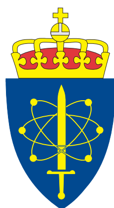

FFI-rapport 2013/01956

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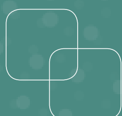

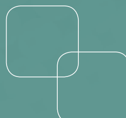

FFI Forsvarets forskningsinstitutt

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Characterization of the material properties of two FR4 printed circuit board laminates

Espen Tunhøvd Haugan and Per Dalsjø

Norwegian Defence Research Establishment (FFI)

10 January 2014

FFI-rapport 2013/01956

1234

P: ISBN 978-82-464-2322-7
E: ISBN 978-82-464-2323-4

Keywords

Kretskort

Laminat

DMA

Viskoelastisitet

Glasstransisjonstemperatur

Lodding

Approved by

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English summary

Most printed circuit boards are based on a laminate of weaved glass fiber cloth and epoxy. These laminates have so-called viscoelastic material properties. This means that properties such as elasticity and thermal expansion drastically change above a certain temperature, called the glass transition temperature. When selecting a laminate, the temperature range of the soldering process and the end application must therefore be taken into account. The objective of this work has been to increase our knowledge on laminates used in printed circuit boards by characterizing two FR4 laminates. This was done by measuring the storage and loss modulus, glass transition temperature, coefficient of thermal expansion and flexural strength. The effect of a typical soldering process was also investigated. The result was detailed material properties for the two laminates and an increased knowledge related to printed circuit board laminates in general. The work reported here was done as part of a summer internship.

Sammendrag

De fleste kretskort er bygget på et laminat av vevd glassfiberduk og epoksy. Disse laminatene har såkalte viskoelastiske materialegenskaper som vil si at materialets elastisitet og termiske utvidelse forandrer seg drastisk over en gitt temperatur, kalt glasstransisjonstemperaturen. Laminatet må derfor velges utifra temperaturområdet til loddeprosessen som benyttes og sluttapplikasjonen. Målet med dette arbeidet har vært å øke kompetansen relatert til laminatet i kretskort ved å karakterisere to FR4-laminat. Dette har blitt gjort ved å måle lagrings- og tapsmodulen, glasstransisjonstemperaturen, koeffisienten for termisk ekspansjon og bøyestyrken. Hvordan en typisk loddeprosess påvirker disse parameterne ble også undersøkt. Resultatet var detaljerte materialparametere for de to laminatene i tillegg til økt kompetanse på laminater for kretskort generelt. Arbeidet rapportert her ble utført som del av et sommerstudentengasjement.

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1 Introduction

Printed circuit boards (PCB) are used in nearly all modern electronic devices and have mainly two functions, which is to mechanically support the electronic components and to create conductive paths to achieve the desired circuit. The most common PCBs are based on a laminate of multiple layers of weaved glass fiber cloth and epoxy, where the mechanical properties can be tailored by the composition and interaction between the two components. This becomes a viscoelastic material with material properties that change significantly around the glass transition temperature (Tg).

When soldering the PCB assembly, the laminate will be exposed to temperatures above the glass transition temperature. The end application may also expose the PCB to a wide range of temperatures. The response of the laminate material as a function of temperature is therefore important. Directives such as the Restriction of hazardous substances directive (RoHS) [1] has resulted in a transition to lead-free solders for the majority of the electronics industry. These lead-free soldering processes require a peak temperature typically 30°C higher than traditional SnPb soldering processes [2]. For low-Tg PCB laminates (<140°C), this means temperatures almost 100°C above Tg. The objective of this work was to increase our knowledge on PCB laminates by studying the effect of exposing standard FR-4 laminates to standard soldering conditions.

Similar research has been performed by Sanapala [3], which investigated the effects of lead-free soldering conditions on key thermomechanical, physical and chemical properties of different FR4 PCB laminate materials. This was done by measuring the laminate material properties by using differential scanning calorimeter (DSC), thermo mechanical analyzes (TMA) and thermo gravimetric analyzer (TGA). Sanapala showed that exposing the different laminates to soldering conditions results in variations in the material properties of certain laminate. The exposure generally tend to lower Tg, the out-of-plane coefficient of thermal expansion (CTE), and time-to-delamination at 260°(T-260) of the material.

In this work we have characterized a low-Tg and a high-Tg FR4 laminate material and analyzed the effect of exposure to typical reflow soldering conditions. This was done by studying the viscoelastic material properties, in-plane CTE and flexural properties before and after exposure, and studying the thermal stability of the laminate material. Dynamic mechanical analysis (DMA) was used to measure storage modulus, loss modulus, Tg and in-plane CTE. A 3-point loading test was used to test the flexural properties. The thermal stability was determined by thermo gravimetric analyses (TGA). The laminate is anisotropic with directionally dependent material properties. Samples were therefore made with three different orientations.

The results show that exposure to typical reflow soldering conditions has a slight effect with a lowering of Tg and the elastic/storage modulus while the loss modulus is increased. The in-plane CTE was not found to be affected. However, the method used to measure CTE has limited accuracy for this type of material.

2 Test material

The material tested was the S1141 FR4 laminate manufactured by Shengyi with a specified glass transition temperature Tg=140°C. The datasheet for the laminate is given in Appendix A. The laminates consisted of 8 layers resulting in a thickness of 1.6 mm. The composite has an epoxy matrix with weaved glass fiber filaments as the reinforcing medium. For more information on the weave, see Appendix B. By studying the laminate material in an optical microscope, it is believed that a 7628 weave style is used. This can be seen by comparing Figure 2.1 to Figure B.1. This style gives two high-strength directions where the fibers are aligned, termed fill and warp. When weaving, the filament in the machine direction is referred to as warp filament, while filament perpendicular to the machine direction is referred to as fill. The performance of the laminate is also improved by additives such as curing agents, flame retardants, fillers and accelerators. The curing agents enhances polymerization in the resin, the flame retardants reduce the flammability of the material, the fillers reduce thermal expansion and the accelerators reduce curing temperature and control cross-linking density [3]. The test samples were cut from 300x100 mm rectangular laminate panels at 0°,45° and 90° relative to the length of the panel. The nomenclature used for the different samples are based on the assumption that the length of the panel is aligned with the warp direction. A few tests where also performed on a FR4 laminate material with a specified Tg=170°C from the same manufacturer. These samples have the additional identifier "high" in their nomenclature.

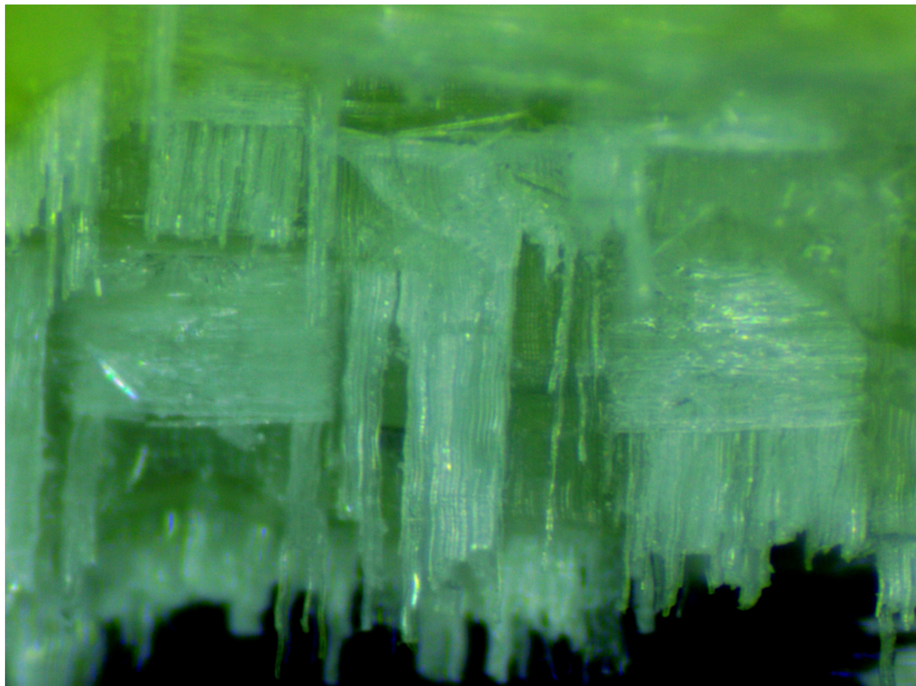


Figure 2.1 Fracture surface of the laminate material showing the weave style of the fibers in the laminate

2.1 Viscoelastic behavior

The laminate is a viscoelastic material. This means that during deformation, the material will exhibit the combined characteristics of an elastic and viscous material [4]. For an elastic material, stress is directly proportional to strain (small deformations), but independent of the rate of strain. For a viscous material however, the stress is directly proportional to the rate of the strain, but independent of the strain itself [5]. The material properties of the viscoelastic laminate are also temperature dependent. At low temperatures (below Tg and in the glassy region), the material will be rigid and somewhat brittle. By increasing the temperature, the glass transition temperature (Tg) is reached. This temperature is where the material changes from a hard, brittle "glass-like" form to a softer, rubberlike consistency [6]. This is because of reversible breakage of Van der Waals bonds between the molecular chains. The measured value for Tg will depend on which mechanical property is measured and the experimental method used. Independent of the measuring method, the Tg for FR4 laminate systems also depends on the epoxy resin used and its percentage composition [3].

By measuring the material's stiffness and damping when the material is exposed to a periodic loading, it is possible to find the storage and loss modulus. The storage modulus is a measure of the energy stored and recovered per cycle, while the the loss modulus is a measure of the energy dissipated as heat per cycle. By studying these two measurements, it can be said that in regions where the storage modulus changes very slowly, the behavior is nearly perfectly elastic. The loss modulus will then also be relatively constant, which on a molecular scale corresponds to the absence of any molecular or atomic adjustments capable of dissipating energy within the period of deformation [5]. At the glass transition temperature however, these adjustments will occur, and a local maximum in the loss modulus will be seen. To describe the relationship between the storage and the loss modulus, a loss tangent is often used. This is defined as the loss modulus divided by the storage modulus, and will mathematically be the tangent of the phase lag (tan delta).

When performing a DMA, there are several options on how to measure the glass transition temperature, as can be seen from Figure 3.3. Both the inflection point of the storage modulus, the maximum of the loss modulus and the maximum of tan delta might be used to give Tg a value. Usually, the Tg value measured using the loss modulus will be several degrees lower than the if tan delta is used. This is due to the maximum of the loss modulus will denote the initial drop from the glassy state into the transition, while the Tg value obtained by using tan delta corresponds more closely to the transition midpoint [7]. In literature, all three of these values can be found to represent the Tg of a material as there is no given standard for measuring this property. Other methods such as DSC and TMA may also be used to measure Tg.

