1 Introduction
ABB provides slot liner strips for insulating and stabilizing copper coils in the rotors of turbo and hydro generators. These slot liners are manufactured in L- or U-shaped sections with a wall thickness of 0.5 to 2.5 mm and a part length of up to 10 meters (Fig. 1). In addition to glass fiber and heat-resistant epoxy resin, thin layers of Nomex® or PTFE can be laminated onto the slot liner to increase the electrical performance. The main requirements of a slot liner are mechanical strength, resistance to heat, and low dielectric losses [1].

![Slot Insulation](image)

Fig. 1. a) Vetresit and b) Vetrelam slot liner insulation

Generator insulation are continuously in operation at high temperatures up to approx. 130 °C. Thermal ageing and thermal cycling determine the material performance over the estimated life-time. This contribution discusses the determination of the glass transition temperature ($T_g$) by various thermal and dynamical mechanical methods by using the material Vetresit 17 as an example. Additionally, dielectric spectroscopy and results from thermal ageing on slot insulation materials will be presented.

2 Influence of Temperature on Phase Transitions
With increasing temperature the mobility of polymeric segments or groups is increasing as well. At a certain temperature, a transition from the rigid glassy state to a more flexible rubbery state takes place. By this transition the volume of the material is increasing, thereby generating more free volume for the polymer to move. This glass transition temperature for thermoset materials should be merely regarded as a process and not just as a single point, like it is represented by the $T_g$-value. The increased mobility of the polymeric segments can be also followed by studying its dielectric response.

The determination of the glass transition temperature is performed by applicable standards [2, 3, 4]. Although all methods determine the glass transition temperature, the physical background of the determined transitions are different and so the values are not directly comparable.

The IEC 61006 (eq. to DIN EN 61006) determines the glass transition temperature by three different methods:

- **Differential Scanning Calorimetry (DSC)** is based on a technique in which the difference in heat flow energy inputs into a tested material and a reference material is measured as a function of temperature while the tested material and the reference material are subjected to a controlled temperature program (Fig. 2).

![DSC Curve](image)

**Fig. 2: Typical DSC curve**
- **Thermal mechanical analysis (TMA)** which is a technique based the deformation of a test specimen under non-oscillatory load and is measured as a function of temperature whilst the test specimen is subjected to a controlled temperature program (Fig. 3).

![Fig. 3: Typical TMA graph](image)

- **Dynamical mechanical analysis (DMA)** technique in which either the storage elastic or loss modulus, or both, of a substance under oscillatory load or deformation is measured as a function of temperature, frequency or time, or combination thereof (Fig. 4). The tan delta or loss factor is defined the ratio of loss to elasticity or in other words, the ratio of energy dissipated to energy stored per cycle of deformation.

![Fig. 4: Typical DMA graph](image)

The glass transition temperature can be determined readily only by observing the temperature range in which a significant change takes place in some specific electrical, mechanical, thermal, or other physical property. Moreover, the observed temperature can vary significantly depending on the property chosen for observation and on details of the experimental technique (e.g. heating rate, frequency of testing or sample dimensions).

Phase transition of polymer can also be observed by following the consequent changes in the dielectric properties of the material. Particularly, polar group tend to orientate themselves to the applied alternating electric field. The complex dielectric properties, the loss factor (tan delta or dielectric losses) and the relative permittivity (dielectric constant), are determined by dielectric spectroscopy. These are isothermal capacitance scans as a function of frequency in accordance with IEC 60250. Fig. 5 shows schematically the set-up.

![Fig. 5: Schematically set-up for dielectric spectroscopy](image)

The ASTM E 1640 applies the DMA-method for the determination of the glass transition temperature. In contrast to the IEC 61006, it is proposed to use the onset of the storage modulus, but the peak of loss modulus or the peak of the loss factor may be taken as well.

![Fig. 6: Schematically drawing of the current (I) for dielectric spectroscopy](image)
With changes in the temperature and frequency, the ratio of the resistive portion to the capacitive portion is changing as well. This is represented in Fig. 6 by the angle (\(\delta\)) between both portions.

The dielectric spectroscopy therefore provides information about the dielectric losses (\(\epsilon''\)) when an alternating current is applied. Additionally, the relative permittivity (\(\epsilon'\) or \(e_r\)) is determined. This value provides information about the extent to which the sample concentrates electrostatic lines of flux (relative to the permittivity of a vacuum). The ratio \(\epsilon''/\epsilon'\) is called loss factor \(\delta\), usually represented by \(\tan\delta\) [5].

