Docket No. SA-522

Exhibit No. 15-D

NATIONAL TRANSPORTATION SAFETY BOARD

Washington, D.C.

Airbus Submission
Thermal Analysis by DMA and MDSC

(20 Pages)

AIRBUS	TECHNICAL NOTE	Page 1

Order - No.:	Copy to (* = only this coversheet)
Preparation:	
Duration:	See page 2

Report No.: TN – ESWCG-1181/02

Author: ----------

Department: ESWCG

Title: Thermal Analysis by DMA and MDSC of CFRP materials Hexcel F913, F550 and AIK EHG 250 after 14 years of service

Date: 24.09.2002

Summary: T_g by DMA Analysis and DSC-Analysis by MDSC has been performed on specimens that were cut out of the composite vertical tail plane (VTP) of an Airbus A300-600. Referenced by testing during qualification (testing period of time 1984-1988) the DMA- and MDSC- tested specimen showed the same level for both wet and dry test specimens. No significant difference could be noticed. As well, the degree of cure was sufficient.

Key Words (Retrieval Terms): CFRP, DMA, MDSC, tg-onset, degree of cure

	Issue	Date	No. of page	Revised pages	Valid from/for
	1	24.09.2002	16		

Name	Prepared	Checked	Approved	Signed	Released
Date	24.09.2002		25.09.2002		
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Content

1 INTRODUCTION

The investigations of this TN were made on specimens which were cut from the fin-box and rudder skins of the vertical tail plane (VTP) of MSN 420 (flight AAL587). Different resin systems were used in these parts. The fin-box is made of the resin system Hexcel F913 carbon tape and fabric and the rudder skins are made from F550 carbon fabric in combination with EHG250 fiberglass fabric. The EHG250 fiberglass fabric was used to adhere the Nomex ® honeycomb core to the CFRP skin and was co-cured with the skin.
All tested specimens were original parts of MSN 420, delivered by the BEA (Bureau d´enquetes et d´analyses, french accident investigation office). Testing was done on behalf of NTSB (National Transportation Safety Board) and witnessed by BEA.

2 EXPERIMENTAL

2.1 Dynamic Mechanical Analysis (DMA)

DMA Analysis has been performed according to AITM 1-0003, issue 2 [1].

AITM 1-0003 is a method for determination of the glass transition temperature by DMA analysis. Tests have been performed for specimens in original “as received” condition and after drying.

In the DMA Analysis the glass transition temperature T_g is defined as the temperature where the sample exhibits a dramatic change in mechanical and damping behavior with increased temperature when connected to an oscillation displacement. Three different T_g values can be determined by the measurement according to AITM 1-0003. The three different T_g values are interpreted in *Fig 1* and described below.

- $T_{g\text{-onset}}$ is defined as the temperature of extrapolated tangents drawn from points on the storage modulus curve before and after the start of the glass transition event.
- $T_{g\text{-loss}}$ is defined as the temperature where the diagram loss modulus versus temperature has its maximum.
- $T_{g\text{-peak}}$ is defined as the temperature where the diagram tan σ (damping) versus temperature has its maximum.

The $T_{g\text{-peak}}$ value is usually several degrees higher than $T_{g\text{-loss}}$ value and corresponds more closely to the transition midpoint while the $T_{g\text{-onset}}$ value more closely denotes the initial drop from the glassy state into the transition. The T_g value that is of interest differs and should be stated in the report.