2.2 Coefficient of thermal expansion

The coefficient of thermal expansion (CTE) describes the dimensional change in a material as a response to a change in temperature, and is defined as a percentage change in length per unit temperature. This phenomenon is often isotropic, but due to the structure of the laminate, this property becomes anisotropic, with different value of CTE for expansion in the plane of the aligned

fibers (in-plane), and out of the plane of the aligned fibers (out-of-plane). The reason for this is the difference in CTE of the glass fibers and the epoxy. As the glass fibers have a CTE of approximately 5-6 ppm/°C, they will expand less than the epoxy, which typically has a CTE of 35-45 ppm/°C [6]. As a result, in the in-plane direction the fibers will limit the epoxy expansion, while in the out-of-plane direction the the epoxy can expand less restricted. The resulting CTE of the composite will not entirely depend on the component's mechanical properties in isolated form, but also on the effectiveness of the chemical and physical bonds between the components, the degree of transfer of the modulus of the stiffer reinforcement materials into the resin, and the volume ratio of the components of the composite. A simplified computational model is the Schapery equation, which says:

$$CTE(composite) = \frac{CTE_1 \cdot M_1 \cdot V_1 + CTE_2 \cdot M_2 \cdot V_2 + \ldots\ldots}{M_1 \cdot V_1 + M_2 \cdot V_2 + \ldots\ldots} \tag{2.1}$$

Where CTE is the effective CTE of the component, M is the effective modulus of the component and V is the volume fraction [6].

CTE should be a concern when it comes to PCBs, as out-of-plane CTE could cause via cracking and delamination, while in-plane CTE may for example cause shear failures in solder joints.

3 Experimental conditions and procedure

3.1 Soldering programs

In order to expose the samples to similar conditions as when soldered, a IBL SLC509 vapour phase reflow machine was used. Two different exposures were used. Soldering program 1 corresponds to one soldering cycle, while soldering program 2 corresponds to three cycles. The profile seen in Figure 3.1 is the temperature profile of one soldering cycle. The time at the plateau varied somewhat for each run as the machine automatically adjusts according to a temperature sensor on the sample tray. This temperature is assumed to represent the temperature in the samples.

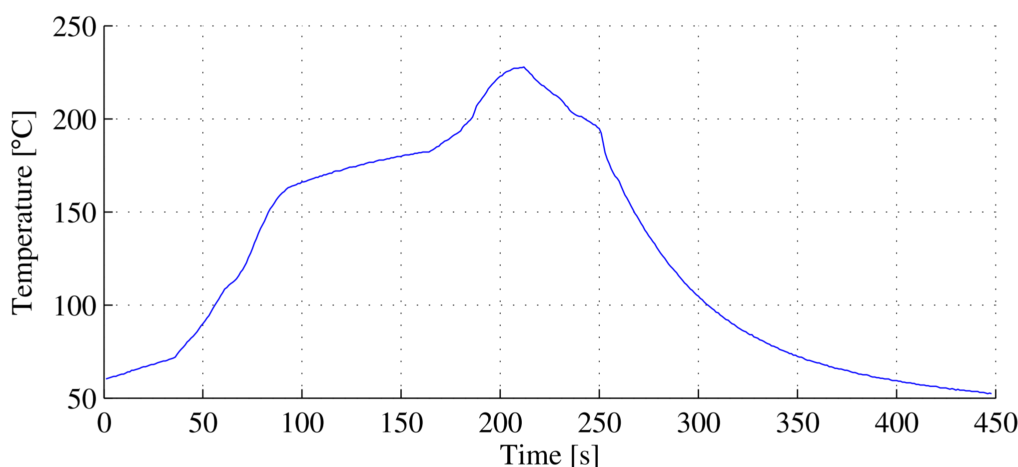


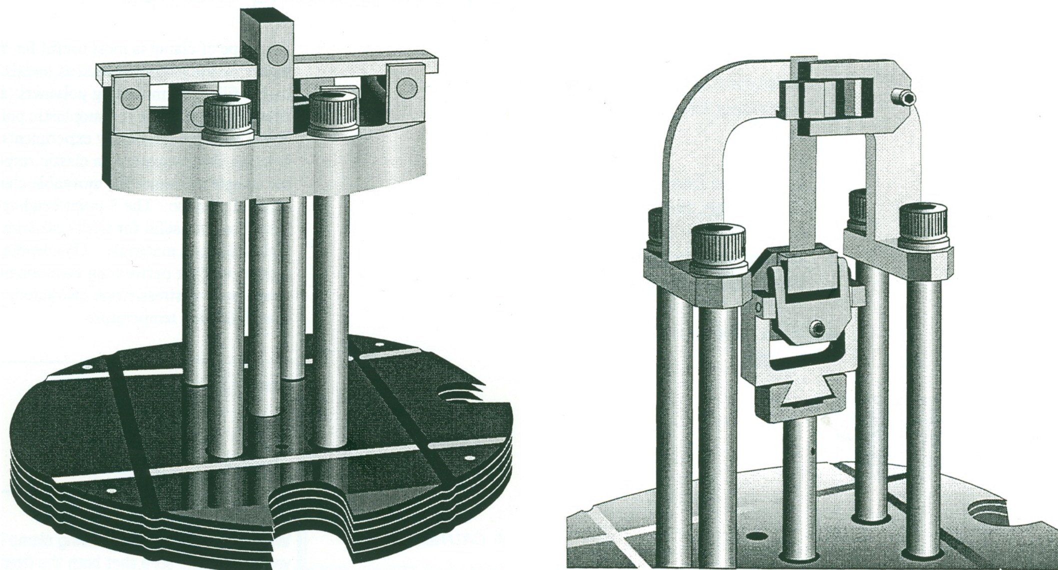
Figure 3.1 The soldering profile used in the two soldering programs.

3.2 Dynamic mechanical analysis

A TA Instruments DMA 2980 was used to measure the storage modulus, loss modulus and glass transition temperature of the laminate. The DMA test method is described in [8]. The laminate was cut into rectangular test samples of about 60 x 14 mm with three different orientations, longest axis parallel with the fill direction, longest axis parallel with the warp direction, and longest axis 45° on both the fill and warp direction. By using abrasive paper, the width of the samples were made to vary less than 0.05 mm. The DMA was done with a 3-point bending clamp as shown in Figure 3.2a. Amplitude and frequency of the deflection was set to respectively 50 μm and 1 Hz. The samples were then exposed to a temperature ramp up of 2°C/min from 30°C to 180°C.

Four samples of each orientation were tested with the above conditions. To examine if the soldering conditions would affect the material, two samples were exposed to soldering program 1, one sample was exposed to soldering program 2, while the last sample was used as a reference and was not exposed. All of the samples were then tested in the DMA once again with the same conditions as in the first test.

To test the behavior of the laminate at low temperatures, one sample of both the fill and warp direction



(a) Illustration of the 3-point bending clamp. The sample is resting on the support in each end, while the clamp in the middle oscillates with given frequency and amplitude.

(b) Illustration of the tension film clamp. The sample is held with a constant force, while the distance between the two points where the specimen is clamped is measured.

Figure 3.2 Illustration of the two clamps used in the DMA [9].

was tested with different conditions. Instead of a start temperature of 30°C, the initial temperature of the experiment was -75°C for the sample in the fill direction, and -60°C for the one in the warp direction [1]. The temperature ramp was still of 2°C/min. To obtain the low temperatures, liquid nitrogen was used, which gave an atmosphere with more nitrogen than in the tests starting at 30°C.

When it comes to the high-Tg laminate material, three samples of each orientation were tested. First, all of the samples went through a run in the DMA with similar conditions as the low-Tg samples. To reduce the time of each run the temperature interval was however set to 60°C to 180°C. Exceptions were two samples in the warp directions (warp_high_1 and warp_high_2) which were tested up to 210 °C. After the first DMA run, two samples of each orientation went through soldering program 2, before all of the samples were tested in the DMA again.

The DMA was also used in controlled force mode in order to measure the in-plane CTE of the different orientations of the laminate. This was done by using the tension film clamp as shown in Figure 3.2b. The applied force was 0.05 N and the temperature range was set to 30°C to 180°, with a ramp up rate of 1°C/min. By compensating for the known thermal expansion of the clamp the thermal expansion of the sample could be found. This expansion was then used to determine the CTE for the given laminate orientation. For more information on this compensation see Appendix C. The samples were rectangular and had dimensions of approximately 35 mm x 3 mm x 1.6 mm. Due to the narrow width of the samples, abrasive paper could not be used to achieve a uniform width. The width therefore varied 0.1 - 0.25 mm for the different samples.

[1] The initial temperature was increased from -75°C to -60°C for practical reasons.

Samples with the same three orientations were used in these tests. Four samples of the warp orientation, and three of the fill and 45°-orientation were run in the DMA to find the initial values of CTE of the samples. The samples were then exposed to soldering program 2, before a new run in the DMA was performed.

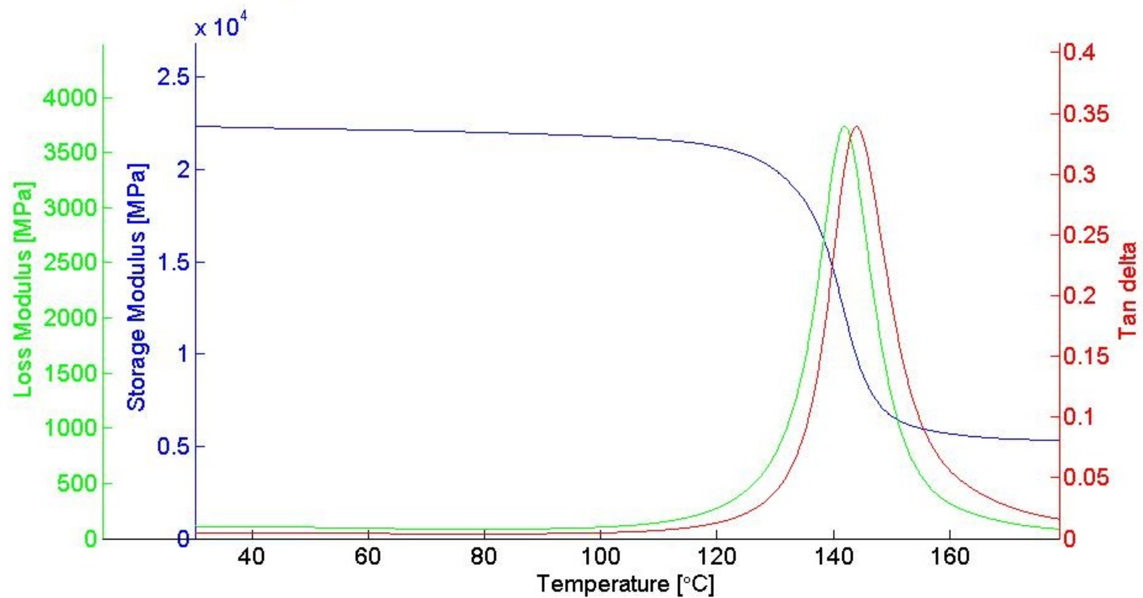


Figure 3.3 Tg-measurement with DMA.