### 2.1 Comparison between TMA and DMA for GF/epoxies

A comparison between TMA and DMA \(T_g\) determination is presented in [4]. It is shown that the glass transition of a certain epoxy is determined by TMA is 121.2 ± 0.4 °C and the onset of the storage modulus from the DMA (linear calculation) is 120.8 ± 4.2 °C. The onset of the storage modulus by logarithmic representation is of 118.6 ± 2.6 °C. Here already a few degree difference are determined although the material properties are not changed.

### 2.2 Calibration method for DMA

In [6] it is stated that the glass transition temperatures measured by the DMA methods can vary as high as 40 °C. Several suggestions to improve the proposed calibration method for DMA measurements are presented. The difference in heating ramp leads to a large difference in the determined glass transition temperature for the epoxy. In the case of a heating rates of 1 and 3 °C/min., the differences between the DSC composite and DMA composite were 6 °C, and 12 °C respectively. These values are a few degree higher than for the neat resin. At a heating rate of 3 °C/min. the sample temperature was 6 °C lower than the instrument readout. A low heating rate could not prevent this difference, so it has been concluded that there is a significant effect of thermal lag between read out temperature and sample temperature on the \(T_g\) measured by DMA.

In the IEC 61006 the 2-point temperature calibration should be performed by determination of the onset temperature of ice (0 °C) and indium (156.6 °C) in the penetration method. However, it is not given how the method should be applied and is referred to the manual of the equipment manufacturer. In case of the DMA 7e from Perkin Elmer, it is stated that an aluminum pan with indium should be positioned on the flat bottom of the sample holder, followed by a thermal program to determine the onset of penetration. This method unfortunately does not take the sample (e.g. thermal conductivity and dimensions) for the 3-point bending into account. Moreover, the thermal wire that determines the sample temperature is not calibrated for the to be analyzed sample and sample position. In the experimental set-up section an improved method used for the calibration is presented.

### 2.3 Influence of the sample aspect ratio

In [7] a study on the influencing factors for DMA testing of fiber reinforced composites was performed. This study found out that the glass transition temperature is independent of the specimen aspect ratio. The aspect ratio is the ratio of the support span width divided by the sample thickness. In case of the glass/epoxy reference an aspect ratio of 27 fitted the results from flexural modulus testing of the DMA and ASTM D790 very well. For high-modulus (carbon/epoxy) a higher aspect ratio is recommended. The thickness of the samples were reduced by polishing in order to change the aspect ratio. The ASTM uses the tangent method for the flexural modulus, so a tangent between 0.05 % and 0.25 % displacement of the load-displacement diagram. However, the DMA uses the secant method and includes also the values below 0.05 % and may include initial machine adjustment errors as well. Therefore, it was recommended for glass fiber composites to use a load for the testing that results in a displacement of at least 0.04 %.

### 2.4 Thermal Ageing

Odegard [8] describes two changes in the molecular structure of an epoxy during thermal ageing. The first change is the reduction of free volume due the locked-in molecular structure. This is a result from the start of cross-linking in the liquid state (not crystalline state), so the amorphous structure is permanently secured by the presence of newly formed rigid crosslinks. The second change is the volume-independent configuration changes in the molecular network. With increasing ageing levels
more energy is required to initiate rubbery phase molecular motions. Experiments show that for ageing below $T_g$ the coefficient of thermal expansion reduces with increasing ageing time.

In [9] the thermal degradation of filled epoxy systems by means of DMA-measurements on samples aged at 160 °C was investigated. It was shown that thermal ageing (up to approx. 2000 h) above glass transition temperature leads to an increase of the storage modulus which results in a decrease in the tan delta values. The glass transition temperature determined from the tan delta values are increased with increasing ageing time with more than 20 °C to approx. 160 °C. This means that the dynamic damping performance is reduced.

In [10] DMA measurements were performed on thermal aged composite materials used for rotating machines. However, here it is shown that with increasing ageing time (from 284 to 1202 hours) the storage modulus decreases. Furthermore, the glass transition temperatures from the loss modulus and tan delta are shifted toward higher values with increasing ageing time. The height of the tan delta peak is reduced from 0.2 to 0.15. In contrast to other publications or standards a frequency of 2 Hz was applied.

