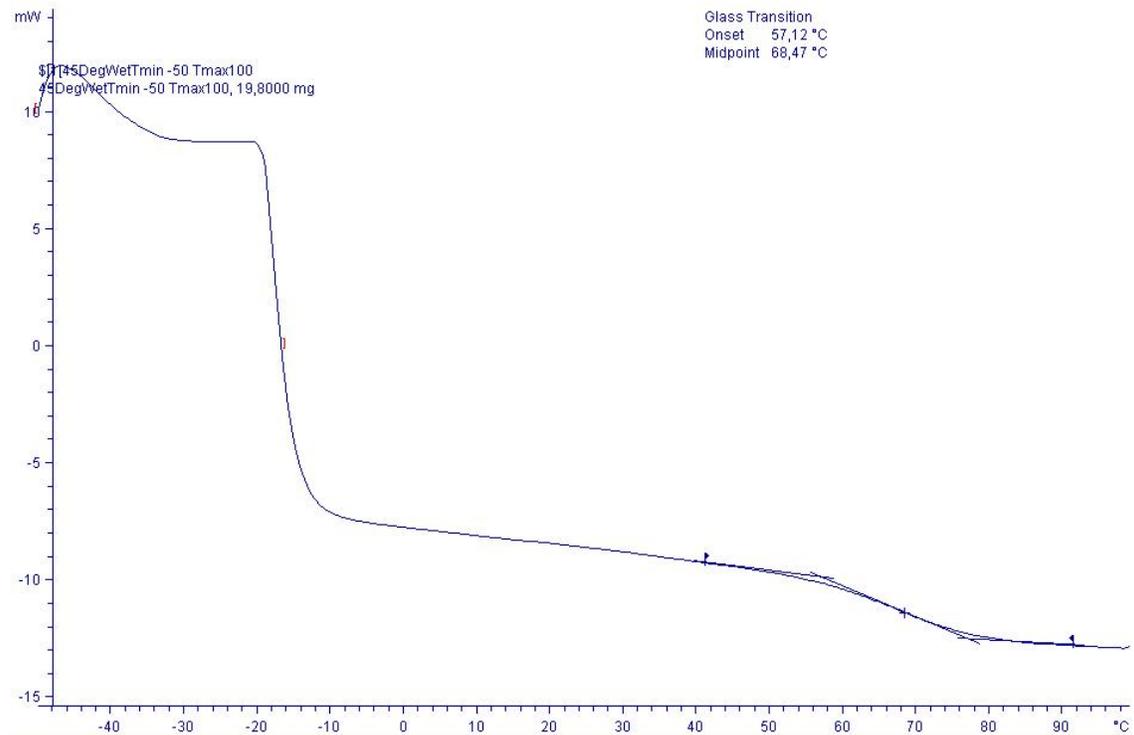


Fig. 32: Glass Transition (Tg) curve wet aged at 45°C

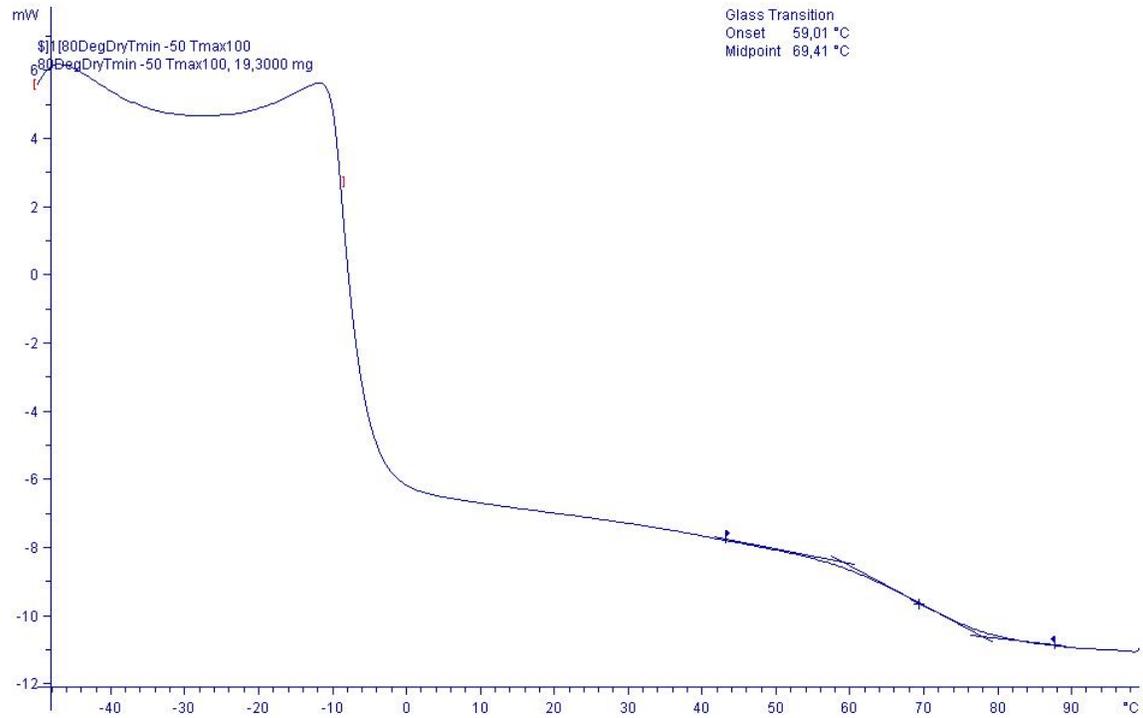


Fig. 33: Glass Transition(Tg) curve dry aged at 80°C