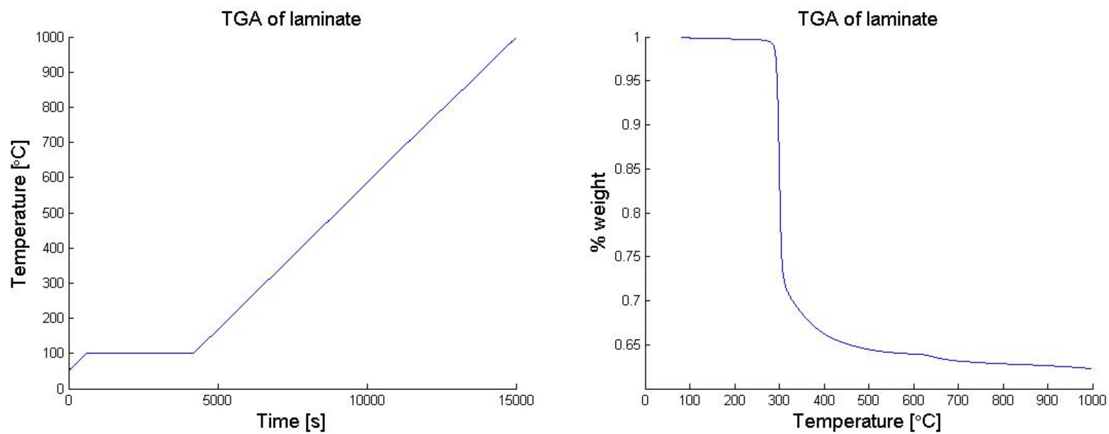
3.3 Thermogravimetric analysis

To examine the thermal stability, a thermogravimetric analysis was performed with Mettler Toledo TGA/SDTA851. The principles of a TGA is described in [10]. This analysis shows at what temperature the epoxy system undergoes irreversible degradation with destruction of the epoxy system (decomposition temperature), reducing the weight of the sample. The analysis was performed by using a small 15.578 mg sample of the laminate. The weight of the sample was measured in a temperature profile from room temperature to 1000 °C with a temperature ramp-up of 5°C/min, which is shown in Figure 3.4a. The change in %-weight of the sample is shown in Figure 3.4b. The experiment was done in an inert nitrogen atmosphere with a purge rate of 50 ml/min.

From the TGA-measurements seen in Figure 3.4b, it is also possible to roughly estimate the %-weight of epoxy in the laminate by studying how much weight that is lost when the epoxy decomposes.

3.4 3-point loading test

A 3-point loading test was performed with a Zwick BZ2.5 on a selection of the samples, to estimate the flexural strength, flexural strain and the elastic modulus of the laminate. This was done by placing the sample on a support, with a load nose pushing the middle of the sample down, as shown in Figure 3.5.



(a) Temperature profile of the TGA-experiment.

(b) Plot of the samples %-weight as a function of temperature.

Figure 3.4 Plots from the TGA-measurements.

The tests were performed with a load nose speed of 2.73 mm/min, and a span-to-depth ratio of 32. Based on the samples thickness of 1.60 mm, the span was set to 51.2 mm for all of the samples [11]. The load nose was displaced until either the sample failed, or the load on the sample was reduced to 80 % of the maximum load. The test method is described in [11]. The samples were the same as the samples used in the DMA to determine the viscoelastic properties. Samples of the low-Tg and the high-Tg laminate material were tested with the same conditions.

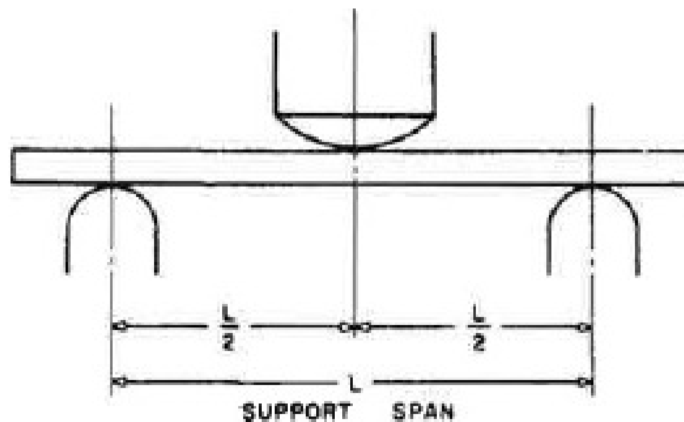


Figure 3.5 Illustration of the 3-point loading test. The sample is supported in both ends while the load nose pushes the middle of the sample down until failure. The fibers are aligned in the plane perpendicular to the load nose [11].

4 Results

4.1 Viscoelastic properties

The storage and loss modulus of the different samples were measured using DMA. The glass transition temperature was estimated based on these measurements and is presented in Table 4.1. Here, the first column identifies the sample. The glass transition temperature is given both for the inflection point of the storage modulus, the maximum of the loss modulus and maximum of the tan delta. Following the first DMA run, all the samples, except the reference samples, were exposed to a soldering program. This is stated in the fifth column. The remaining columns present the estimated glass transition temperatures from the second DMA. The corresponding storage and loss modulus at 60°C is presented in Table 4.2.

The results for the low-Tg material given in Table 4.1 is illustrated in Figure 4.1. The data for each orientation is plotted in a column, where fill is to the left, warp in the middle and 45° is to the right. Where there are more than one measurement value available, the average is plotted with the standard deviation. Inside each column, the green marker represents Tg based on the storage modulus, the blue marker represents Tg based on the loss modulus and the red marker represents Tg based on tan delta. There are also four subcolumns, the first presenting the initial values from the first DMA run. The second subcolumn presents the values from the second DMA run for the reference sample. The third and forth subcolumns presents the values from the second DMA run for samples exposed to soldering program 1 and 2 respectively. These subcolumns are also described in the legend. An equivalent illustration of the high-Tg material is given in Figure 4.2.

The measured storage and loss modulus at 60°C, given in Table 4.2, is plotted respectively in Figure 4.3 and 4.4. The results are plotted as function of exposure (Initial, None, SP1 - Soldering program 1, SP2 - Soldering program 2).

For samples with the same material, orientation and exposure the measured values are fairly stable, which makes it possible to analyze trends. From the second DMA run the reference samples show a slightly increased Tg, a slightly reduced storage modulus and an increased loss modulus. The samples exposed to the elevated temperatures of soldering program 1 and 2 show varying trends when compared to the initial values. The low-Tg fill and warp samples show a reduction in Tg, while the equivalent high-Tg samples show a stable or a slightly increased Tg. All samples, however, show a reduced storage modulus and an increased loss modulus.

Table 4.1 Estimated glass transition temperatures.

	First DMA run				Second DMA run		
Sample ID	Tg Storage modulus [°C]	Tg Loss Modulus [°C]	Tg tan delta [°C]	Exposure	Tg Storage modulus [°C]	Tg Loss Modulus [°C]	Tg tan delta [°C]
fill_1	141.64	141.84	144.23	Program 1	139.41	140.00	142.11
fill_2	140.82	141.13	143.52	Program 1	140.25	140.25	142.35
fill_3	140.60	141.00	143.40	None	144.28	144.58	146.58
fill_4	139.92	140.52	142.91	Program 2	138.57	139.07	141.17
mal_1	141.83	141.93	143.94	Program 1	138.20	138.20	140.30
warp_1	139.47	139.67	141.97	Program 1	139.03	139.23	141.23
warp_2	139.98	140.48	142.78	None	143.95	144.35	146.34
warp_3	139.03	139.23	141.63	Program 2	138.11	138.41	140.61
45_1	135.60	137.00	143.09	Program 1	139.55	137.55	142.95
45_2	134.30	137.71	143.59	Program 1	136.25	137.25	142.85
45_3	136.29	137.49	143.59	None	142.59	141.69	147.07
45_4	136.09	137.69	143.68	Program 2	135.90	135.80	141.10
fill_high_1	133.79	134.29	136.99	Program 2	134.83	135.33	137.93
fill_high_2	134.05	134.45	137.15	Program 2	135.98	136.18	138.88
fill_high_3	134.21	134.51	137.31	None	139.50	139.70	142.00
warp_high_1	135.89	136.39	138.99	Program 2	134.43	135.43	138.33
warp_high_2	135.39	135.99	138.39	Program 2	134.48	135.37	138.07
warp_high_3	136.20	136.79	139.29	None	140.46	140.76	142.96
45_high_1	131.55	132.35	138.64	Program 2	135.62	133.72	139.12
45_high_2	129.88	130.98	137.78	Program 2	133.45	133.84	139.24
45_high_3	131.23	131.73	138.23	None	139.79	138.49	143.69

Table 4.2 Measured storage and loss modulus at 60°C.

