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Making and Analyzing Polymer Nanocomposites

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APPLICATION NOTE

No. LR-68

Producing high-performance polymer-composites by embedding nanoparticles using twin screw extrusion

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Key words
Compounding, Carbon nanotubes, Composites, Twin screw extrusion

Introduction
Carbon nanotubes are graphite sheets rolled into seamless tubes, with diameters of just a few nanometers and lengths up to centimeters. Nanotubes have received much attention because of their unique mechanical, electrical and thermal properties.

There are a large number of potential applications for CNTs, especially in the field of polymer compounds, where they are used to improve mechanical and electrical properties. Polymer nanocomposites are frequently used in the automotive and aviation industries, as well as in construction materials for windmill blades.

Key to unleashing the unique properties of the polymer nanocomposites is dispersion of the CNTs thoroughly in the polymer matrix. Only when the CNT particles are dispersed homogeneously within the polymer and the formation of larger clusters is avoided, can the desired property improvements be achieved. The improved mechanical properties of the final compound can be tested by means of dynamic mechanical thermal analysis (DMTA) which can be performed, for instance, with a rotational rheometer [1].

One approach that can lead to a homogeneous distribution of the CNT particles within the polymer matrix is the use of CNT suspensions for the extrusion process. For this the CNTs are functionalized first (i.e. by amination) and dispersed afterwards in a carrier liquid like ethanol by means of high shear mixing or ultra sonic treatment. The obtained CNT suspension is then feed into the extrusion process. Using CNT suspensions in the extrusion process also avoids the formation of CNT dust in the laboratory environment.

The aim of this report is to demonstrate that CNT suspensions can be used to produce polymer nanocomposites by means of twin screw extrusion. With the described procedure a homogeneous distribution of the CNTs in the polymer matrix can be achieved in order to obtain the desired property improvements for the polymer nanocomposite.

Material and methods
Test material
- Base Polymer: Polypropylene Metocene HM562S (LyondellBasell)
- Two CNT-Ethanol suspensions with different functionalization (Rescoll/France)

Test equipment
- Torque rheometer system Thermo Scientific™ HAAKE™ PolyLab OS System
- Co-rotating twin screw extruder Thermo Scientific™ HAAKE™ Rheomex PTW16 OS System (L/D = 40)
- Gravimetric RotoTube feeder for pellets
- Liquid feeding pump for the suspensions
- Vacuum pump
- Strand line with Varicut pelletizer

Test conditions
- Screw speed: 250 rpm
- Temperature profile: 20°/230°/250°/250°/230°/220°/220°/200°/200°
- Feed rate PP: 0.919 kg/h
- Feed rate CNT-suspension: 0.114 kg/h (equivalent to 0.5 % CNT in PP)

Test procedure
The complete extruder and screw configuration is presented in Fig. 1. In the first stage (zone 1) the polypropylene was added and molten in the first mixing section (zone 2). The CNT suspension was dosed into the second feeding port (zone 3) into the polypropylene melt by means of a liquid feeding pump. The ethanol of the suspension was removed from the extruder using an atmospheric venting port in zone 4 and a vacuum venting in zone 9.