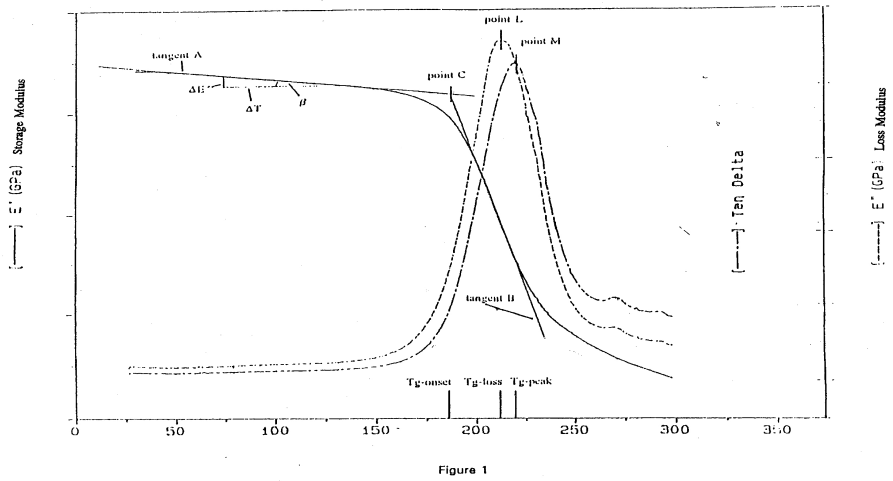

Figure 1

Fig. 1 Three different Tg values $T_{g\text{-}onset}$, $T_{g\text{-}loss}$, and $T_{g\text{-}peak}$ are interpreted in the diagram [1]. The unit on the x-axis is °C.

2.1.1 Sample preparation for DMA and Moisture Content

The DMA specimens were cut in order to have the faces parallel to the fiber direction. After machining, the test specimens were conditioned before testing according to *tables 1 and 2*. In minimum one specimen was kept in an oven chamber at a temperature of 90 °C. This so called Moisture Content Specimen indicates the moisture absorption of the component during lifetime.

2.1.2 Testing parameters

The relevant test parameters according AITM 1-0003 were used. Prior to the thickness of the DMA specimen the heating rate was sometimes reduced to 2 °C/min.

The DMA analysis were performed according to:

Instrument:	DMA 983 (Dynamic Mechanical Analyses)
	Thermal Analyst 2100, Du Pont
Method:	AITM 1-0003 A, issue 2
Frequency:	Resonant frequency
Amplitude:	0.2 mm
Rate:	normally 3 °C/min; thick specimen: 2 °C/min
Moment:	7 lbs
Nitrogen flow:	None

Note: Integrity of the test results was insured by calibration measurements and data correlation to previously performed DMA tests using the same DMA 983 equipment.

Table 1 DMA test specimens for 913

Specimen	**1** (VTP)	**2** (VTP)	**3** (VTP)	**4** (VTP)
Condition	as received	as received	as received	1) drying at 90 °C

1) After machining the test specimen was dried to a constant level prior to DMA analysis

Table 2 DMA test specimen for F550/EHG250

Specimen	**5** rudder skin	**6** rudder skin	**7** rudder skin	**8** rudder skin	**9** rudder skin	**10** rudder skin
Condition	as received	as received	as received	1) Drying at 90 °C	1) Drying at 90 °C	1) Drying at 90 °C

1) After machining the test specimen was dried to a constant level prior to DMA analysis

2.1.3 Moisture Content Specimen

Comparing figures of moisture pick-up, it is important to know to what base they are related (dry weight), so as a consequence the so-called “Moisture Content Specimens” were prepared taken account for:

- Calculation of the actual moisture content of the “as received” sample, prior to testing
- Testing of DMA-specimen in real dry condition

The moisture content specimens were dried in a 90 °C-oven. Related to the initial moisture content, the loss of weight was recorded to have the asymptote of the curve.

2.2 MDSC Analysis

Note: Calorimetric measurements were made for comparative reasons only.

The MDSC technique measures the amount of energy (or heat) absorbed or released by a material as it is either heated, cooled or maintained at a constant (isothermal) temperature. This heat flow/temperature data provides valuable information of such physical/chemical properties as:

- glass transition event
- determine the level of curing

MDSC analysis has been performed according AITM 3-0008, issue 1 [2]. The used MDSC equipment and testing parameters are the following:

Instrument: DSC Q 100 (Modulated Differential Scanning Calorimetric), Du Pont

Sample weight 5 – 10 mg punctured out the laminate cross section

Method: AITM 3-0008, issue 1

Rate: 10 °C/min

Nitrogen flow: 7 ml/min

Note: Integrity of the test results was insured by calibration measurements

The investigated specimens are shown in *tables 3 and 4*.