	First DMA run			Second DMA run	
Sample ID	Storage modulus [MPa]	Loss Modulus [MPa]	Exposure	Storage modulus [MPa]	Loss Modulus [MPa]
fill_1	20302	91	Program 1	19415	111
fill_2	20346	89	Program 1	19801	110
fill_3	19945	95	None	19572	103
fill_4	19772	87	Program 2	19542	107
mal_1	22158	93	Program 1	22062	102
warp_1	22361	79	Program 1	21758	100
warp_2	21823	80	None	21277	86
warp_3	22088	83	Program 2	21595	100
45_1	13523	111	Program 1	13038	147
45_2	13187	112	Program 1	12710	152
45_3	13274	115	None	12951	126
45_4	13177	109	Program 2	12918	146
fill_high_1	20600	88	Program 2	19876	99
fill_high_2	20470	83	Program 2	19435	92
fill_high_3	20495	81	None	19901	101
warp_high_1	22534	75	Program 2	22116	91
warp_high_2	22749	77	Program 2	21732	97
warp_high_3	22358	73	None	22232	84
45_high_1	13986	105	Program 2	13027	131
45_high_2	13776	106	Program 2	14071	144
45_high_3	13800	109	None	13202	121

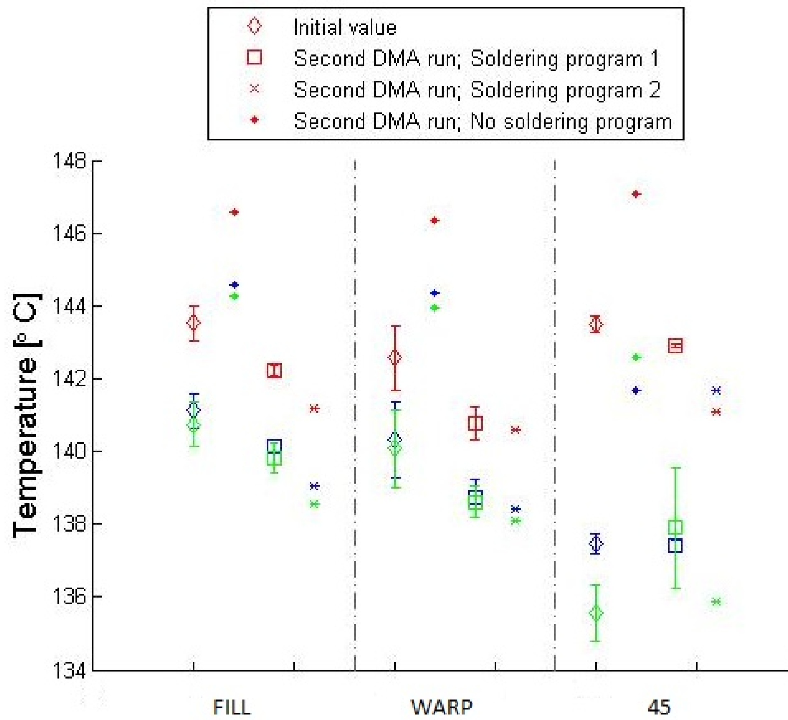


Figure 4.1 *Illustration of the results in Table 4.1 for the low-Tg laminate material. Green markers represents Tg based on the storage modulus, blue markers represents Tg based on the loss modulus and red markers represents Tg based on tan delta.*

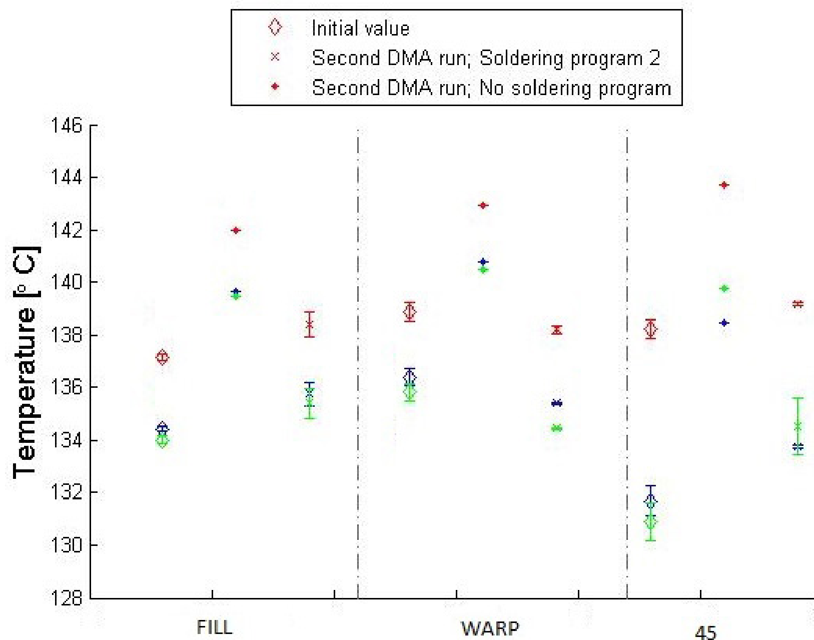


Figure 4.2 *Illustration of the results in Table 4.1 for the high-Tg laminate material. Green markers represents Tg based on the storage modulus, blue markers represents Tg based on the loss modulus and red markers represents Tg based on tan delta.*

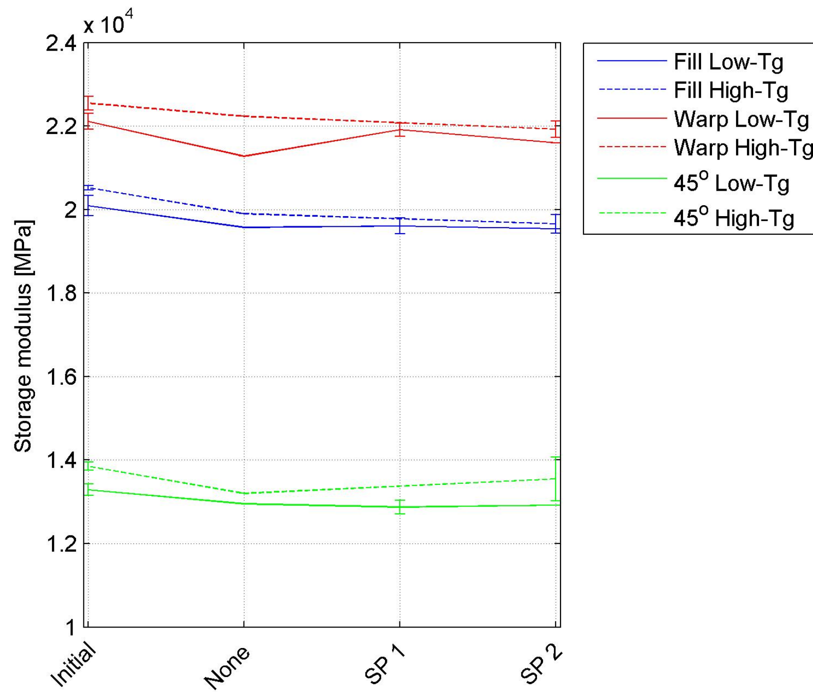


Figure 4.3 Plot of the measured storage modulus at 60°C as function of temperature exposure, sample orientation and laminate material. (SP1 - Soldering program 1, SP2 - Soldering program 2)

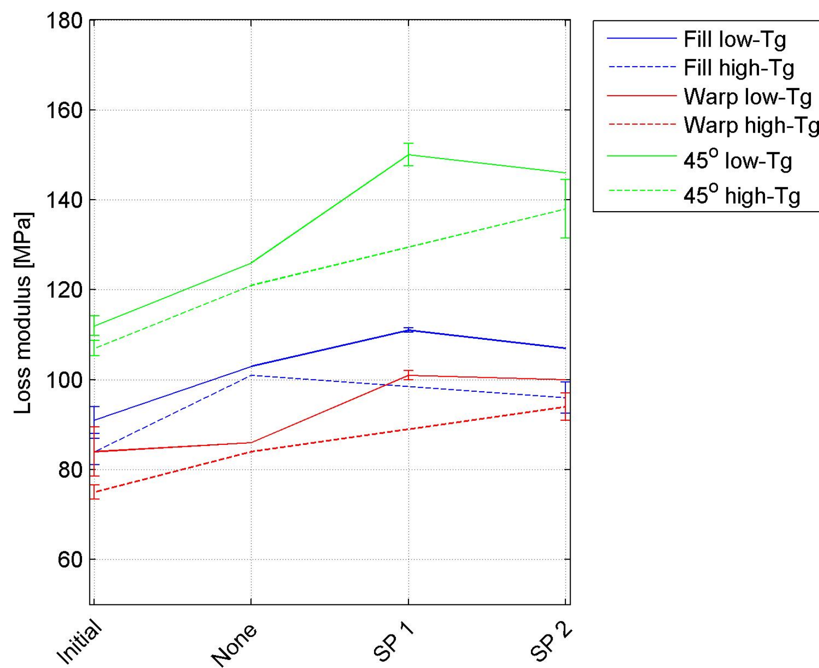


Figure 4.4 Plot of the measured loss modulus at 60°C as function of temperature exposure, sample orientation and laminate material . (SP1 - Soldering program 1, SP2 - Soldering program 2).

4.2 Coefficient of thermal expansion

The coefficient of thermal expansion (CTE) was measured only for the the low-Tg material using the experimental procedure described earlier. As the temperature increases, the length of the sample increases[2] linearly until approximately Tg, where the slope changes. This is illustrated in Figure 4.5. By measuring the slope above and below Tg and compensating for the expansion of the clamp itself, the CTE of the sample above and below Tg is found. To make sure the measurements were done in regions with a stable slope, the values between 75°C - 85°C and 165°C - 175°C were used. A plot of the established CTE values is given in Figure 4.6. Below Tg the CTE for all three orientations were comparable. The fill orientation had the highest CTE, while the warp orientation had the lowest. Above the glass transition temperature the CTE followed the same trend with regard to orientation. The relative difference between the orientations however, increased significantly. Exposing the samples to the soldering program 2 did not seem to affect the CTE.

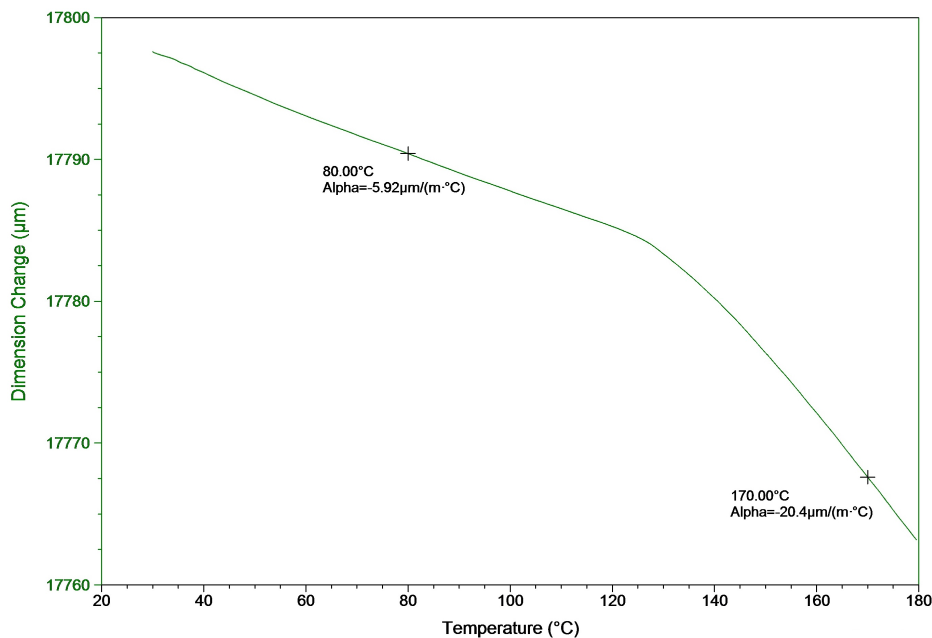


Figure 4.5 The measured displacement of the lower tension film clamp as a function of temperature. (Not corrected for the expansion of the clamp itself).