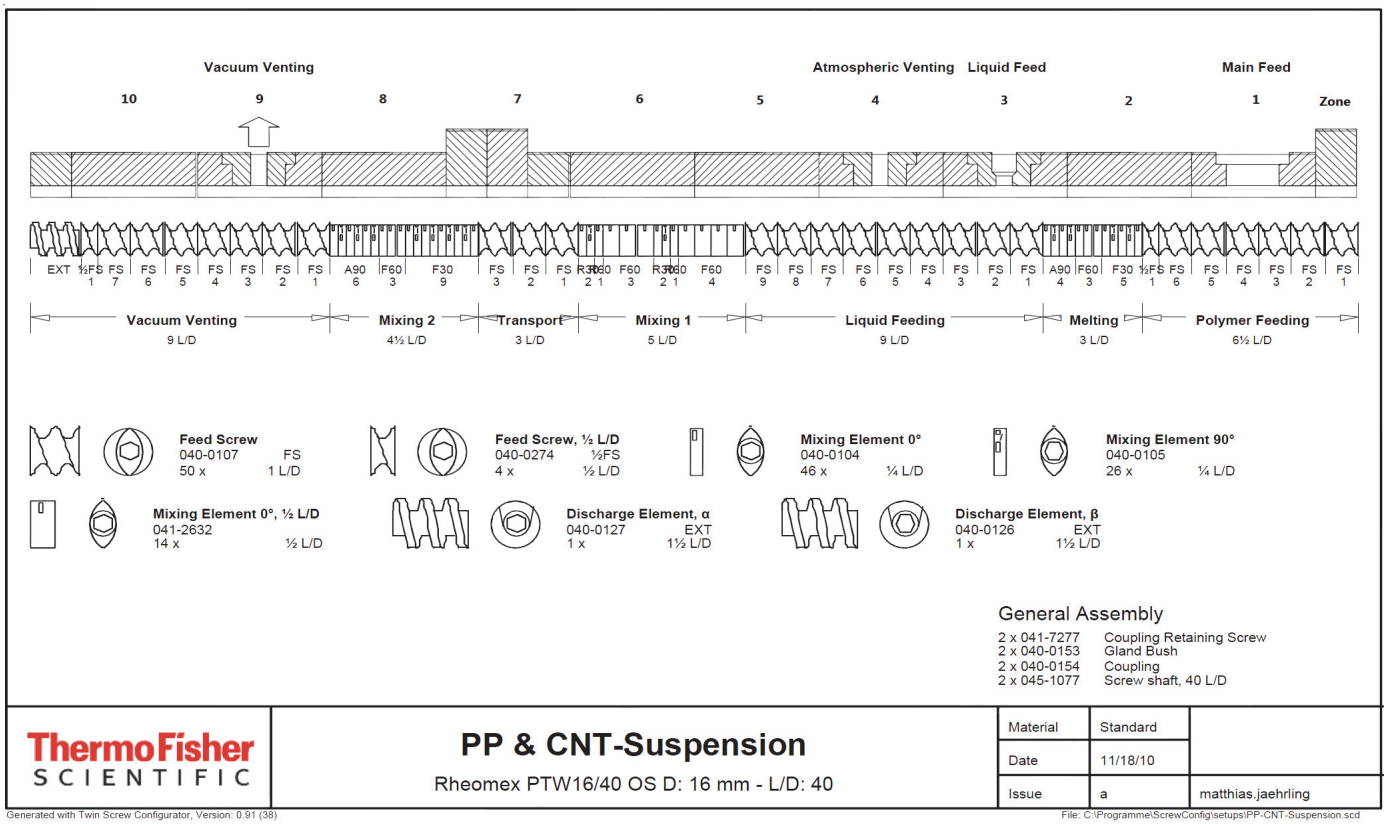

Fig. 1: Extruder- and screw configuration.