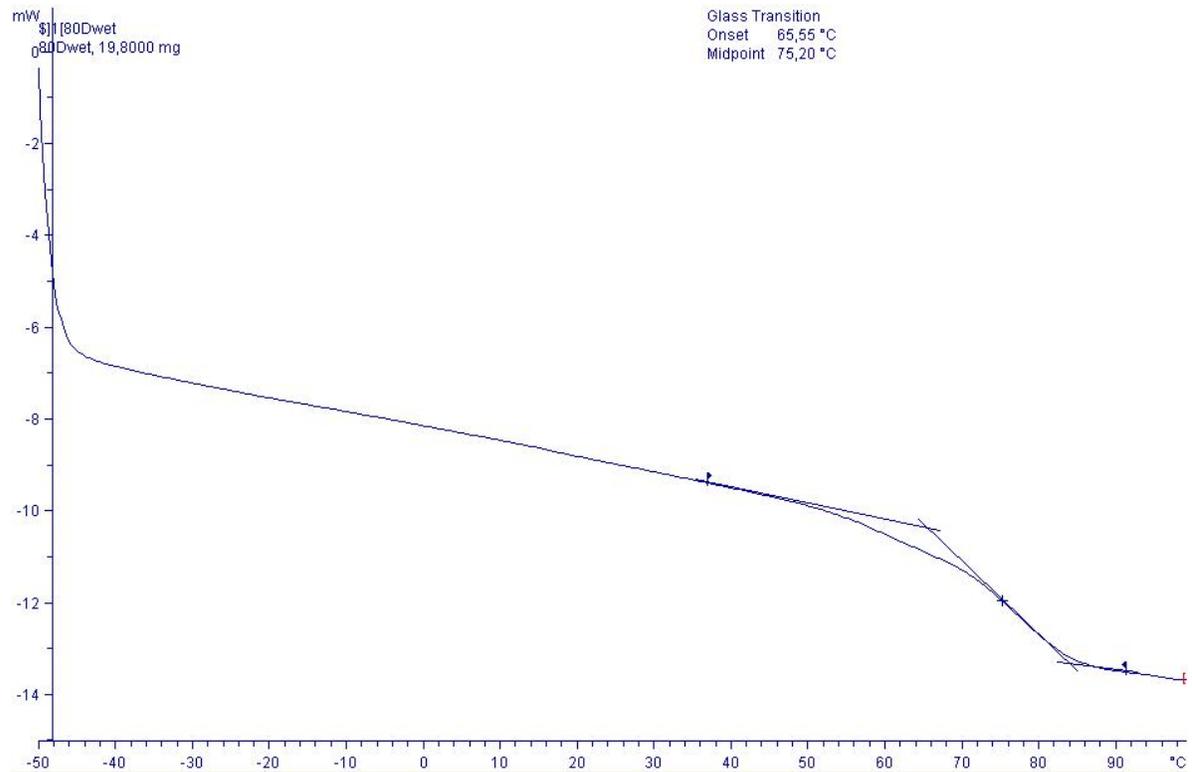


Fig. 34: Glass Transition(Tg) curve wet aged at 80°C

### 9.3.2 Stress-Strain Curves