The accuracy of these measurements above the glass transition temperature is uncertain as the samples become soft. This may explain the negative CTE for the warp direction. This will be further addressed in the discussion section. As a consequence, the emphasis of these results should be on the measurements below Tg. The same problem is also described by Brown and Sottos [12].

[2]The length of the sample increases, which results in a downward displacement of the lower clamp in the tension film clamp fixture 3.2b.

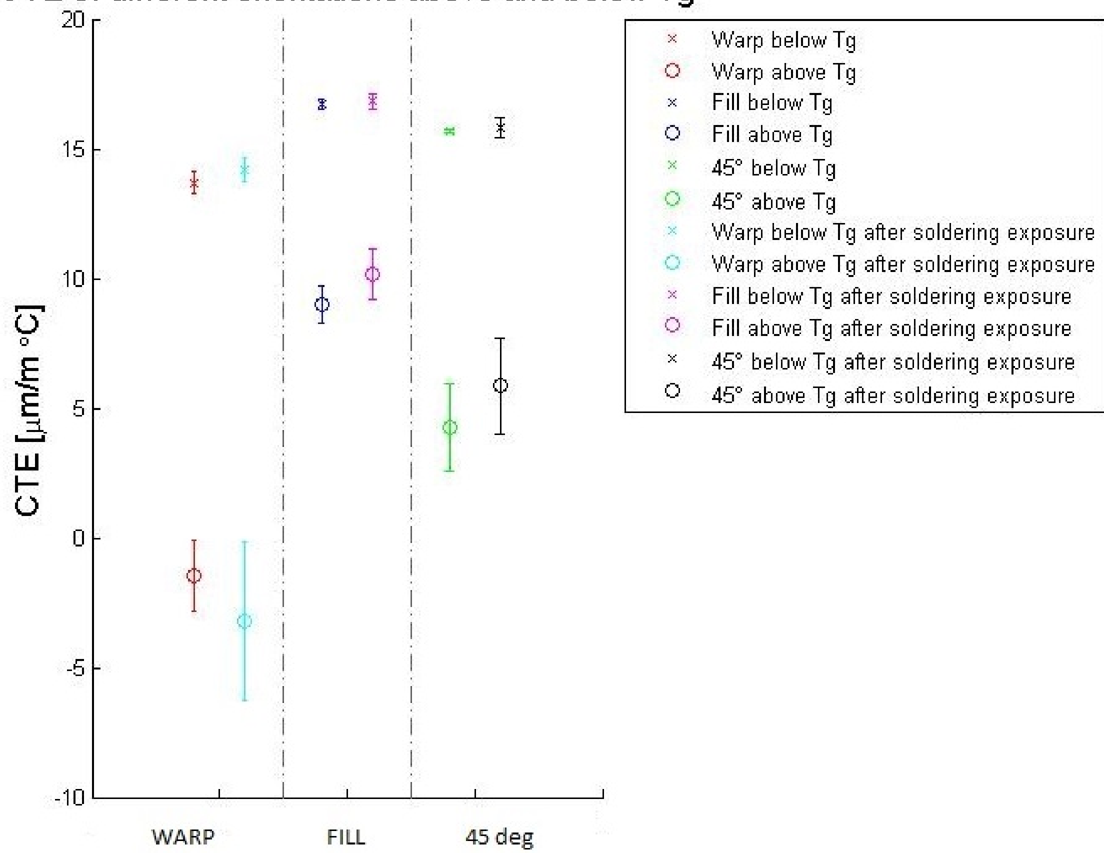
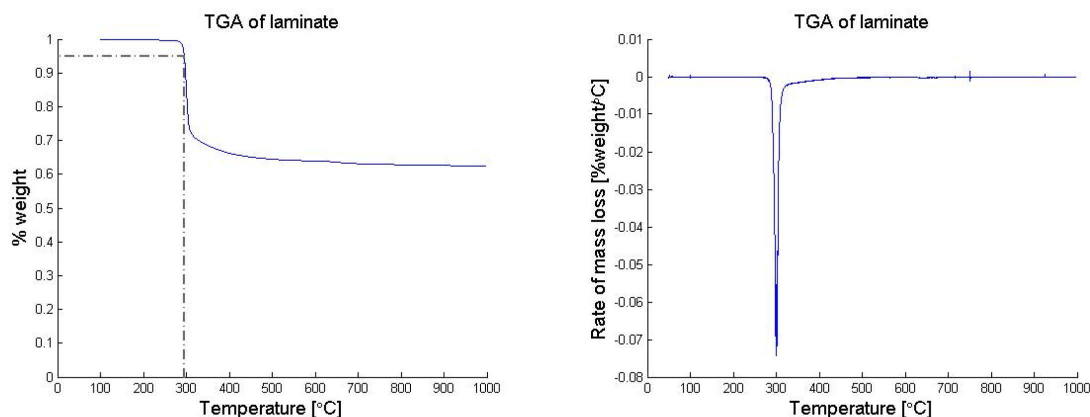


Figure 4.6 Measurements of the CTE for different orientations.

4.3 Thermal stability

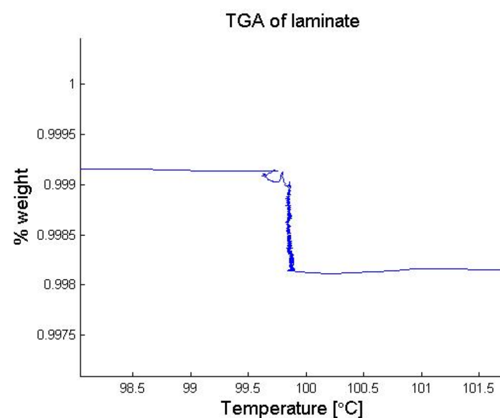
To determine the thermal stability of the laminate a TGA was performed on a low-Tg laminate material sample. The results from this measurement are presented in Figure 4.7a and 4.7b, where Figure 4.7a shows the weight of the sample compared to the initial weight, and Figure 4.7b shows the rate of mass change as a function of temperature. From Figure 4.7a, the thermal decomposition temperature is estimated to be 295 °C. This indicates that the epoxy should not decompose during soldering program 1 and 2. Figure 4.7c shows the evaporation of water from the laminate. From this the water content in the laminate is estimated to be low, only about 0.1 %-weight.

When the decomposition takes place, about 36 % of the weight of the sample is lost. This weight corresponds to the decomposed epoxy and shows that there is about 36 %-weight epoxy in the laminate.



(a) The %-weight of the sample as a function of temperature in the TGA-measurement.

(b) Rate of mass change in the TGA-measurement



(c) Mass loss at 100°C, corresponding to water evaporating.

Figure 4.7 Figures showing the results from the TGA-measurement.

The thermal stability of the laminate at low temperatures is also of interest. Figure 4.8 shows the result of a DMA run starting at -75°C. Here a slight increase in the storage and loss module can bee seen below -60 °C. The reason for this will be discussed in the Section 5.1.2.

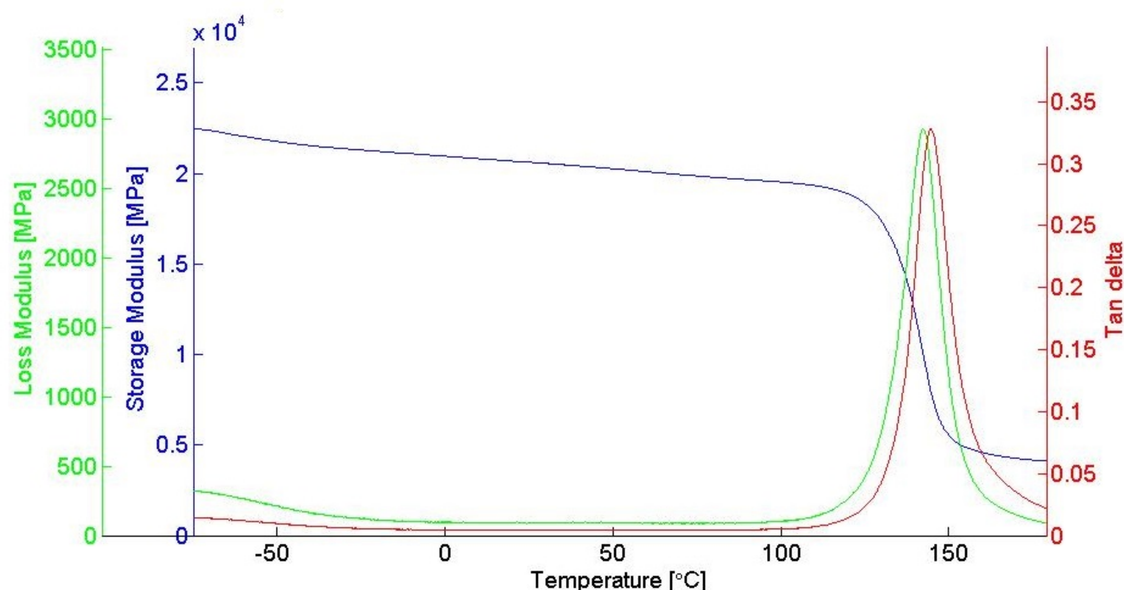


Figure 4.8 Results from a DMA run of a fill direction sample with an initial temperature of -75°C.

4.4 Flexural properties

Using the 3-point loading test the flexural strength, flexural strain and elastic modulus was measured. The results are presented in Table 4.3. A plot of the load as function of displacement and orientation for three low-Tg material samples is given in Figure 4.9. The flexural strength and strain is calculated based on the load at failure, the geometry of the sample and boundary conditions given by the 3-point loading test. The elastic modulus is calculated based on the linear part of the plot. For both the low-Tg and high-Tg material, the warp orientation has the highest values.

The load when failure occurs is highly dependent on small flaws that cause high stress concentrations. The flexural strength and strain is therefore not a accurate parameter. The 45° orientation is significantly more compliant than the warp and fill direction. As a result, these samples flexed and did not fail. This means that the flexural strength and strain could not be established.

Table 4.3 The measured flexural properties of the laminate.