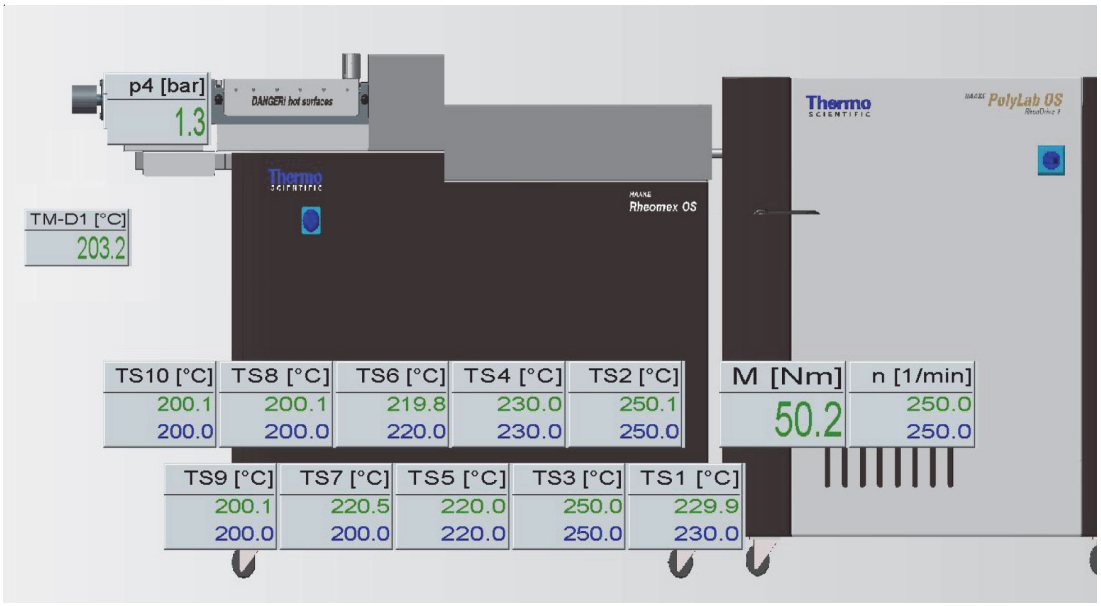

Fig. 2: Extrusion conditions.

The CNTs and the polypropylene were thoroughly mixed and sheared in two mixing sections in zones 5/6 and zone 8.

Results

During the test, the melt pressure at the die was measured. Fig. 3 shows this melt pressure as an overlay of three different extrusion tests. One test was done with the pure polypropylene, one test with the addition of CNT suspension “1“ and one with CNT suspension “4“.

It can be clearly seen that the pressure increased when a CNT suspension was added. The pressure difference between the two different suspen-sions itself was not significant. The extruded material was then formed into a strand, which was cooled down in a water bath and cut into pellets by a pelletizer.

Using our mini injection moulding machine, the Thermo Scientific™ HAAKE™ MiniJet System those pellets were injection moulded into specimens like disks and DMTA bars for further investigation.

Fig. 4 shows a microscopic picture taken from specimens made from the PP compound containing 0.5% CNT from suspension “1“.

In this picture no agglomeration can be seen and the CNTs seem to be evenly distributed in the polymer matrix. Fig. 5 shows a microscopic picture taken from the PP compound containing 0.5% CNT from suspension “4“. This picture shows a large amount of agglomerates. The dispersion seems to be much worse than the result we got from suspension “1“.

