

# Dynamic Mechanical Thermal Analysis (DMTA) on Polymer Composites with the HAAKE MARS Rheometer

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## Introduction

For many modern technical applications, polymer composites are the materials of choice because their properties like e.g. specific strength, chemical resistance and shape can be tailored to the individual application. The production process involves embedding fibres or fibre fabrics in a liquid polymer matrix. Subsequently, to control this process, the rheological characterization of the liquid matrix is a must. To test the mechanical properties of the final composite is at least difficult if not impossible with classical rheological setup. Due to the high hardness and smooth surface of many composites, samples are difficult to shape and often slip after being put between parallel plates.

To extend its range of testing methods into the field of composites, the Thermo Scientific HAAKE MARS can be equipped with solids clamps (Figure 1), an accessory for its Controlled Test Chamber (CTC). The patented design of the CTC, which uses a combination of radiation heating and convection heating, creates a large uniform heating zone inside its gold plated test chamber (see Figure 1) thus allowing testing larger samples under uniform temperature conditions.



Fig. 1: Solids clamps holding a solid sample in front of the right half of the CTC

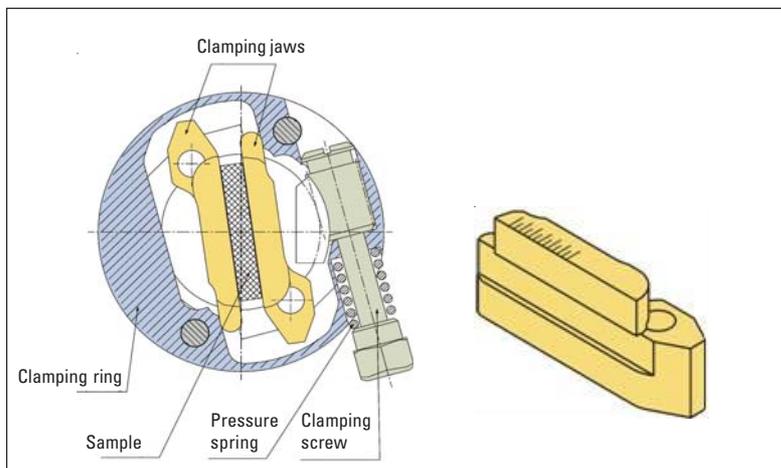


Fig. 2: Left side: Schematic top view on one of the solids clamps holding the sample perfectly centred with its 2 moving jaws (depicted in yellow). Right side: detail view of one of the moving jaws.

The solids clamps can be equipped with special jaws for soft, medium or hard samples. With the latter ones they are even able to fix hard composite materials with smooth surfaces during oscillation testing. Due to their unique design with 2 moving jaws, the solids clamps automatically position the sample in the axis of the rheometer, which is mandatory to avoid any error from eccentric placement (Figure 2).

## Carbon Fibre Enforced Sample

The first sample was a light weight carbon fibre enforced sample like e.g. being used in airplane construction. A constant oscillation at 1 Hz in controlled deformation mode (CD) with a deformation  $\gamma = 0.1\%$  was chosen. According to the typical temperature range for such an application, the sample was tested in a temperature range between  $-100\text{ }^{\circ}\text{C}$  and  $+240\text{ }^{\circ}\text{C}$  to determine its Storage Modulus  $G'$  at low temperatures and its Glass Transition Temperature  $T_G$ .

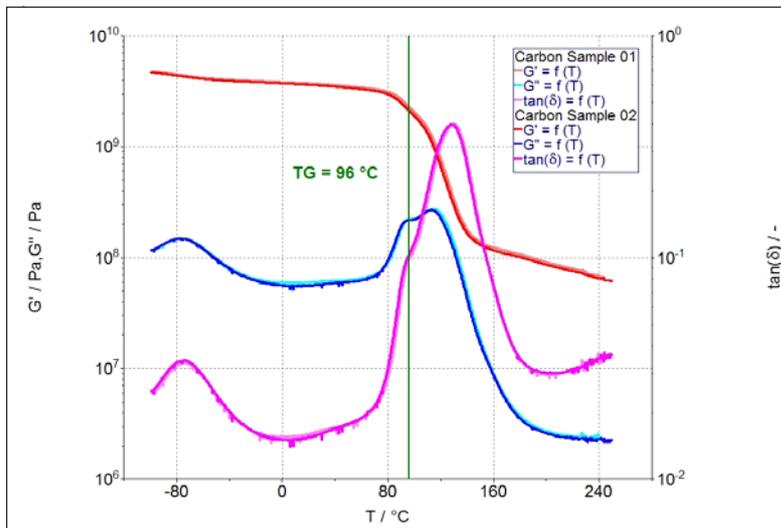


Fig. 3: Storage Modulus  $G'$  (red), Loss Modulus  $G''$  (blue) and  $\tan(\delta)$  (pink) as a function of temperature for the carbon based sample. The glass transition temperature  $T_G$  is indicated by the green line. The results of 2 independent tests (light and dark colour) run on fresh samples each show the excellent reproducibility of the results.