Table 3 MDSC test specimens for 913

Specimen	**11** (VTP)		**12** (VTP)		**13** (VTP)		**14** (VTP)	
Condition	as received		As received		as received		as received	
Tested for	residual heat (J/g)	Tg (°C)	residual heat (J/g)	Tg (°C)	residual heat (J/g)	Tg (°C)	residual heat (J/g)	Tg (°C)

Table 4 MDSC test specimen for F550/EHG250

Specimen	**15** rudder skin	**16** rudder skin	**17** rudder skin	**18** rudder skin	**19** rudder skin	**20** rudder skin
Condition	as received	as received	as received	1) drying at 90 °C	1) drying at 90 °C	1) drying at 90 °C

1) After machining the test specimen was dried to a constant level prior to DMA analysis

3 RESULTS

3.1 Moisture Content Specimen

3.1.1 Moisture content for 913

The "Zero Weight Specimen" were dried in an oven at 90 °C and by gravimetric measurements the loss of weight is calculated which will correspond to the loss of moisture. In t*able 5* the weight loss of 913 is shown for different times. After this model is established it will be possible to introduce a correction in the "wet" (as received) DMA values if necessary.

The moisture content in the dried specimens is viewed by ca. 0.55-0.60 % by weight*, see figure 2.*

Table 5 Moisture content (weight %) in the test specimen after re-drying for 913

Exposure date 12. Apr		Specimen Nr.4 m_0 (g)=	14.0142
Exposure time: 10.15			Weight %
Date	Time (h)	m1 (g)	M [%]
12. Apr	0	14.0142	0
12. Apr	3	13.9924	-0.16
12. Apr	5	13.9893	-0.18
15. Apr	77	13.9489	-0.47
16. Apr	101	13.9376	-0.55
18. Apr	149	13.9336	-0.58
19. Apr	173	13.933	-0.58

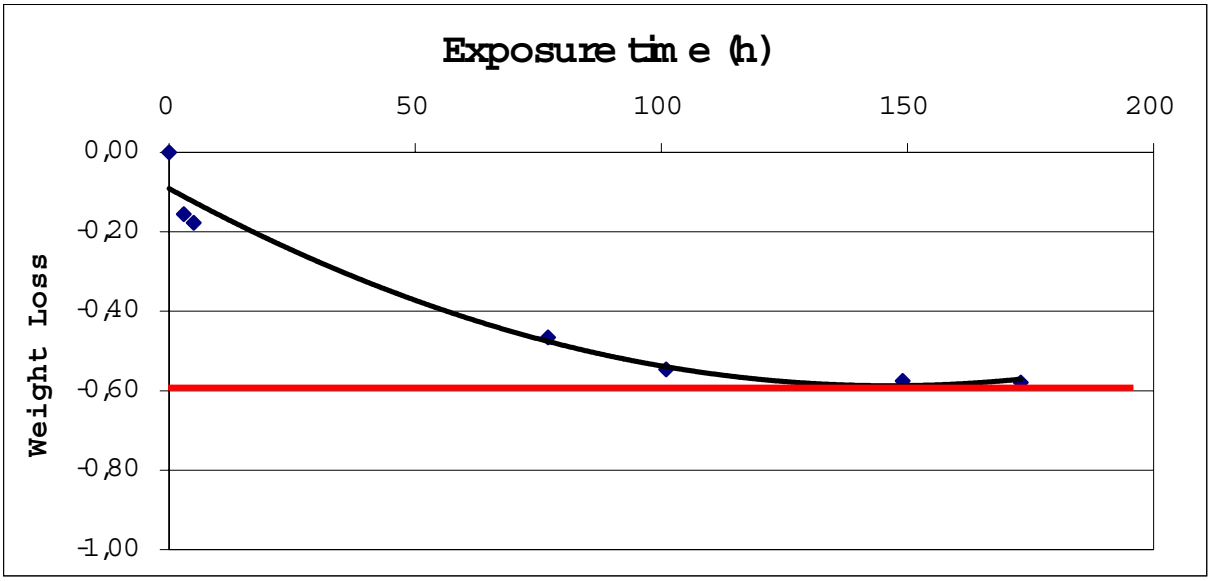

Fig. 2 Moisture content (weight %) in the test specimen after drying

3.1.2 Moisture content for F550/EHG250

The moisture content of F550/EHG250 is shown in *table 6*. After drying the weight loss is about 0.80 % by weight. The experience has shown that the moisture absorption until saturation for a climate of 70 °C/70 % RH for F550 and EHG 250 is between 0.75 and 0.9 %. Therefore the drying of the F550/EHG250 sample has reached the dried state.