The described methods can be used for quality control directly after manufacturing, but also provide valuable information about the material quality during operation (e.g. influence of thermal ageing or dynamic loading).

3 Experimental Part

For the experiments in this contribution, Vetresit 17 material was supplied by ABB Micafil Laminate Technologies (Klingnau, Switzerland). The glass fiber reinforced heat resistant epoxy samples have an overall thickness of 1.11 – 1.14 mm. Samples in various dimensions were cut out of the large plate in the manufacturing direction.

For the thermal analyses by means of the DSC, samples with a weight of 64 to 73 mg were placed in a DSC 7 from Perkin Elmer to determine the heat flow as function of the temperature. The measurements were performed under nitrogen with a heating rate of 25 K/min.

The TMA-measurements were performed by a TMA 402 F1 supplied by Netzsch under a helium flow of 20 ml/min with a heating rate of 3 K/min. The sample size was approx. 4.0 x 4.0 mm. This equipment can perform modulated force thermomechanometry as well.

For the DMA-measurements the sample length was 23 mm and the width 4.0 mm. Various support width having a lengths of 10, 15, or 20 mm were used. The static and dynamic forces were also varied for the measurements between 200 and 2880 mN in the 3-point bending mode. The frequency for the measurements was set to 1 Hz; only a few measurements were performed at a frequency of 0.2 and 5 Hz. The measurements were again performed under a helium flow of 20 ml/min with mainly a heating rate of 3 K/min.

In order to determine a temperature difference over the sample length indium was placed at two different locations in the measuring cell or furnace. Position #1 is at the tip of the support and the position #2 is located underneath of the probe (Fig. 7).

![Fig. 7: Set-up to determine the temperature distribution](image-url)

During heating indium will soften, the probe penetrates the material and indicates that the temperature of 156.6 °C has been reached. In case of a thermal difference two penetration onset temperatures will be recorded. The thermal wire is located on the same height at the sample.

Dielectric spectroscopy measurements were performed isothermally in the frequency range $10^{-2}$ – $10^{7}$ Hz at various temperatures from 40°C to 200°C using a Novocontrol Alpha analyzer. Temperature control was achieved by a Novocontrol Quatro cryosystem (temperature stability better than 0.1°C). Round electrodes (Au over Cr), 30 mm in diameter,
were deposited on both sides of \(38 \times 38 \text{ mm}^2\) samples to ensure good electrical contacts (Fig. 8).

The frequency of the dielectric spectroscopy is varied between \(0.01 \text{ Hz}\) and \(1 \text{ MHz}\), and the temperature in 13 steps between \(40 \degree C\) and \(200 \degree C\).

The mechanical testing was performed in accordance to the DIN ISO 178 with support radius of \(5 \text{ mm}\) (Fig. 9). As the average sample thickness is \(1.12 \text{ mm}\), a sample width of \(25.0 \text{ mm}\) and a sample length of \(80 \text{ mm}\) were selected.

The tests were performed in a universal testing machine provided by Zwick. A climatic chamber was installed to measure the flexural strength and modulus at RT, and at elevated temperatures of \(130 \degree C, 155 \degree C,\) and \(180 \degree C\). These temperatures correspond to the temperatures classes B, F, and H which are provided in IEC 60085.

Due to the elevated temperatures, it was required to use a load cell of \(100 \text{ kN}\). Previous investigations showed a negligible/small difference between the mechanical data of the more suitable \(5 \text{ kN}\) and the large \(100 \text{ kN}\) load cell.

4 Results

4.1 DMA Calibration set-up

With the set-up for the DMA calibration (Fig. 7) a thermal run was performed. The recordings of the thermal wire at various positions are presented in Fig. 10. Initially, three different support lengths (10, 15, and \(20 \text{ mm}\)) were investigated.

As can be seen, the support length has no significant influence on the onset temperature of the first penetration. A higher helium flow of \(40 \text{ ml/min}\) leads to a small change of onset of only approx. \(4 \degree C\). This clearly indicates that the middle of the sample (pos. \#2) has a temperature that is approx. \(30 \degree C\) lower than the temperature at the support (pos. \#1). The heating rate was also varied from 3, 5 and \(10 \text{ K/min}\). Here also similar temperature differences of \(30 \degree C\) were observed, so the low thermal conductivity of the glass epoxy materials is not of influence. Apparently, the metallic probe tip/knife subtracts heat from the furnace and determines therefore the temperature underneath of it, which is the location where the bending occurs. Furthermore, the cold purge gas (helium) is guided along the probe holder and cools the metallic structure.