Sample ID	Width [mm]	Thickness [mm]	Exposure	Flexural strength [MPa]	Flexural strain [mm/mm]	Modulus of elasticity [MPa]
fill_5	14.08	1.60	None [3]	467	0.0268	20640
fill_4	14.24	1.61	Program 2	505	0.0293	20202
fill_2	12.89	1.61	Program 1	424	0.0213	19787
fill_3	12.98	1.61	DMA [1]	395	0.0198	20563
warp_4	14.07	1.59	None [3]	542	0.0221	24838
warp_3	13.58	1.60	Program 2	503	0.0263	23695
warp_1	13.82	1.60	Program 1	569	0.0244	23813
warp_2	14,16	1.61	DMA [2]	577	0.0249	23342
45_5	12.93	1.60	None [3]	-	-	14186
45_4	14.11	1.61	Program 2	-	-	12345
45_2	12.79	1.61	Program 1	-	-	13237
45_3	12,63	1.61	DMA [1]	-	-	13413
fill_high_1	13.73	1.60	Program 2	452	0.0244	20114
fill_high_2	13.31	1.60	Program 2	486	0.0265	19932
fill_high_3	12.57	1.60	DMA [1]	453	0.0245	20223
fill_high_4	15.05	1.59	None [3]	431	0.0230	21152
warp_high_1	13.94	1.61	Program 2	620	0.0270	23410
warp_high_2	13.97	1.60	Program 2	662	0.0286	23485
warp_high_3	13.56	1.62	DMA [1]	579	0.0251	23168
warp_high_4	15.65	1.59	None [3]	572	0.0269	24286
45_high_1	13.26	1.60	Program 2	-	-	12882
45_high_2	14.34	1.60	Program 2	-	-	12422
45_high_3	13.54	1.60	DMA [1]	-	-	13481
45_high_4	15.40	1.60	None [3]	-	-	14522

[1] Two runs in the DMA as described in the experimental section.

[2] Three runs in the DMA, two as described in the experimental section and one from 30°C to 230°C with a ramp up rate of 2°C/min.

[3] Non-exposed laminate material.

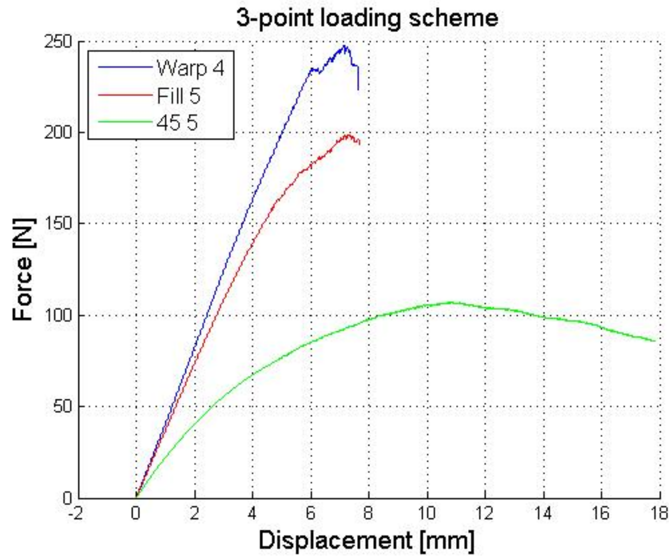


Figure 4.9 Comparison of the flexural properties of the different orientations for the low-Tg laminate material.

Plots of the load as a function of displacement for the low-Tg fill, warp, and 45° samples are given respectively in Figure 4.10, 4.11 and 4.12. It is difficult to identify any effect of the temperature exposure on the flexural strength due to the inaccuracy of this parameter. The results indicate however, that temperature exposure lowers the elastic modulus. Untreated samples have a slightly higher elastic modulus compared with samples that have been through DMA tests. More severe temperature exposure in the form of soldering program 1 and 2 reduces the elastic modulus further.

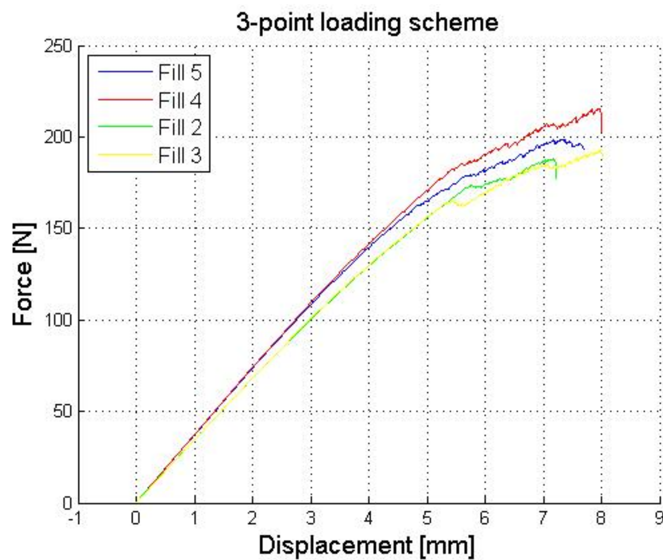


Figure 4.10 Results of samples in fill direction for the low-Tg laminate material.

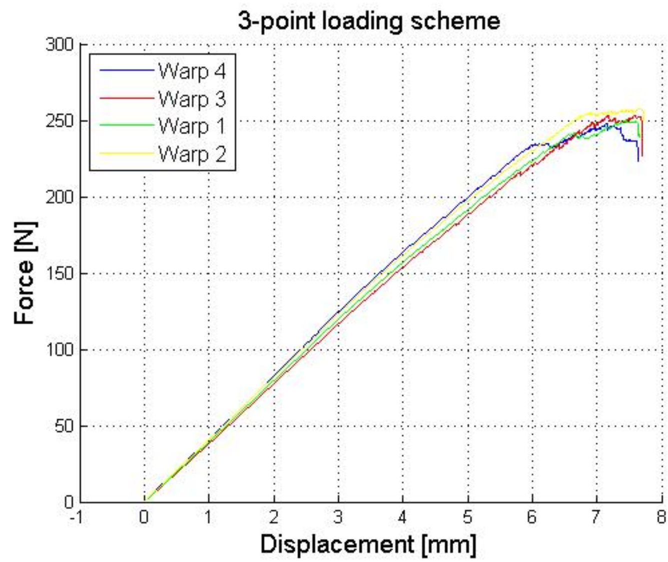


Figure 4.11 Results of samples in warp direction for the low-Tg laminate material.

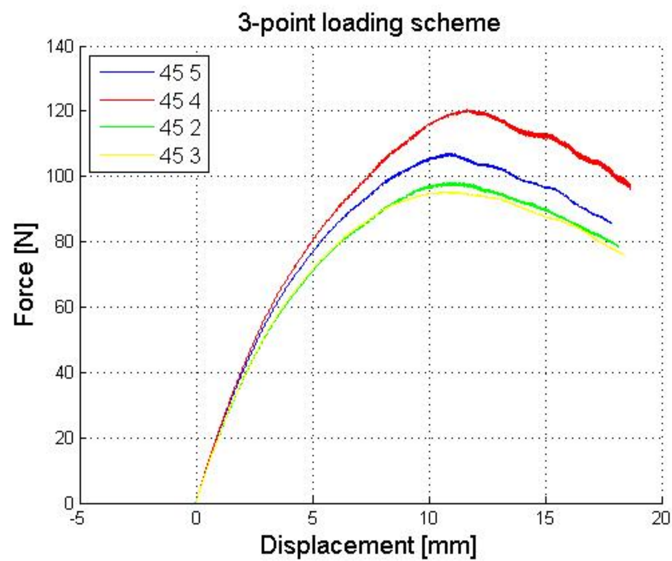


Figure 4.12 Results of samples in 45°-orientation for the low-Tg laminate material.

5 Discussion

5.1 Pre-exposure results

5.1.1 Low-Tg laminate material

When performing the first run in the DMA, the fill and warp direction had approximately the same Tg-values independent of how Tg was measured. For the 45°-orientation the mean value of Tg was approximately 3°C lower than the mean value for the fill and warp direction if the loss modulus was used, and approximately 5°C lower if the storage modulus was used. This shows that the method used to determine Tg produce different values. The absolute differences are small and are not considered very important.

The results from the TGA measurements indicate that the decomposition temperature of the laminate material is 295°C. This suggests that the laminated material is thermally stable in both soldering programs. The TGA however, only registers changes in weight. Reactions that do not alter the mass will therefore not be registered using the TGA. It should also be noted that the TGA is performed in a nitrogen atmosphere.

Figure 4.9 clearly shows that the laminate material has the highest elastic modulus in the warp direction. This is supported by the plot of the measured storage modulus given in Figure 4.3. The elastic and storage modulus in the fill direction is about 85 % of the modulus in the warp direction, while it is only about 60 % in the 45° orientation. This can be explained by the alignment of the fibers and the weave style. The orientations where the fibers are aligned are stiffer and stronger. Much of the stiffness and strength of the laminate material is lost in the 45° orientation. This is important to take into consideration if this orientation is used in an application. The difference between the strength in the fill and warp direction is consistent with what was found by Brown and Sottos [12], and can be explained by the density of bundles and the tension of the fibers in the two different directions. For more details, see Appendix B.

The CTE-measurements gave comparable values in all the in-plane directions (Figure 4.6). The CTE-value in the fill direction was higher than in the warp direction. This is expected as the fiber tension and the amount of fibers is lower in the fill direction providing less restriction for the expanding of epoxy (Equation (2.1)). Why the fill direction has a higher CTE-value than the 45° direction is however difficult to explain. Equation (2.1) is not valid for this case as the fibers are not aligned with sample geometry.

Above Tg the CTE is reduced. This can be explained by Equation (2.1). The CTE and storage modulus of the glass fibers are virtually constant in the temperatures encountered during the tests. The storage modulus of the epoxy resin however, is significantly reduced above Tg. Therefore, the CTE will decrease in the in-plane directions when Tg is exceeded. As mentioned in the result section, the absolute value is hard to establish from the experimental setup used in this study.

Figure 4.8 shows the results of a DMA run of a fill orientation sample with an initial temperature

-75°C. The plot shows that the slope of the storage and loss modulus is somewhat reduced above -50°C. This is assumed to be due to a so-called beta transition[3], where localized movements in the side chains of the polymer backbone can occur [13].

5.1.2 High-Tg laminate material

The high-Tg laminate material had actually a slightly lower glass transition temperature than the low-Tg material, which means that the Tg was approximately 40°C lower than the specified 170°C. The other measured characteristics where also similar to the low-Tg material. It is therefore suspected that the two laminates are actually the same but from two separate batches. However, the quality assurance documentation following the shipment all specify Tg=170°C for the high-Tg laminate. Moisture absorption may cause a reduction in Tg and will be discussed in the following section.

5.2 Effect of soldering conditions

5.2.1 Low-Tg laminate material

Table 5.1 shows the average change in Tg for the different temperature exposures. For the reference samples, which have only been exposed to the temperatures of the DMA, Tg increases. This increase may be due to curing in the first DMA run, increasing the density of cross-linking. This implies that the laminate was not fully cured when it was received from the manufacturer. Whether this is the case is uncertain since at the same time the storage modulus was slightly reduced and the loss modulus was increased.