Table 6 Weight loss of F550/EHG250 (rudder skin)

Specimen		Date	Xav. 1)	**18** rudder skin	**19** rudder skin	**20** rudder skin
m_0	[g]	20.08.02		0.5314	0.5441	0.5365
m_1	[g]	10.09.02		0.5270	0.5397	0.5322
weight loss	[%]		**0.81**	0.83	0.81	0.80

1) Xav.: average

3.2 DMA

3.2.1 Results for 913

The test results from the T_g analysis for the tested specimens are shown in *table 7.*

Typical DMA curves from the T_g measurement are shown in the appendix (1) as examples.

Table 7 The T_g test results for the "as-received"specimens (resin: 913)

Specimen	Xav. 1)	**1** (VTP)	**2** (VTP)	**3** (VTP)
Tg-onset [°C]	***134***	*137*	*132*	*134*
Tg-loss [°C]	***156***	*158*	*152*	*159*

Note 1) Xav.: mean value

For comparison reasons relevant values of the system 913C Fabric (see Qualification report W6/87, authorized in 1988 [3]) are summarized in *table 8* and *figure 3*.

Table 8 Moisture content (weight %) of traveler specimen exposed till saturation

Tg onset of DMA specimen exposed till saturation

Exposure in Climate % rel. Humidity	Moisture content by weight %	Tg onset (°C)		
		X average	s	n
-	0	**144**	5	33
50	0.7	**122**		4
70	1.3	111	5	11
85	1.6	102	3	11
95	2,1	96	2	11

X: mean value
s: standard deviation
n: number of tested specimen

When comparing the observed $T_{g\text{-onset}}$ value, see *table 7*, it can be noticed that the mean average value of 134 °C for the specimens in "as received condition" do not show a large difference for both the dry specimens ($T_{g\text{-onset}}$ = 144 °C) and the wet specimens after saturating at 50% relative humidity ($T_{g\text{-onset}}$ = 122 °C), see *Table 8,* which were referenced in the cited Qualification report.

For a better understanding of the observed level of 134 °C, the relationship between moisture content and $T_{g\text{-}onset}$ was introduced in *figure 3,* which shows a linear correlation between moisture content and $T_{g\text{-}onset.}$

By the indicated moisture content of about 0.55-0.60 % by weight, and after extrapolating that value in *figure 3* it is obvious that at this moisture level a theoretical $T_{g\text{-}onset}$ of about 129 °C should be reached. This extrapolated value is well comparable to the experimentally measured $T_{g\text{-}onset}$ value of 134 °C.