Especially for a small support width of \(10 \text{ mm}\), this temperature gradient is approx. \(6 \degree C/\text{mm}\). Here it is...
unclear to which extent the determined material properties are influenced by this high temperature gradient.

The observations were verified with a prepared sample in which thermal wires were imbedded. The results from these observations match with the results from the indium experiments. The position for calibration at the bottom of the measuring cell has the same temperature as the top of steel support system (pos. #1) and is therefore a wrong position for calibrating the three point bending set-up in the DMA. Measurements performed in [11] confirm similar large differences on the DMA furnace.

In case of an not correct calibration position of the equipment, large difference in the recorded thermal behavior can be expected, leading to e.g. broader peaks in the loss modulus and tan delta, the onset of the storage modulus will be reduced as well. The performed measurements clearly show the importance of correct calibration with the to be analyzed sample and measurement settings.

**4.3 Glass transition temperature of Vetresit 17**

Important for the final material application is to know the glass transition temperature or even better the glass transition temperature range. DSC, TMA, and DMA-measurements with the given settings in section 3 were performed.

The DSC measurement of Vetresit 17 showed a clear \( T_g \) (\( T_{\text{mid-point}} \)). Especially in the TMA measurement (Fig. 11) is can be seen that glass transition is merely a process over a large temperature range, and is not a single point.

Fig. 11. TMA-measurement in thickness direction of Vetresit 17 (2\textsuperscript{nd} run)

By definition of the standard, the onset of the sample expansion is the glass transition temperature.

Fig. 12 shows the DMA measurement of Vetresit 17.

The measurements already clearly show that there is a variety of 5 °C on the determined glass transition temperature of the same material.

Instead of using the 3-point bending samples, one could use the dynamic compression mode in the TMA as well. Suitable devices can modulate the force, so a change in the elastic behavior of sample can be detected as well. A thermal scan of the sample under sinus-shaped modulated forces enable the observation of loss modulus and tan delta in compression (Fig. 13). As in this contribution only a closer look at the temperature is given, no absolute values for the loss modulus and tan delta are provided for this measuring mode. The difference

### Table 1: Various \( T_g \)-values of Vetresit 17

<table>
<thead>
<tr>
<th>Method</th>
<th>Difference in ( T_g ) (compared to ( T_g, \text{TMA} ))</th>
<th>Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC (2\textsuperscript{nd} run) +2 °C heating rate: 25 K/min</td>
<td>heating rate: 25 K/min</td>
<td></td>
</tr>
<tr>
<td>TMA (2\textsuperscript{nd} run) 0 heating rate: 3 K/min</td>
<td>heating rate: 3 K/min</td>
<td></td>
</tr>
<tr>
<td>DMA +1 °C mid point lin. storage mod.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMA 0 peak of loss modulus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMA +4 °C peak of tan delta</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 12: DMA-Measurement of Vetresit 17 (2\textsuperscript{nd} run)

The peak of the loss modulus was clearly detected and had the same value as the \( T_g, \text{TMA} \). The peak of tan delta is 4 °C above the value of a \( T_g, \text{TMA} \).

A summary of the various glass transition temperatures is presented in Table 1.
between the \( T_g \), \( T_{\text{TMA}} \) (determined in the same measurement) and the peak of loss modulus and peak of the tan delta, is approx. 25 to 35 °C. The static force was 960 mN, and the dynamic force was set to 800 mN. The penetration tool with a tip of 1 mm was used.

![Fig. 13: Loss modulus, tan delta, and sample height of Vetresit 17 as a function of temperature measured in the compression mode with modulated forces](image)

The advantage of this method is that the sample are small, so little temperature difference in the sample are available. However, several samples need to be measured as the small samples could have locally different mechanical properties, especially in the case of woven fabric reinforced composites. Another disadvantage is that the sample need to be heated up to temperature 30 to 50 °C above the \( T_g \), \( T_{\text{TMA}} \) in order to obtain clear peaks in the loss modulus and in the tan delta curves.