For samples that have been exposed to the soldering programs Tg was slightly reduced. The TGA-measurement however indicate that the material should be stable at the temperatures encountered in the soldering program. An increase in the free-volume will make the material more hydrophilic and thereby more susceptible to moisture absorption [14]. Absorbed water will act as a plasticizer, which leads to a reduction in Tg [3]. To see if the water content of the laminate material had increased, a new run in the TGA could have been performed.

Table 5.1 The average change in Tg for different temperature exposures and different measurement methods for the low-Tg laminate material.

Exposure	Tg Storage modulus [°C]	Tg Loss Modulus [°C]	Tg tan delta [°C]
Soldering program 1	-0.16	-1.13	-1.425
Soldering program 2	-0.82	-1.39	-1.78
None[1]	4.65	3.88	3.41

[1] One run in the DMA as described in the experimental section.

The effect of the different temperature exposures on the elastic modulus is shown in Table 5.2. Since the 3-point loading test is destructive, the same sample can only be tested once. Untreated samples

[3] The glass transition is also referred to as the alpha transition

of the same orientation were therefore used as a reference. In general, exposure to the soldering programs seems to lower the elastic modulus. Soldering program 2 lowers the elastic modulus the most, which is assumed to be due to the samples being exposed to elevated temperatures for a longer time period. The same trend is also seen when analyzing the storage modulus (Figure 4.3).

Table 5.2 The average change in elastic modulus for different heat exposures compared to untreated samples.

Exposure	Mean change compared to untreated samples [MPa]
Two DMA runs	-782
Soldering program 1	-942
Soldering program 2	-1141

The below Tg in-plane CTE of the laminate does not seem to be affected by the soldering programs. However, small changes would be difficult to measure due to the limited accuracy of the experimental setup.

The different measurements performed in this work show that the properties of the laminate material are to some extent affected by exposure to elevated temperatures. However, the changes are not dramatic. The glass transition temperature and elastic/storage modulus are slightly lowered, while the loss modulus is increased. The coefficient of thermal expansion is seen to be fairly stable. However, the method used has a limited accuracy for this type of material. The changes can be seen in relation to whether the property is dominated by the fibers or the epoxy resin. The elastic/ storage modulus and CTE are fiber dominated and therefore show no significant change. The glass transition temperature and loss modulus are however resin dominated, hence are more affected by exposure to elevated temperatures. Excessive exposure of the material to elevated temperatures is expected to produce more significant changes in the material properties. Lead-free soldering conditions for example have a peak temperature 15-20°C higher than the peak temperature used in soldering program 1 and 2 [2].

5.2.2 High-Tg laminate material

The high-Tg material showed much the same response as the low-Tg material. Table 5.3 shows the average change in Tg for the different temperature exposures.

Table 5.3 The average change in Tg for different heat exposures and different measurement methods for the high-Tg laminate material.

Exposure	Tg Storage modulus [°C]	Tg Loss Modulus [°C]	Tg tan delta [°C]
Soldering program 2	1.37	0.91	0.60
None[1]	6.04	5.31	4.61

[1] One run in the DMA as described in the experimental section.

5.3 Various

The samples were cut from the larger panel using a circular saw, which resulted in samples with non-uniform width. This was solved by the use of abrasive paper. Some of the samples had to be polished more than others, resulting in rounding of the corners. This was the case for fill_1, fill_2, warp_3, 45°_1, fill_high_1, fill_high_3 and 45°_high_3. Based on the results given in Table 4.1, this does however not seem to have affected the results.

The samples with 45°-orientation seemed to be too compliant for the test procedure used in the DMA. At temperatures slightly above the glass transition temperature, the value of the static force was below the recommended value of the instrument in order to get accurate measurements. By visual inspection, it was also possible to see that these samples became permanently deformed after a single run in the DMA. This may have affected the results, and could explain the odd shape of the tan delta graph from the tests performed on these samples. This can be seen at approximately 160°C in Figure 5.1. However, close to the the glass transition temperature, the static force was inside the recommended interval. The measured Tg-values for these samples are therefore still used in the results. In future work another clamp more suited for softer materials is recommended for samples of this orientation.

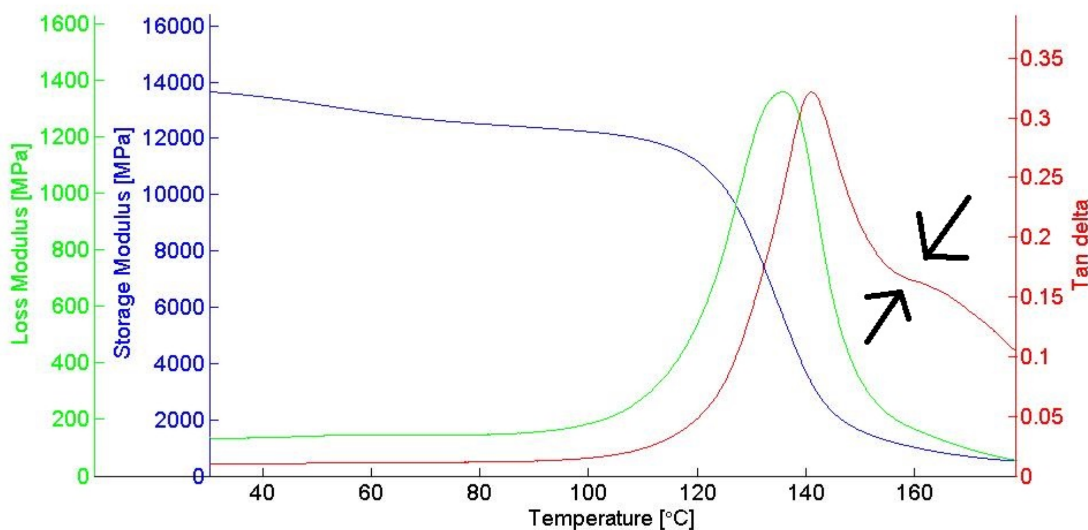


Figure 5.1 Result of DMA run of a sample with 45° orientation, showing possible inaccuracy in the measurement of the storage and loss modulus.

The measurements of the in-plane CTE above Tg are considered less accurate. In order to measure the CTE with a TA DMA 2980, a tension film clamp is used were the clamps in both ends of the sample exert pressure in the z-direction (through thickness direction). The upper clamp is fixed while the bottom is used to measure the deformation of the sample. The CTE is then calculated based on the measured deformation. When the temperature increases above Tg, the epoxy becomes soft. At this point it is suspected that the pressure from the clamps on the sample is relaxed, thereby changing the effective length of the sample. This is assumed to cause the odd formation on the

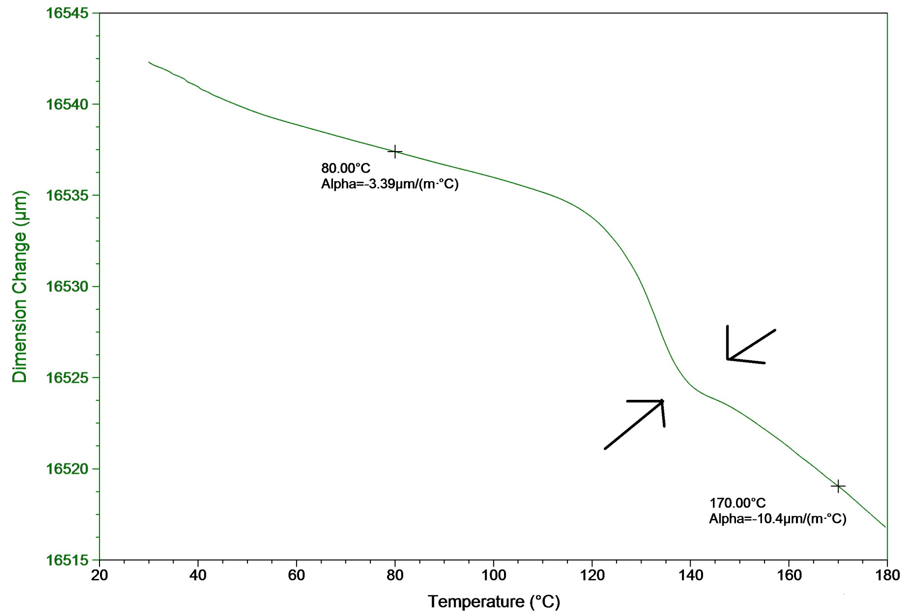


Figure 5.2   Illustration of DMA-measurement of CTE, with an unexpected shape of the curve. The cause is possibly the experimental setup.

curve of the measured displacement shown in Figure 5.2. The calculated negative CTE for the warp samples above Tg is credited to this effect. The tension film clamp is therefore not suited to accurately measure CTE above Tg. However, it is believed that the measurements show the trend of decreasing CTE above Tg. When investigating this effect measurements were performed with a rigid steel sample with CTE of approximately 11 ppm/°C. These measurements showed that the clamps behaved as expected for a rigid material. In future work it is suggested to use for example thermomechanical analysis (TMA) to measure the CTE above Tg.

As shown in Figure 5.3, exposure to soldering program 1 and 2 turned the samples brown. This is due to surface oxidation, where sequences of seven or eight double bonds in the polymer chain (allylic bonds) are produced [6]. This does in most cases not represent any degradation of the mechanical properties and did not seem to significantly affect the properties of our samples either. However, if the laminate is exposed to the same temperatures as in soldering program 1 and 2 for longer durations, the oxidized layer may have a negative effect.