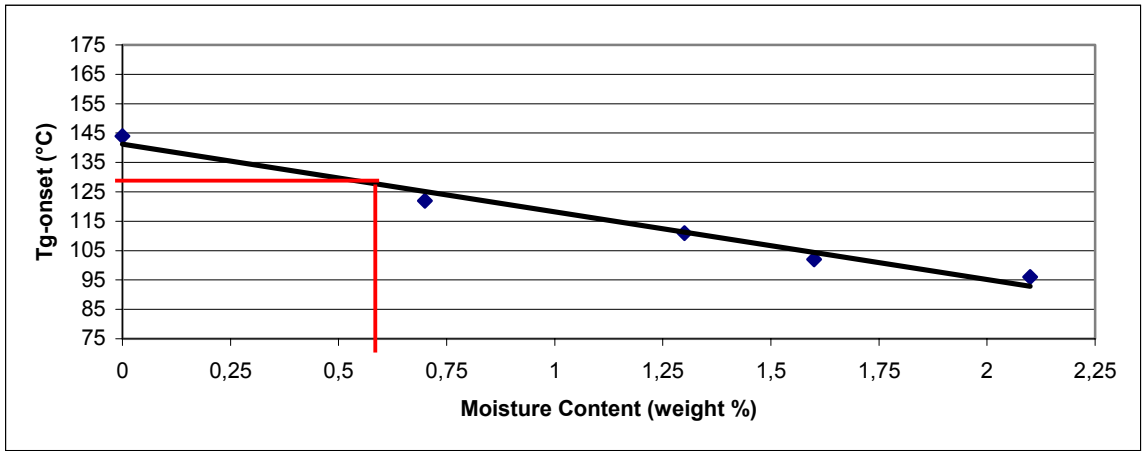

Fig 3. Correlation between moisture pick-up and Tg-onset

The dried test specimen have shown an increase in the $T_{g\text{-}onset}$ value, see *table 9.*

By comparing this MSN 420 $T_{g\text{-}onset}$ result of **149 °C**, it is noticeable that this figure is comparable to the $T_{g\text{-}onset}$ value of **144°C** of the previously performed DMA tests obtained at qualification testing, see *table 9*.

Table 9 The T_g test results after drying for 913

Specimen	**4**
Tg-onset [°C]	***149***
Tg-loss [°C]	*181*

It has been verified that the observed values didn't show any offset.

No significant difference of Tg-performance between MSN 420 - and previously DMA-tested specimens was observed

Remark

The first two DMA specimen showed a secondary relaxation peak in the temperature region between 90 and 110 °C. After slightly removing the gray paint this secondary relaxation peak has not been observed anymore.

3.2.2 Results for F550/EHG250

The DMA results for F550/EHG250 of “as received” and “dried” specimen are shown in *table 10 and 11*.

Table 10 DMA results for “as received” specimen for F550/EHG250

Specimen		**5** rudder skin	**6** rudder skin	**7** rudder skin	**average**
Condition		as received	as received	as received	
Tg-onset	[°C]	81.6	83.1	84.0	**82.9**
Tg-loss	[°C]	132.4	137.2	136.8	135.5

Table 11 DMA results after drying for F550/EHG250

Specimen		**8** rudder skin	**9** rudder skin	**10** rudder skin	**average**
Condition		dry 1)	dry 1)	dry 1)	
Tg-onset	[°C]	97.9	105.0	104.5	**102.5**
Tg-loss	[°C]	140.1	143.7	137.7	140.5

1) Dried at 90°C

Previous investigations showed a similar Tg-onset for F550/EHG250 [5]. After analyzing the diagrams of [5] according to AITM 1-0003 [1] there were the following values for dry and wet (70 °C/70 % RH) specimens:

- dry ca. 102 °C
- wet ca. 75 °C

Compared to the values shown in *table 10 and 11* there is no significant difference observed.

3.3 MDSC

3.3.1 Results or 913

The test results from the residual heat analysis and the Tg measurements for the tested specimens are shown in *table 7.*

Typical *MDSC* curves are shown in the appendix (2 and 2a) as examples.

For kinetic calculations relevant values, which were reported in test report K219/94 [4], were used for the matrix system 913C.

When comparing the measured residual heat release values it is verified that this low value of 4.5 J/g indicates that this minimal excess of energy is correlative with a **sufficient degree of cure of > 97%.**

The observed Tg value (154 °C) has the same level as the DMA-$T_{g\text{-}loss}$ (156 °C)

Table 7 The residual heat values and T_g test results

Specimen Condition	Xav. 1)	**5** as received		**6** as received		**7** as received		**8** as received	
		res. Heat (J/g)	Tg (°C)	res. Heat (J/g)	Tg (°C)	res. Heat (J/g)	Tg (°C)	res. Heat (J/g)	Tg (°C)
	4.5 J/g 154 °C	2.8	155	7.0		4.3	155	3.8	152

Note 1) Xav.: mean value

The observed physical/chemical properties show no difference prior to qualification performance.

3.3.2 MDSC results for F550/EHG250

None of the investigated specimens of F550/EHG250 have shown a residual heat for “as received” or dried specimens. **The degree of cure is 100%**. The diagrams are shown in the appendix (3).

4 DISCUSSION / COMMENT

$T_{g\text{-}onset}$ measurements by DMA and DSC-Analysis by MDSC have been performed. The tested specimens were cut out of the composite VTP (vertical tail plane) of the Airbus A300-600, MSN 420 (flight AAL587). Referenced by testing during qualification (testing period of time 1982-1988) the DMA - and MDSC - tested specimens showed the same level for both wet and dry test specimens.