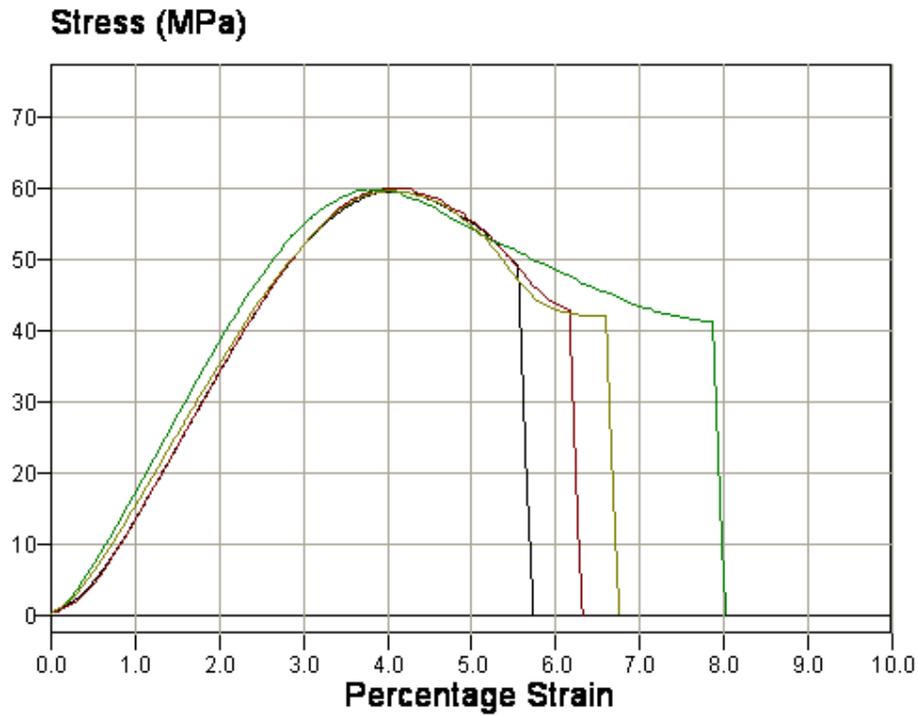


Fig. 35: Stress-Strain curve dry aged at 45°C

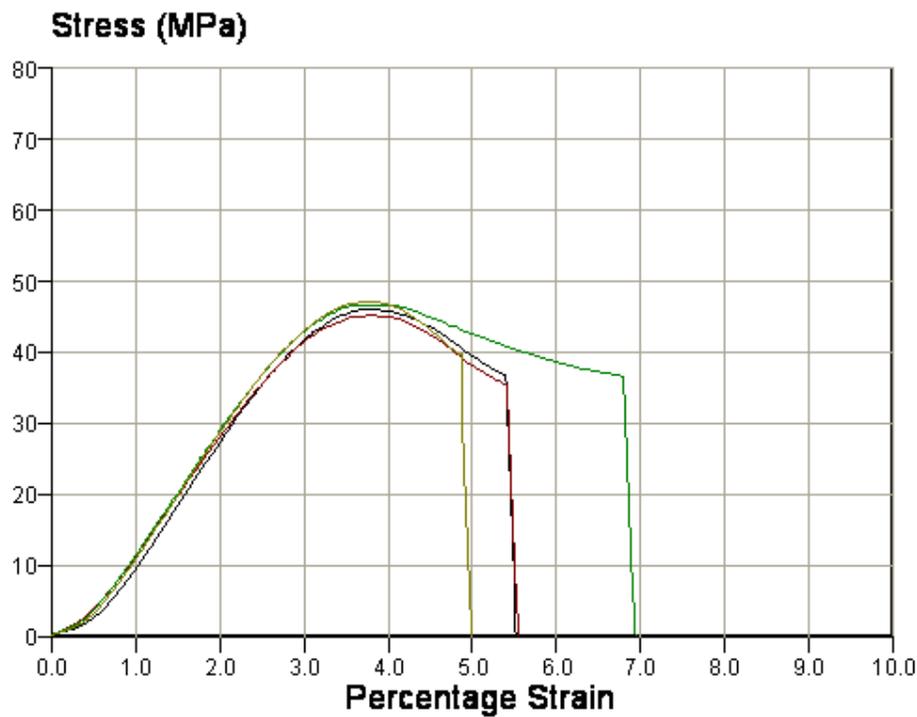


Fig.36: Stress-Strain curve wet aged at 45°C