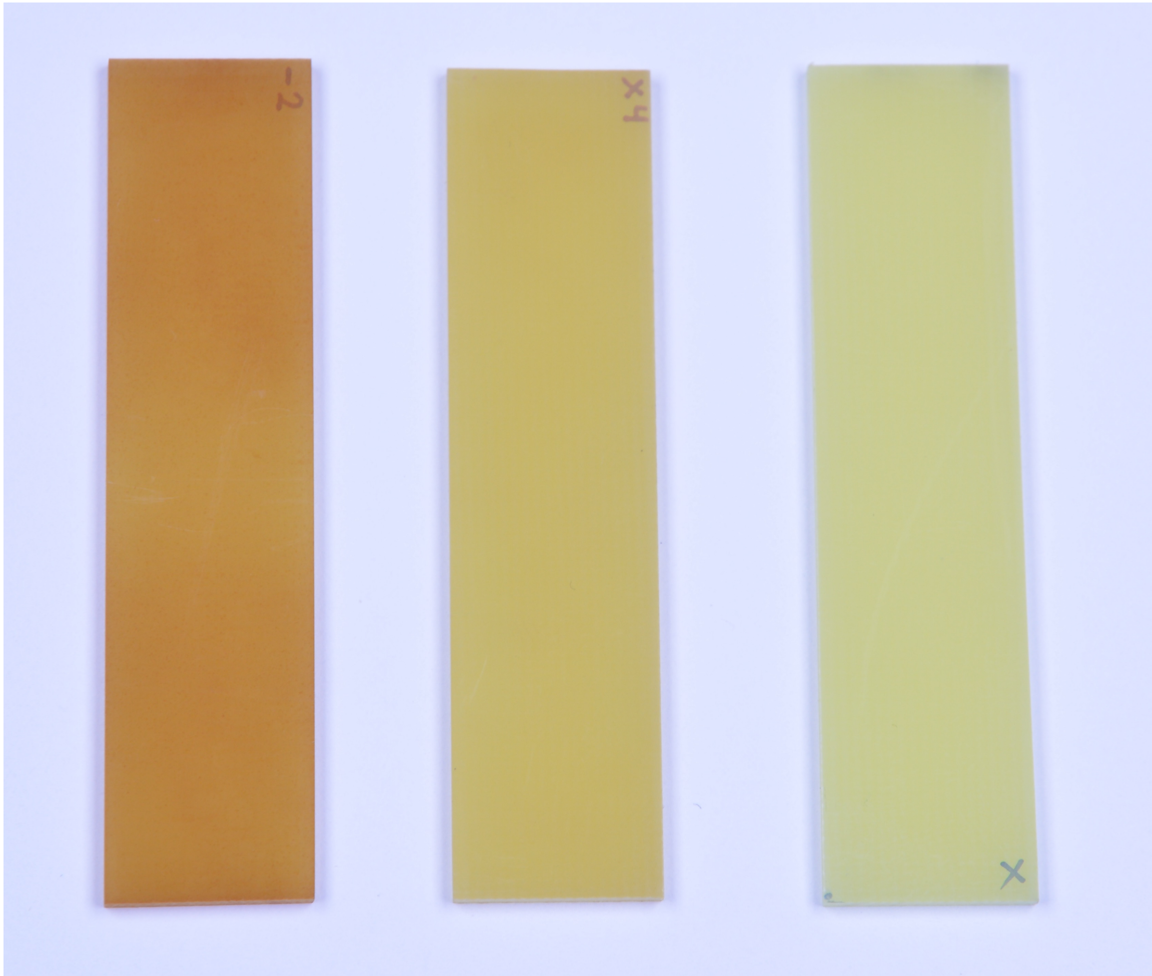


Figure 5.3 *Picture of samples with different temperature exposure. The sample to the left has been through a run to 230 °C in the DMA, the sample in the middle through soldering program 2 and the one to the right is untreated.*

6 Conclusion

The performed tests have illustrated the significance of how a PCB is orientated relative to the fiber glass weave reinforcing the epoxy filled laminate. A PCB orientated at 45° relative to the glass weave will have an elastic/storage modulus that is approximately 40% lower than a PCB aligned with the glass fibers. The limited stiffness of test samples of this orientation meant that the flexural strength of this orientation could not be established with the 3-point loading test used. The measured flexural properties of the so-called warp (0°) and fill (90°) orientations are comparable but the warp orientation show the highest values.

For the low-Tg laminate material the measured glass transition temperature is in good agreement with the specified value Tg=140°C. The high-Tg laminate material was shown to also have a similar glass transition temperature, much lower than Tg=170°C specified in the documentation included with the laminates. Since the other material properties for the two laminates are also in good agreement, it is assumed that the two laminates actually are the same. This will be discussed with the laminate supplier and manufacturer.

The in-plane coefficient of thermal expansion was also measured. Below Tg the values agree well with values given in literature and the dependence on sample orientation seems to be limited. Above Tg the in-plane CTE was seen to be lower due to the glass fiber weave becoming structurally dominant when the stiffness of the epoxy is significantly reduced. The absolute values above Tg were not established as the measurement method used was determined not to provide sufficient accuracy above Tg. In future work a thermomechanical analysis (TMA) should be used to measure the CTE.

How the measured material properties are affected by exposing the laminate to temperatures above Tg was also investigated. This was done by testing samples that had been exposed to one reflow soldering cycle, three repeated cycles and retesting samples that had only been exposed to the elevated temperatures of the DMA. The repeated DMA test, the least severe, seemed to increase Tg slightly. The most severe exposure, three repeated reflow soldering cycles, resulted in a slight lowering of the Tg. The same tests showed a slight reduction in the elastic/storage modulus and increase in the loss modulus. An effect of high temperature exposure on CTE was not found. This may be due to the limited accuracy of the method used.

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Appendix A Material Data Sheet

A.1 Data sheet S1141

S1141

(UL ANSI:FR-4)UV Blocking

特点

- Tg140℃（DSC）。
- UV Blocking/AOI兼容。
- 优良的机械加工性能。

应用领域

电脑、仪器仪表、摄像机、通讯设备、电子游戏机、汽车、航空等。

FEATURES

- Tg140℃（DSC）.
- UV Blocking/AOI Compatible.
- Excellent mechanical processability.

APPLICATIONS

Computer,Instrumentation,VCR, communication equipment,electronic game machine,automotive electronics, aviation,and etc.

GENERAL PROPERTIES

Test Item		Treatment Condition	Unit	Property Data	
				SPEC	Typical Value
Tg		DSC	℃	≥130	140
Flammability		C-48/23/50	Rating	V-0	V-0
		E-24/125			
Volume Resistivity		After moisture resistance	MΩ-cm	$\geq 10^6$	5.2×10^8
		E-24/125		$\geq 10^3$	5.2×10^6
Surface Resistivity		After moisture resistance	MΩ	$\geq 10^4$	5.4×10^7
		E-24/125		$\geq 10^3$	5.6×10^6
Arc Resistance		D-48/50+D-0.5/23	S	≥60	120
Dielectric Breakdown		D-48/50+D-0.5/23	KV	≥ 40	60
Dielectric Constant (1MHz)		C-24/23/50	-	≤5.4	4.6
Dissipation Factor (1MHz)		C-24/23/50	-	≤0.035	0.015
Thermal Stress	Unetched	288℃,solder dip	-	>10s No delamination	60s No delamination
	Etched				
Peel Strength	1oz Cu. Foil	288℃,10s	N/mm	≥1.05	1.8
		125℃		≥ 0.70	1.6
Flexural Strength	LW	A	MPa	≥ 415	600
	CW			≥ 345	500
Water Absorption		D-24/23	%	≤0.80	0.15
CTE Z-axis	Before Tg	TMA	μm/m℃	-	65
	After Tg	TMA	μm/m℃	-	300
	50~260℃	TMA	%	-	4.5
Td		10℃/min,N_2,5% Wt Loss	℃	-	310
T260		TMA	min	-	15
T288		TMA	min	-	2
CTI		IEC60112 Method	V	PLC 3(175V--249V)	PLC 3

Remarks: 1.Specification sheet:IPC-4101/21, is for your reference only.
2.All the typical value is based on the 1.6mm specimen,while the Tg is for specimen ≥0.50mm.
3.All the typical value listed above is for your reference only, please turn to Shengyi Sci.Tech.Co., Ltd . for detailed information, and all rights from this data sheet are reserved by Shengyi Sci.Tech.Co., Ltd .

Explanations: C = Humidity conditioning; D = Immersion conditioning in distilled water; E = Temperature conditioning.

The figures following the letter symbols indicate with the first digit the duration of the preconditioning in hours, with the second digit the preconditioning temperature in ℃ and with the third digit the relative humidity.

-5-

Appendix B Weave styles

The glass fibers in the laminate material are weaved to form a certain pattern, which decide many of the properties of the material. When weaving, the filament in the machine direction is referred to as warp filament, while filament perpendicular to the machine direction is called fill. Common weave styles for FR-4 laminate materials are 1080, 2116 and 7628, where the numbers are codes defined by a IPC standards. From this standard, the number of bundle ends per length (the count), the number of fill and warp yarn length, the number of twists of the fill yarn and the diameter of a single glass fabric is given. 1080 has the lowest fabric density and fabric thickness, while 7628 has the highest. Therefore, a laminate material with a 7628 weave style will have a larger fraction of fiber to resin and will be a stiffer material. Data for typical weave styles are given in Table B.1. The weave styles are also illustrated in Figure B.1.

Table B.1 Data for different weave styles [15] [16].

Style	Bundle thickness [mm]	Fiberglass thickness [μm]	Counts (warp x fill) [ends/50mm]
1080	0.0584	5	118 x 93
2116	0.0965	7	118 x 114
7628	0.1727	9	87 x 63

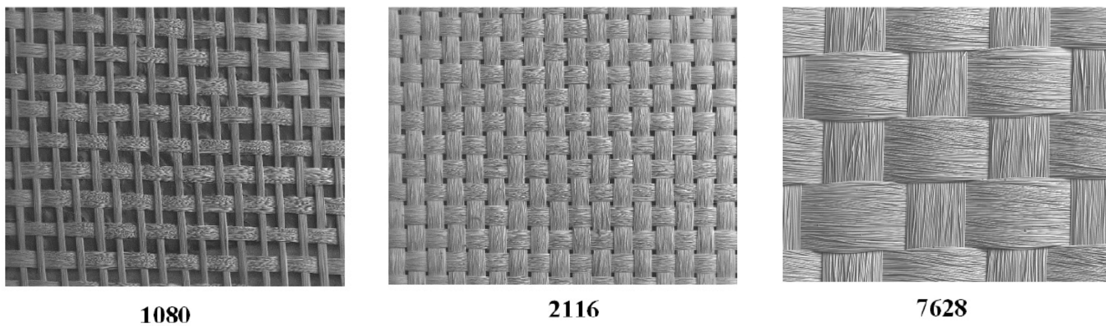

Figure B.1 Pattern of the three different weave styles 1080, 2116 and 7628 [15].

As there is a difference in the count in the warp and fill direction for both 1080, 2116 and 7628, there will be a difference in the stiffness in the warp and fill direction for all of these weave patterns. The differences can also be due to the varying degree of flexibility in the two directions due to changes in the tension of the warp and fill fiber bundles during weaving [16].

Appendix C Compensation CTE

The tension film clamp used in the DMA to measure CTE will also expand during the test. This has to be compensated for in order to get the correct result. To find the compensation, measured data for a titanium grade 2 sample with known CTE was used. The sample had been run with five different lengths, and the compensation needed to get the correct CTE value was noted. The results were plotted, and by using curve fit in Matlab, the compensation as a function of sample length was determined to be

$$y = -0.0060127 \cdot x^3 + 0.36105 \cdot x^2 - 7.3371 \cdot x + 70.994, \quad \text{(C.1)}$$

where y is the compensation and x is the sample length in millimeters.

The compensation was also checked against a known rigid steel sample in the temperature range used for the laminate material samples, and proved to be applicable with the test conditions used in this study.