- **No significant difference in material performance could be noticed.**
- **The curing of the matrix was sufficient.**

5 REFERENCES

[1] AITM 1-0003 (issue 2), Determination of the glass transition temperatures (1995)

[2] AITM 3-0008 (issue 1), Determination of the extent of cure by Differential Scanning Calorimetric (1995)

[3] Qualification report W6/87, authorized in 1988

[4] Test report K219/94

[5] TN-BT25-21/82, „*Mechanische Untersuchungen zur Harz-Kompatibilität für FVW-Hybride im Airbus-Seitenleitwerk (Phase 2), Teil 1: Torsionsschwingungsmessungen“* (1982)

Record of Revisions

Issue	Date	Page	§	Reason of Revision
1	24.09.2002	-all-	-all-	

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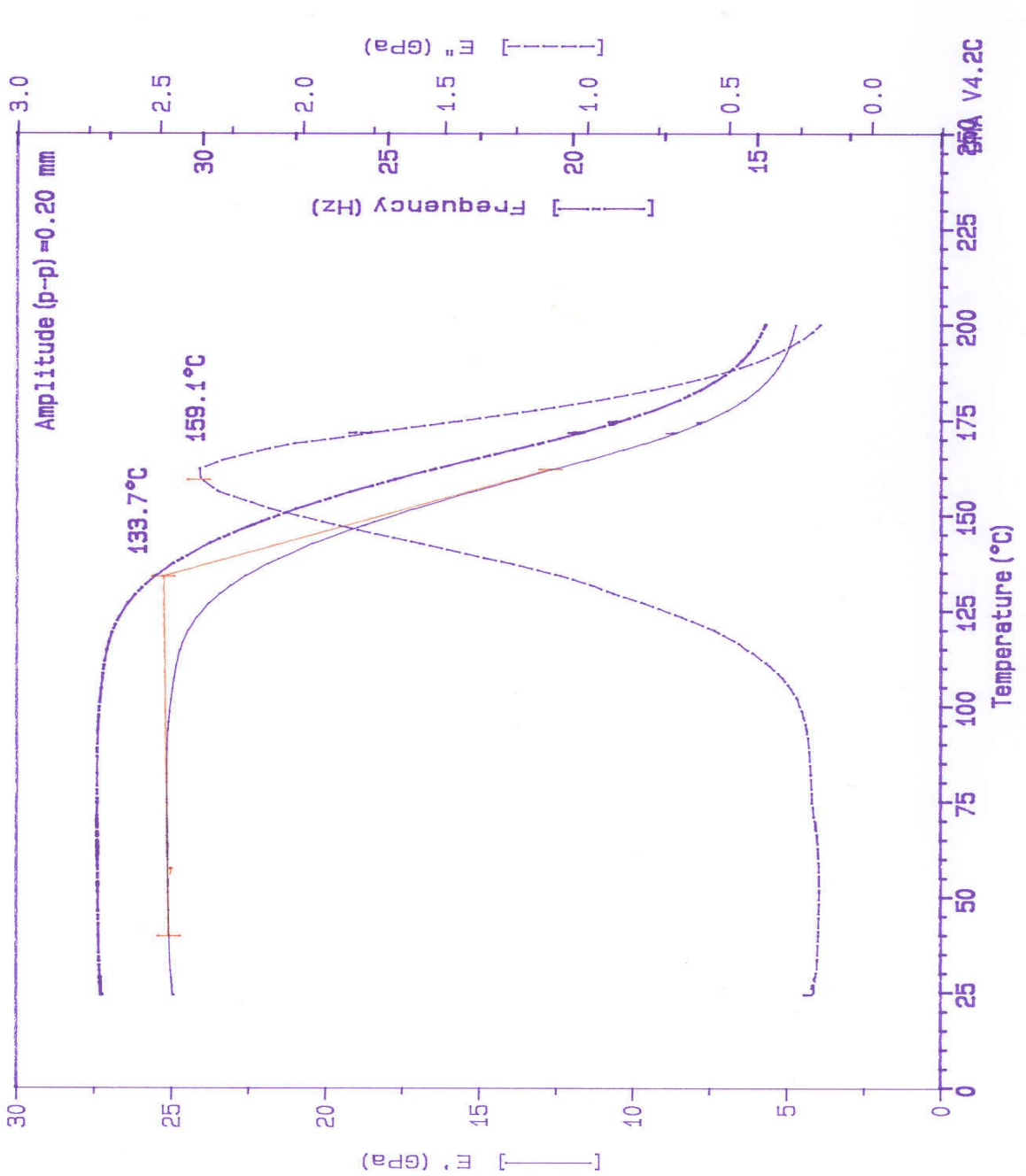
Appendix 1