It is obvious that the temperature influences the coefficient of thermal expansion as well (Table 2).

**Table 2: Comparison of coefficient of thermal expansion of Vetresit 17**

<table>
<thead>
<tr>
<th>Temperature range [°C]</th>
<th>Thermal expansion (thickness direction) ([10^{-6}/\text{K}])</th>
<th>Thermal expansion (fiber direction) ([10^{-6}/\text{K}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 – 100</td>
<td>35 - 50</td>
<td>14 - 16</td>
</tr>
</tbody>
</table>

The coefficient of thermal expansion in the thickness direction of the sample is changed significantly from approx. 35-50 \([10^{-6}/\text{K}]\) below the glass transition temperature to approx. 4-times this value above the glass transition temperature.

As the slot insulation is a thin sheet of 1 mm, the relative thermal expansion from RT to 130 °C in thickness direction is only 5 µm. Also in fiber direction the thermal expansion is small for the range of RT to 130 °C. Although the parts can be up to 10 m, the thermal expansion would be 15 mm.

### 4.4 Mechanical testing and comparison to DMA measurements

The flexural modulus of Vetresit 17 was determined in accordance with ISO 178 and is illustrated in Fig. 14. Five samples were measured and resulted in the given error bars with 95 % confidence intervals. The flexural modulus decreased from 20 GPa at 130 °C to 15 GPa at 180 °C. The flexural strength at 155 °C is approx. 270 MPa (± 10 %).

![Fig. 14: Flexural strength and modulus as function of the testing temperature](image)

In order to make the relation between mechanical tests and DMA-measurements the aspect ratio should be similar. The support span in the DMA was set to the maximum value of 20 mm, the tool used for the flexural modulus had a fixed span of 25.4 mm. Furthermore the applied forces in the DMA must be high enough in order to obtain a similar deformation.

From the load displacement diagram (Fig. 15) it can be seen that up to 1.2 % is deformation the material has a linear elastic behavior, so high forces can be applied without reaching the viscous region. Moreover this also explains the low tan delta value of the DMA measurements.
INFLUENCE OF TEMP. ON PHASE TRANSITIONS IN GF/EP FOR ELECTRICAL SLOT INSULATION

Fig. 15: Flexural strength – deformation diagram of Vetresit 17 at 155 °C

Fig. 16 shows a DMA-measurement, where the support width was set to 20 mm in order to be as close as possible to the support width of the mechanical testing set-up. The forces of the measurement were set to 2880 mN (static) and 2400 (dynamic) in order to generate an amplitude of approx. 40 µm at room temperature. This value corresponds to a deflection of 0.07 %. At increased temperatures the amplitude increases to 60-65 µm, which corresponds to a deformation of 0.10 % and is on the lower range as where the flexural modulus (ISO 178) is determined (0.05 % and 0.25 %).

When the values of the storage modulus are added to the values of the loss modulus the complex modulus is obtained [11]. Fig. 16 illustrated the difference in the moduli from the mechanical testing and the dynamic mechanical analyses.

The DMA has in each cycle a point where little dynamic force is applied.

- The radius support structure and the radius of the probe are different (sharp edges versus a radius of 5 mm)

However, the tendency of both measurements are quite similar at elevated temperatures.

Performing 3-point bending tests at increased temperatures is generally time consuming and requires a lot of effort. Here, the DMA has advantages as this measurement is performed with little effort. Additionally, the DMA provides usually easy to be detected peaks in the tan delta values. Especially, for dynamical mechanical loaded parts, the DMA could provide useful information about the material quality as well.

The tan delta value provides besides the T_g, also information about the damping performance. In a further experiment, the equipment was heated up to the T_g, Tan Delta max and three different supports spans (10; 15, and 20 mm) were varied. Then the tan delta values were determined by changing the applied forces (Fig. 17).

Fig. 16: Comparison of the storage modulus (DMA) with mechanical determined values flex. modulus

As can be seen the values from the DMA measurements are similar to the flexural modulus, especially near T_g. Possible causes for deviation are:

- The way of measuring (secant method or tangent method) leads to some difference.