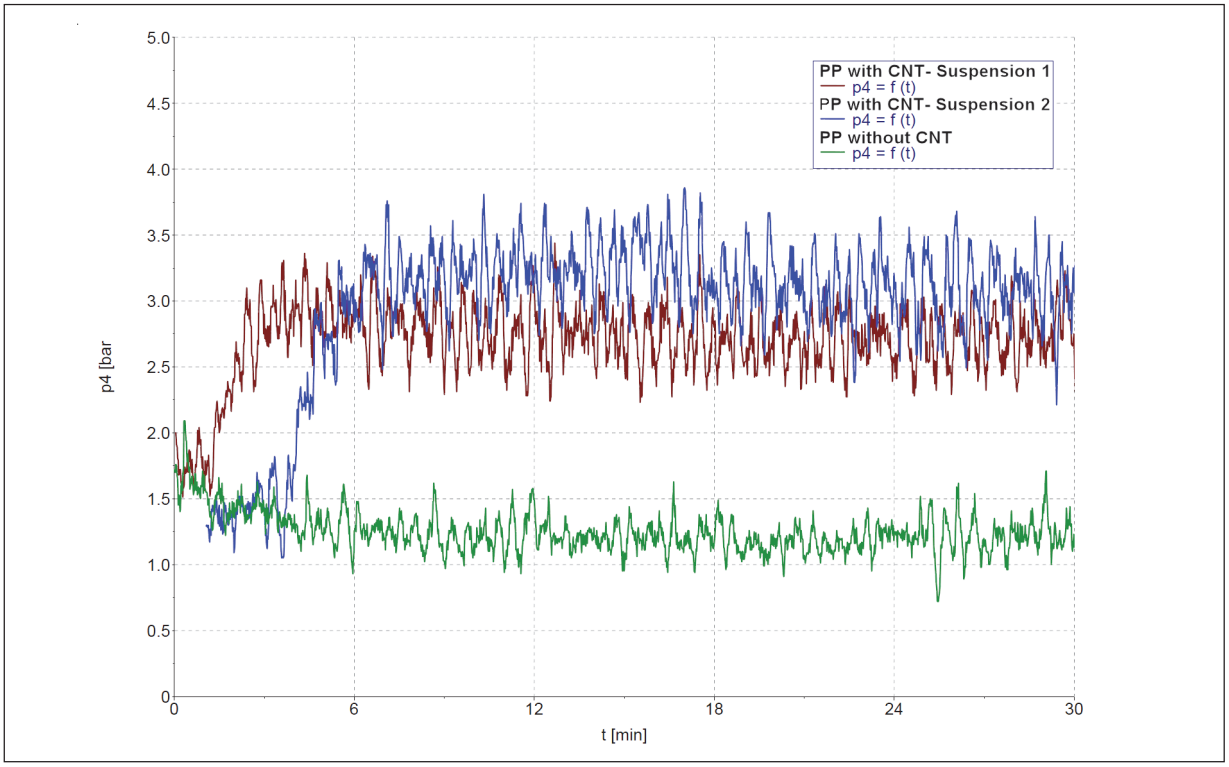

Fig. 3: Pressure at Die-Had.

Fig. 4: PP with 0.5% of CNT "1".

Fig. 5: PP with 0.5% of CNT "2".

Conclusion

The PolyLab System with the lab scale twin screw compounder, Rheomex PTW16, can be used to prepare compounds from polymers and CNTs using CNT suspensions.

The result of these tests shows significant differences between the compounds made with the differently functionalized CNTs.

Acknowledgement

We would like to thank the Fraunhofer Institute for Manufacturing Engineering and Automation IPA in Stuttgart, Germany for their input and the Research Company RESCOLL in Pessac, France for their kind co-operation and supplying the CNT-suspensions. We also thank Volker Räntzsch from the Karlsruhe Institute of Technology in Germany for providing the microscopic images.

Reference

[1] Thermo Scientific Application note V241 "Dynamic mechanical thermal analysis (DMTA) on polymer nanocomposites" Fabian Meyer, Klaus Oldörp and Frits de Jong

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APPLICATION NOTE

Dynamic mechanical thermal analysis (DMTA) on polymer nanocomposites

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Key words

DMTA, Solids clamping tool, Glass transtion

Introduction

Polymer nanocomposites (PNC) are materials that consist of a polymer matrix with embedded particles with a size of 100 nanometers or smaller. Typical nanoparticles are nanoclays, carbon nanotubes or nanofibers and graphenes. Compared to unfilled polymers, polymer nanocomposites show improved properties that make them interesting for various technical applications. In particular, the greater mechanical strength of polymeric materials combined with low weight are desired properties. Additionally the incorporation of nanocomponents can lead to an improved heat and chemical resistance as well as electric conductivity. Nowadays, polymer nanocomposites are frequently used in the automotive and aviation industries, as well as in construction materials for windmill blades.

Polymer nanocomposites can be produced by mixing the nanoparticles into the molten polymer matrix using extrusion. One way to achieve proper mixing during the extrusion process is to use nanoparticles that are predispersed in a carrier liquid and to feed the dispersion into the extruder. Only when the particles are distributed homogeneously inside the polymer matrix and no larger clusters are formed, the composite material exhibit the desired properties.

For testing the mechanical properties of a polymer nano-composite, dynamic mechanical thermal analysis (DMTA) can be used. DMTA can be performed in torsion with a rotational rheometer. The material is exposed to oscillatory shear while the temperature is changing continuously. The obtained data is used to identify characteristic phase changes such as the glass transition or the occurring of melting and crystallization. In addition to this, DMTA is used to determine the solid material's mechanical performance with important application related properties such as stiffness, brittleness, damping or impact resistance. The rheological parameters storage modulus (G'), loss modulus (G'') and the loss or damping factor (tan δ) are obtained from DMTA. The storage modulus represents the elastic, and the loss modulus represents the viscous properties of a material. For solids, the storage modulus is larger than the loss modulus and vice versa for fluids. The loss factor is the ratio of G'' and G' and is also a measure for the damping properties of a material. Fig. 1 shows the schematic diagram for DMTA on a semi-crystalline polymer. The glass transition can be identified using different approaches. The most common approach for rheological tests uses the maximum of the loss modulus (Fig.1). The onset of the decrease of the storage modulus or the maximum in the tan δ (G''/G') are two alternative methods. At room temperature, polymer nanocomposites are usually in the glassy state and show high values for G', indicating the high stiffness of the material. Compared to the unfilled polymers, polymer nanocomposites show higher G' values in the glassy state indicating their greater mechanical strength.