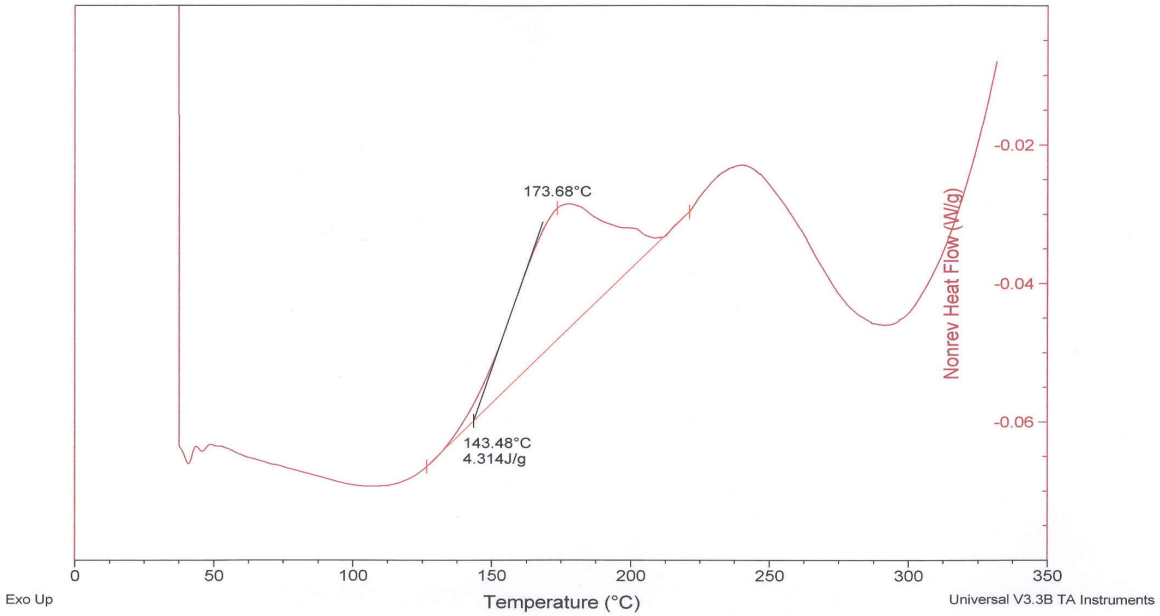


DMA-testing of C-913

Tg-performance (sample 3) in "as received " condition

	Issue 1					
	Date Prepared Checked					

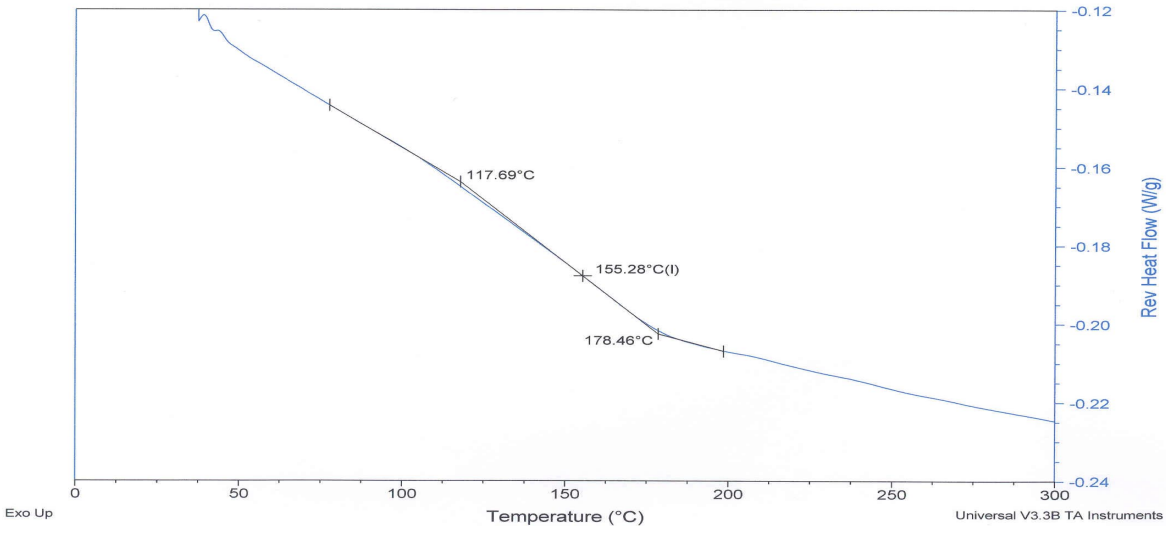
Appendix 2



MDSC-testing of C-913