The excellent reproducibility of the test results could be shown by comparing the results of 2 independent tests run on 2 samples from the same material. The 2 sets of curves shown in Figure 3 are almost perfectly identical.

During the measurement the Thermo Scientific HAAKE MARS applied a constant small pulling force on the sample to compensate any thermal expansion or contraction (see black curve in Figure 4). Thus, the distance between the two clamps follows any change in sample length. This information can be used to check whether the clamps were able to hold the sample or might have lost their grip. In a plot of the sample length as a function of temperature, any slipping of the sample between the jaws of the clamps would show as a step-change. The smooth progression of the orange curve in Figure 4 documents the clamps' steady grip even on such a hard sample.

Apart from its diagnostic value, the data shown in Figure 4 contains valuable information about the sample itself. The length decrease with increasing temperature reflects the negative temperature expansion coefficient ( $\alpha$ ) some carbon fibre enforced materials show in fibre direction. We even can see from the change in slope that the sample's  $\alpha$  changes around  $T_G$ .

### Glass Fibre Enforced Sample

The temperature dependant behaviour of two different glass fibre enforced polyphenylene-sulfid (PPS) samples has been tested in CD-mode with  $\gamma = 0.01\%$  between  $30\text{ }^\circ\text{C}$  and  $250\text{ }^\circ\text{C}$ . Materials like these are used for applications where a high mechanical and thermal stability is required. So again the solids clamps were used to be able to properly fix the samples for testing.

In addition to the glass transition of the PPS at  $103\text{ }^\circ\text{C}$  we see for both samples, a secondary maximum in  $G''$  and  $\tan(\delta)$  is clearly visible at approx.  $70\text{ }^\circ\text{C}$  for Sample A, indicating an additional compound in the matrix of Sample A. This modification leads to a softer behaviour of the compound material between  $40\text{ }^\circ\text{C}$  and  $100\text{ }^\circ\text{C}$ . Above  $100\text{ }^\circ\text{C}$  both materials show similar properties.

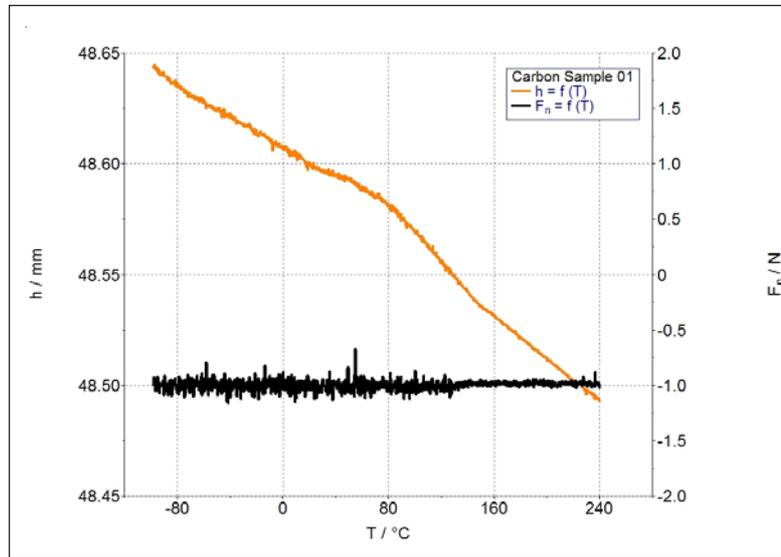


Fig. 4: Constant normal force (black) and decreasing sample length (orange) during a temperature increase from  $-100\text{ }^\circ\text{C}$  to  $240\text{ }^\circ\text{C}$  on the carbon fibre enforced sample.