Fig. 17. Tan delta values of Vetresit 17 for 10, 15 and 20 mm of support span measured at T_g, Tan delta (solid markers) and the corresponding amplitude (open markers)

It can be seen that low forces lead to differences in the absolute tan delta value. The modulus determination is not yet performed in the linear elastic region. At higher forces (above 5280 mN) the tan delta value is quite constant. Furthermore, the higher tan delta value for the 10 mm support width indicated that higher loss are generated in the sample, like is presented in [7].

The effect of an increase of the applied bending force for an elastic material should lead to an
increase in the deflection as well. In the case of the DMA the deflection is represented by the amplitude. For the various applied forces up to 6600 mN, the amplitude is determined and a quite linear behavior is visible. This means the measurements with a total 2880 mN static force and 2400 mN dynamic forces are in the constant region and correct measurements are performed.

In case of using the tan delta values of the DMA for quality control, one should take of course the same sample thickness, but also use the same support span to determine a similar graph like in Fig. 17.

One further setting of the DMA is of influence on the value of the glass transition temperature. This setting is the measuring frequency of the probe. In the IEC 61006 a frequency of 1 Hz is proposed, but also other values may be taken. On the Vetresit 17 samples, the glass transitions temperatures the tan delta peaks are determined at frequencies of 0.2, 1, and 5 Hz (Fig. 18).

As can be seen the temperature difference on the peaks of tan delta are approx. 7 °C. With the lower frequency the polymer can more easily follow the oscillations, and softens at lower temperatures than for higher frequencies.

4.5 Dielectric spectroscopy

Dielectric spectroscopy results, namely the dielectric constant and the dielectric losses as a function of frequency for the various temperatures indicated in the plot, are shown in Fig. 19 and Fig. 20, respectively.

Fig. 18: Tan delta of Vetresit 17 as function of the temperature measured with various frequencies

As can be seen the temperature difference on the peaks of tan delta are approx. 7 °C. With the lower frequency the polymer can more easily follow the oscillations, and softens at lower temperatures than for higher frequencies.

Fig. 19: Dielectric constant (\(\varepsilon^\prime\)) of Vetresit 17 as function of the frequency at various temperatures

Fig. 20: Dielectric losses (\(\varepsilon^\prime\)) of Vetresit 17 as function of the frequency at various temperatures

At low temperatures (70 °C) the dielectric constant (\(\varepsilon^\prime\)) is fairly flat having a value of about 5.9 and the dielectric losses (\(\varepsilon^\prime\)) are low (below 0.01) showing only a small increase at low frequencies (< 1 Hz). For higher temperatures, close to and above to the polymer’s glass transition, a significant increase is observed. In particular, a broad loss shoulder appears on the low frequency side, at around 1 Hz for 125 °C, shifting to higher frequencies as temperature increases. This dielectric relaxation is attributed to the glass transition of the amorphous phase (often called dynamic glass transition), involving cooperative motions of the polymeric chains. As it is known, dielectric relaxations appear as steps in \(\varepsilon^\prime\) as and peaks in \(\varepsilon^\prime\). Here, the relaxation associated with the glass transition, often also called as \(\alpha\) relaxation, appears more as a shoulder in \(\varepsilon^\prime\) since conductivity contributions (charge carrier motions released at temperatures above \(T_g\)) are superimposed on its low frequency side.

The above trends are also depicted in the isochronal representation of Fig. 21 (\(\varepsilon^\prime\) and \(\varepsilon^\prime\)) as a function of temperature for a fixed frequency). Here the frequency of 50 Hz has been chosen due to its importance in electrical applications. As it is seen \(\varepsilon^\prime\) shows a weak temperature dependence. It should be also noted that the normal operation temperature of
Vetresit 17 material is always below that temperature. For higher temperatures, a strong deviation to significantly higher values is observed. Below \( T_g \) no/little motion of the dipoles is allowed, while above \( T_g \) the polar groups of the epoxy matrix can move more freely as a result of the increased free volume, hence the dielectric constant increases from this point on.

Fig. 21: Dielectric constant and losses of Vetresit 17 as function of temperature at 50 Hz

The discussed above determination of the glass transition temperatures and the influence of the various settings will now be applied on analyses on thermally aged rotor slot insulation.

### 4.6 Thermal Ageing of Slot Insulation

Changes in storage and loss modulus and tan delta, as determined by DMA-measurements, due to polymer degradation have been reported in [7]. In order to observe the thermal ageing influence on the Vetresit 17 slot insulation, samples were placed in a hot air oven at both 155 °C and 180 °C for 28 days.