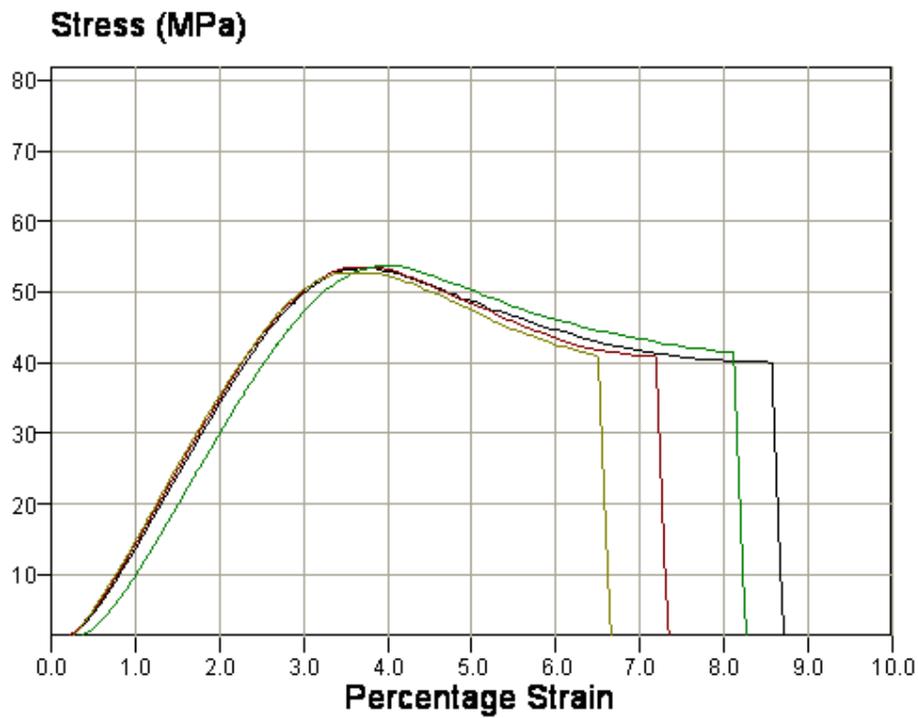


Fig.37: Stress-Strain curve dry aged at 80°C

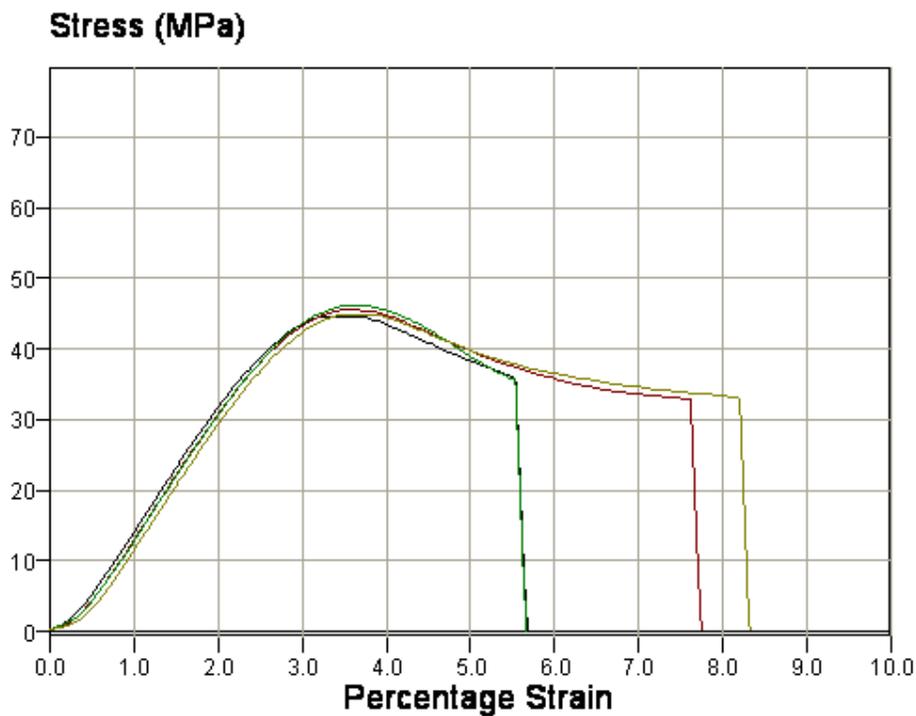


Fig.38: Stress-Strain curve wet aged at 80°C