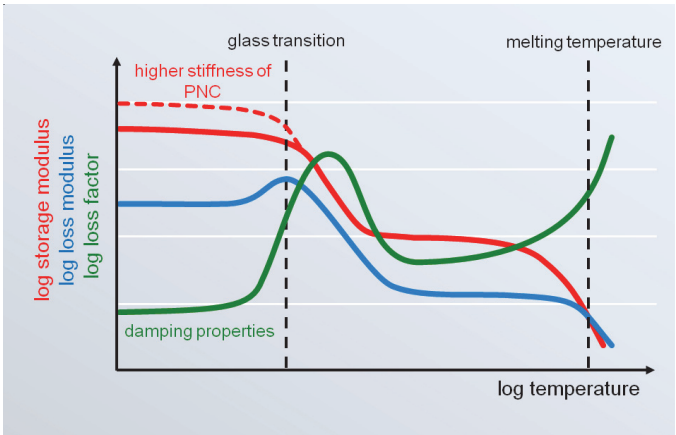

Fig. 1: Schematic drawing of dynamic mechanical thermal analysis results of a semi-crystalline polymer.

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Smaller phase transitions at temperatures way below the main glass transition can occur for copolymers and polymers that carry side chains. The additional peak in the damping factor can improve the impact resistance of a polymer. An example for such a material would be high impact polystyrene (HIPS), an engineering plastic with a polystyrene backbone and rubber side chains.

Fig. 2: Solids clamping tool with carbon fiber enforced composite sample.

Material and methods

To extend its range of testing methods into the field of composites and other solids, the Thermo Scientific™ HAAKE™ MARS™ rheometer can be equipped with a solids clamping tool [1]. The temperature control for this setup is provided by the Controlled Test Chamber (CTC) (Fig. 2).

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 Fig. 2) thus allowing testing of larger samples under uniform temperature conditions. The solids clamping tool can be equipped with special jaws for soft, medium or hard samples.

With the latter, the jaws are even able to fix hard composite materials with smooth surfaces during oscillatory testing. Due to the unique design with two moving jaws, the solids clamping tool automatically positions the sample in the axis of the rheometer, which is mandatory to avoid any error from eccentric placement.

Two different composite materials were tested using the HAAKE MARS rheometer, CTC and solids clamping tool. The first sample was a lightweight carbon fiber enforced material, which could be used, for instance, in airplane construction. The second sample was a glass fiber enforced polyphenylene-sulfide (PPS). Such materials are used for applications where a high mechanical and thermal stability are required.

DMTA was performed with both samples. The carbon fiber enforced material was tested in a temperature range between -100 °C and +240 °C. A constant oscillatory deformation γ of 0.1% was applied with a frequency of 1 Hz. During the entire test, a constant axial force of -1 N (pulling force) was applied.

The glass fiber enforced PPS was tested from 30 °C to 250 °C. A constant oscillatory deformation of 0.01% was applied at a constant frequency of 1 Hz. The axial force was kept constant at zero Newton during the tests.
All tests were performed with a heating rate of 2 °C/min.

Results and discussion

Fig. 3 shows the results of the DMTA tests with the carbon fiber enforced sample. The data reveals the high stiffness of the material at room temperature, with a storage modulus G' of more than 3 x 10^9 Pa. The results also show three transition temperatures of the sample represented by the local maxima of the loss modulus G''. The biggest change of the rheological properties occurs between 80 and 150 °C. The two maxima of G'' at 99 °C and 115 °C indicate the glass transitions of two different components in this temperature range. The excellent reproducibility of the test results was shown by comparing the results of two independent tests run with two different specimens of the same material. The two sets of curves shown in Fig. 3 are almost perfectly identical.