For the testing at room temperature no change in the flexural modulus is observed after the ageing. The aged samples tested at 155 °C show only a small increase of 10 %, which is however within the confidence intervals of the not aged and aged materials.

The \( T_g \)-values for the DSC were difficult to see, although large samples were used. However, an increase of 10 and 13 °C was observed compared to the unaged sample. In the DMA the increase was 7 to 9 °C.

The glass transition temperatures measured by DSC, TMA, and DMA are summarized in Table 3.

<table>
<thead>
<tr>
<th>Method</th>
<th>Difference in ( T_g ) (compared to ( T_g ), TMA)</th>
<th>Aged at 155 °C ( T_g )-Value</th>
<th>Aged at 180 °C ( T_g )-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC (2nd run)</td>
<td>+2</td>
<td>+12</td>
<td>+15</td>
</tr>
<tr>
<td>TMA (2nd run)</td>
<td>0</td>
<td>+11</td>
<td>+13</td>
</tr>
<tr>
<td>DMA (peak loss mod.)</td>
<td>0</td>
<td>+8</td>
<td>+11</td>
</tr>
<tr>
<td>DMA (peak tan delta)</td>
<td>+4</td>
<td>+11</td>
<td>+13</td>
</tr>
</tbody>
</table>

Especially the DMA-measurement show a significant change in the tan delta values (Fig. 22).

Accordingly, the higher ageing temperature of 180 °C does not lead to a further reduction of the tan delta value compared to the value of 155 °C. The tan delta value decreased 40 %, indicating that the sample performs more elastic (storage modulus) and reduced the viscous contribution (loss modulus). An explanation for this are that not bonded side groups had the possibility to react or smaller compounds are outgassed of the samples [9].

Fig. 22: Tan delta value from DMA experiments

Dielectric spectroscopy results presented in Fig. 23 are in line with the above mentioned statement.
Fig. 23: Dielectric losses of Vetresit 17 (non aged, aged at 155 °C, and aged at 180 °C samples) as a function of frequency above \( T_g \).

Even though it is difficult to check any effects of ageing on the position of the \( \alpha \) relaxation process (associated to the glass transition) due to the superposition of conductivity contributions, an apparent decrease in the AC conductivity with ageing is observed (see inset in Fig. 25 where for low frequencies \( \sigma' \) decreases at about one order of magnitude upon ageing). This implies existence of less ionic species contributing to conduction due to either their reaction and incorporation into the crosslinked network or their removal as volatiles (outgassing). The inset also shows the corresponding frequency dependence of \( \sigma' \) (real part of AC conductivity, with \( \sigma' = 2\pi f \varepsilon_0 \varepsilon'' \) where \( f \) is the frequency and \( \varepsilon_0 \) the permittivity of free space).

5 Conclusions and Summary

From the performed measurements above, the following can be concluded:

- The various glass transition temperatures of Vetresit 17 determined by TMA, DMA, and DSC show differences in the values of 5 °C.
- Modulated force TMA measurements show peaks of the loss modulus and tan delta that are approx. 30 °C above the \( T_g,_{TMA} \). However, this technique provide besides a clear \( T_g \) also information about the mechanical performance.
- The flexural modulus from mechanical testing for the evaluated materials is higher than the value of the DMA measurements. At elevated temperatures (130 °C and 155 °C) a good similarity is shown. High forces on the DMA equipment are required in order to generated a high enough amplitude or deformation.
- DMA is suitable for the \( T_g \) determination of composite materials. The \( T_g \)-values are a few degrees lower than the \( T_g \)-values by means of TMA. However, in the case of the DMA thermal difference up to 30 °C in the sample are present due to the support structure and probe holder.
- Dielectric measurements support the findings obtained by mechanical and thermal characterization techniques. In particular, the dielectric constant increases significantly at temperatures close to and above \( T_g \).
- Ageing at 155 °C and 180 °C lead to an increase of the glass transition temperature up to 9 °C, accompanied by a decrease in the AC conductivity at low frequencies.
- Tan delta values as determined by DMA-measurements before and after ageing show a decrease of 40 %. The increased \( T_g \) indicate that probably the cross link density has been increased and so the loss modulus and tan delta decreased.

6. References