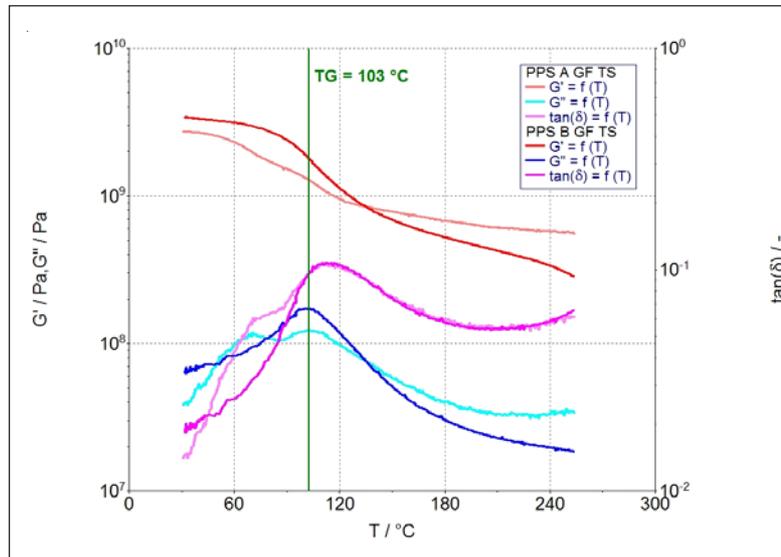


Fig. 5: Storage Modulus  $G'$  (red), Loss Modulus  $G''$  (blue) and  $\tan(\delta)$  (pink) as a function of temperature for 2 different glass fibre enforced PPS samples (light and dark colour). The glass transition temperature  $TG$  is indicated by the green line.

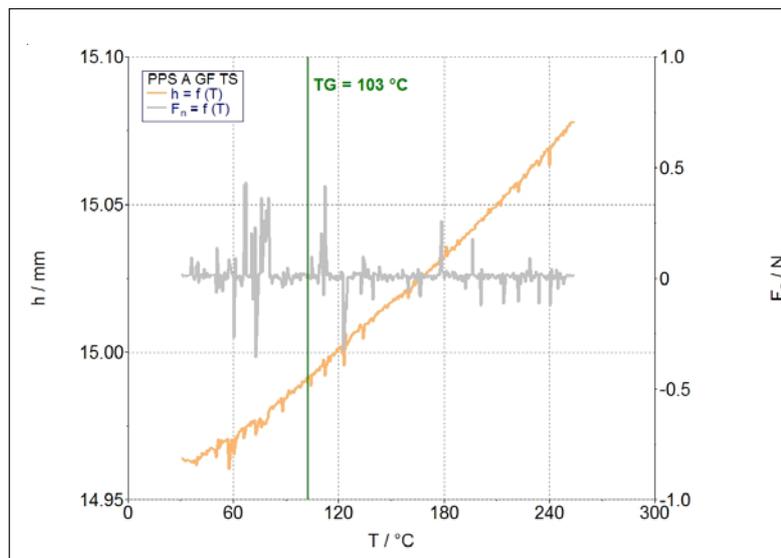


Fig. 6: Constant normal force (black) and increasing sample length (orange) during a temperature increase from  $30\text{ }^\circ\text{C}$  to  $250\text{ }^\circ\text{C}$  on one of the glass fibre enforced PPS samples.

Regarding the sample length over temperature confirms also in this case the perfect grip of the Thermo Scientific HAAKE MARS solids clamps. Compared to the carbon fibre enforced sample, these samples have a positive thermal expansion coefficient, which does not change around  $T_G$ . From the data in Figure 6 a constant coefficient of approx.  $\alpha = 3.3 \times 10^{-6} \text{ K}^{-1}$  can be calculated.

### Summary

The special design of the Thermo Scientific HAAKE MARS' solids clamps combines easy handling with high precision and perfect reproducibility of the testing results. Different composite samples with very hard and smooth surfaces have been tested giving very good results.

Using the rheometer's lift and normal force sensor in combination provides an easy way to verify the perfect grip on the sample and thus the reliability of the data collected. Due to the unique precision of both lift and normal force sensor, important data about the thermal expansion of the samples can be collected simultaneously. This allows e.g. the calculation of the sample's thermal expansion coefficient.

With its Controlled Test Chamber and its solids clamps, the HAAKE MARS is able to extend its range of testing capabilities into the field of dynamic mechanical thermal analysis (DMTA). In combination with a classical rheological setup like e.g. a Peltier temperature control and cone/plate geometries the HAAKE MARS is the perfect and cost efficient solution for testing polymer composites and their liquid base materials on one instrument.

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