During the measurement, the rheometer applied a constant small pulling force on the sample to compensate for any thermal expansion or contraction (see black curve in Fig. 4). This results in a lift motion of the rheometer, that reacts to 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 Fig. 4 documents the clamp's steady grip even on such a hard material.

Apart from its diagnostic value, the data shown in Fig. 4 contains valuable information about the sample itself. The length decrease with increasing temperature reflects the negative temperature expansion coefficient (α) some carbon fiber enforced materials show in fiber direction. One can even see from the change in slope, that the material's α changes around the major transition temperatures starting at 80°.

Fig. 5 shows the results of the DMTA tests with the glass fiber enforced material. Also this material shows a high stiffness at room temperature with a storage modulus G' of above 3 x 10^9 Pa. The glass transition temperature,

indicated by the maximum in the loss modulus G'', was occurring at 101 °C. At temperatures above the glass transition, the material transformed into a rubber elastic condition, where the moduli data changed less with increasing temperature.

Also for this measurement, the sample length over temperature plot shows the perfect grip of the solids clamping tool. Compared to the carbon fiber enforced sample, this material has a positive thermal expansion coefficient, which does not change around the glass transition temperature. From the data in Fig. 5, a constant coefficient of approximately $\alpha = 3.3 \times 10^{-6}\ K^{-1}$ can be calculated.

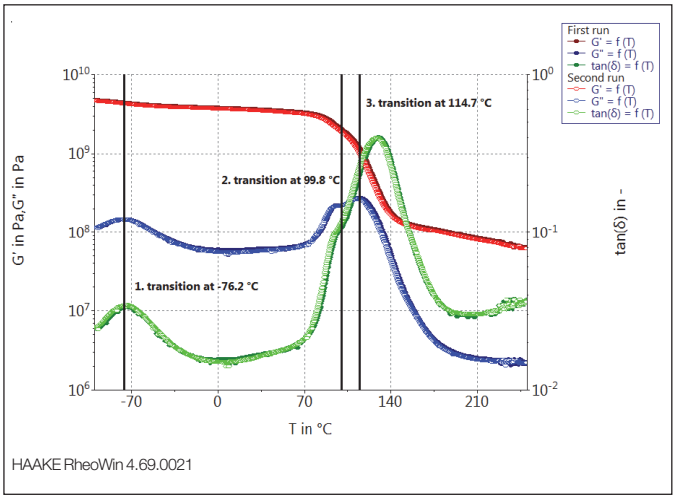

Fig. 3: Storage modulus G' (red), loss modulus G" (blue) and tan (δ) (green) as a function of temperature for the carbon based sample. The glass transition temperature T_G is indicated by the green line. The results of 2 independent tests (open and filled symbols) run on fresh samples each, show the excellent reproducibility of the results.

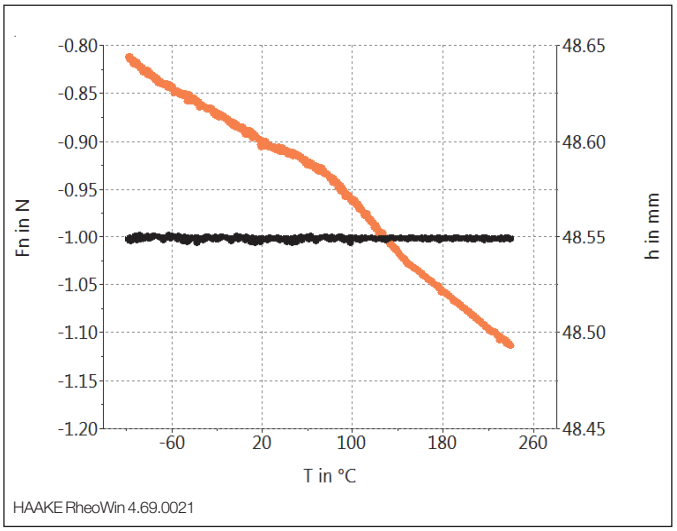

Fig. 4: Constant normal force (black) and decreasing sample length (orange) during a temperature increase from -100 °C to 240 °C on the carbon fiber enforced sample.