determination the residual level of curing

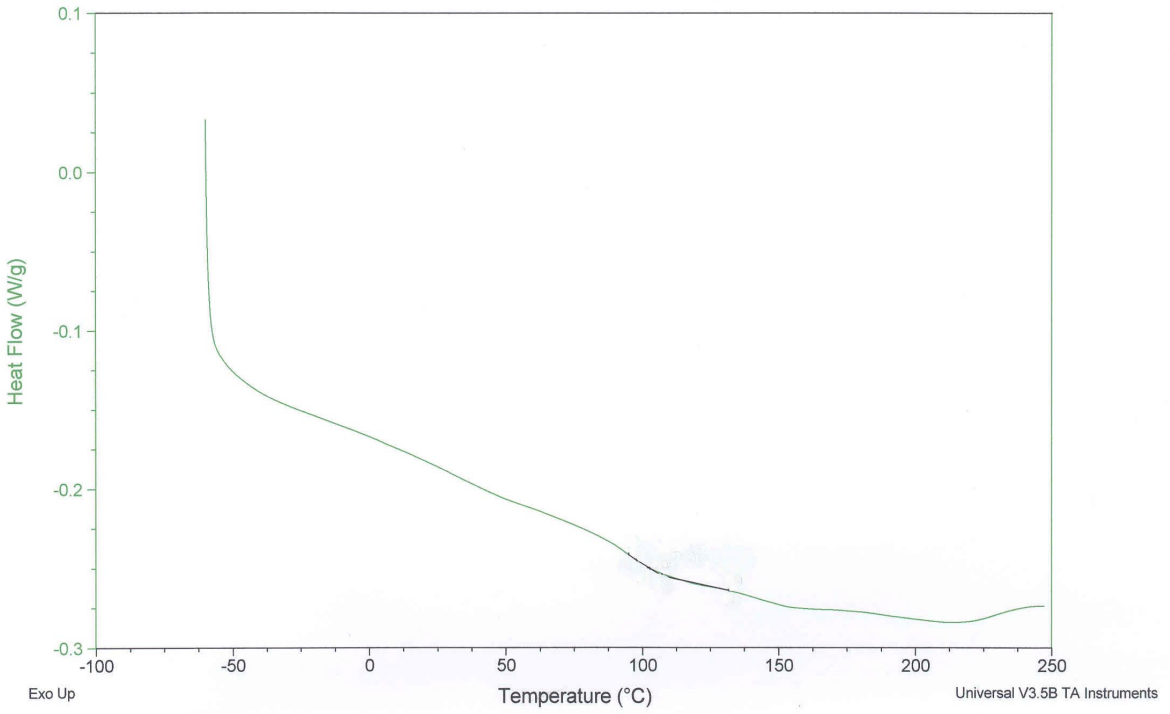
Appendix 2a



MDSC-testing of C-913

determination of the glass transition event

Appendix 3



MDSC-testing of F550/EHG250

no significant level of residual heat release could be analysed