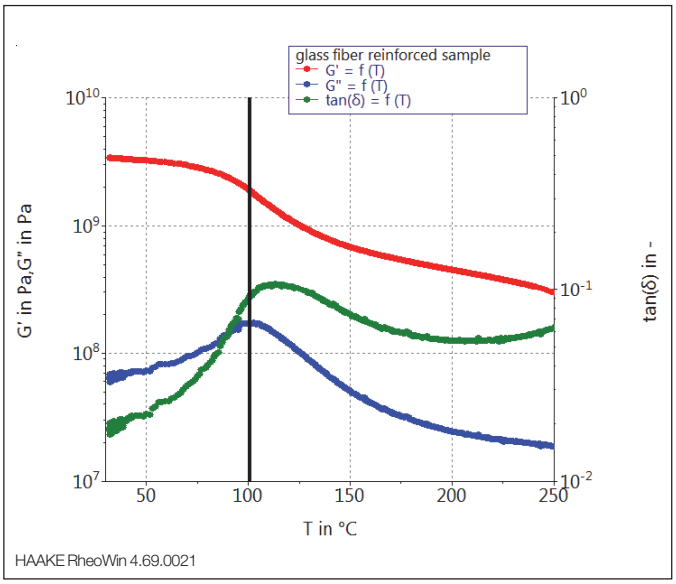

Fig. 5: Storage modulus G' (red), loss modulus G" (blue) and tan (δ) (green) as a function of temperature for a glass fiber enforced PPS sample. The glass transition temperature TG is indicated by the black line.

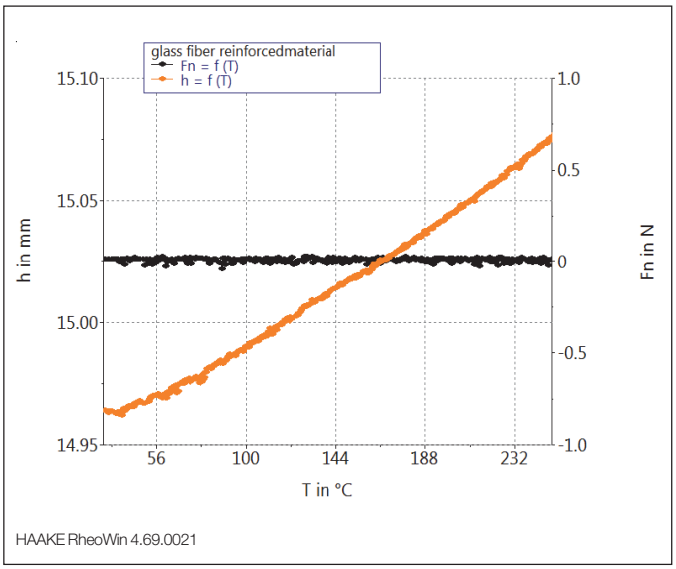

Fig. 6: Constant normal force (black) and increasing sample length (orange) during a temperature increase from 30 °C to 250 °C on one of the glass fiber enforced PPS samples.

Summary

The special design of the solids clamping tool accessory for the HAAKE MARS rheometer combines easy handling with high precision and perfect reproducibility of test results. Different composite samples with very hard and smooth surfaces have been tested with both yielding very good results.

Using the rheometer's lift and normal force sensor in combination with the solids clamping tool 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, for example, the calculation of the sample's thermal expansion coefficient.

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With the Controlled Test Chamber and solids clamping tool, the HAAKE MARS rheometer is able to extend its range of testing capabilities into the field of dynamic mechanical thermal analysis. In combination with a classical rheological setup like a Peltier temperature control module and cone & plate geometries, the HAAKE MARS rheometer is an ideal and cost-effective solution for testing polymer composites and their liquid base materials on one instrument.

Reference

[1] Thermo Scientific Product Information P004
"Solids clamping tool for Dynamic Mechanical Thermal Analysis (DMTA) with HAAKE MARS rheometers"
Cornelia Küchenmeister-Lehrheuer, Fabian Meyer and Klaus Oldörp

Find out more at thermofisher.com/rheometers

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