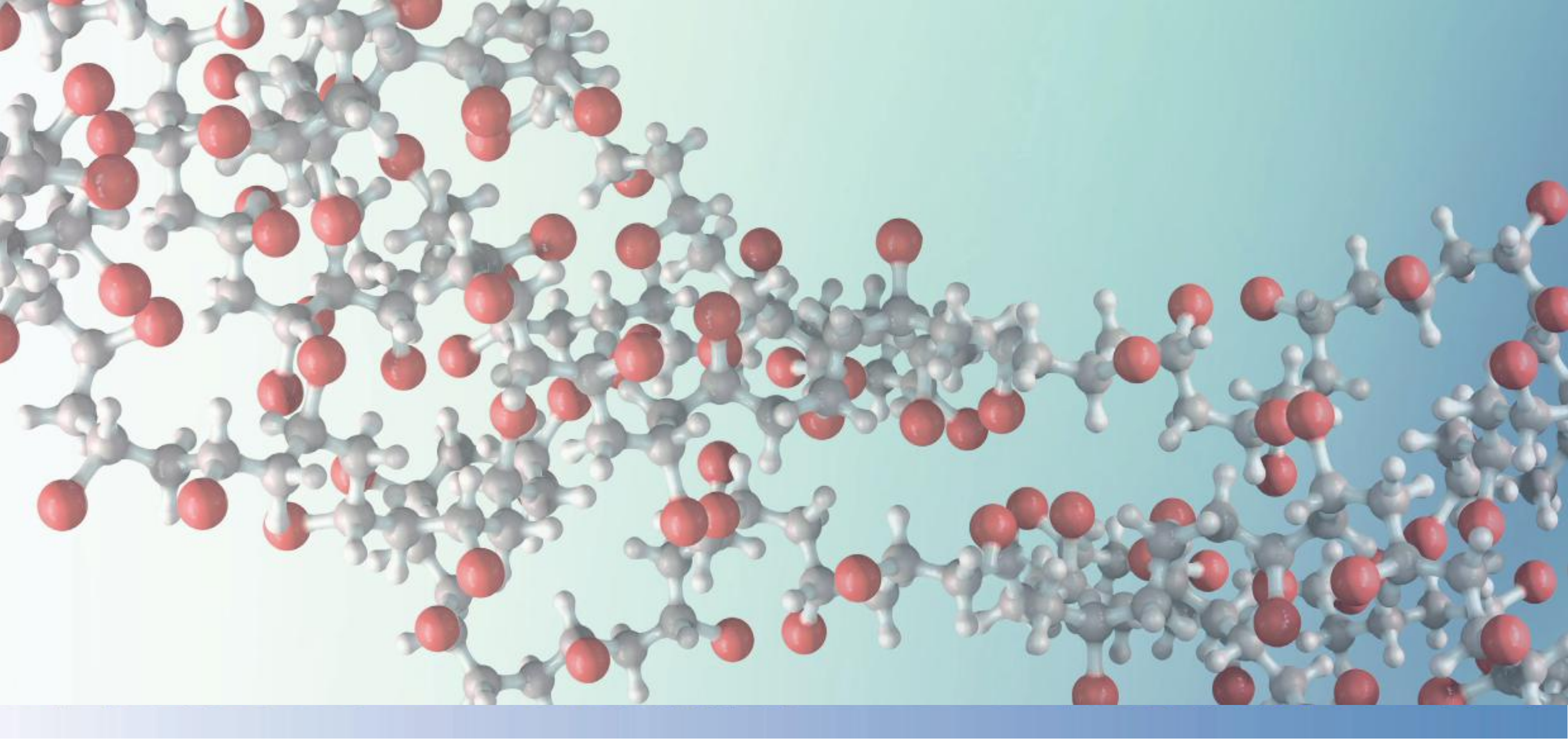

Thermo Scientific

HAAKE MARS Rheometers for Polymer Analysis

Table of contents

Polymer rheology

Polymers are large molecules consisting of repetitive units of smaller molecules bonded together to long chains. They are used in a broad variety of applications and are ubiquitous in our everyday life. In solution for example, polymers can be used as thickeners or stabilizers in food and personal care products. In solid state they are used for casings, packaging and composite materials. For these types of applications polymers are processed at elevated temperatures in a molten state.

Due to their chemical structure and high molecular weight, polymers exhibit a complex flow and deformation behavior. They are so called viscoelastic materials, showing both, viscous and elastic properties. Which behavior is dominating depends on the molecular structure itself, as well as the testing or processing conditions. Too much elasticity can lead to flow anomalies and unwanted effects during many common processing steps. One example is the swelling of a melt stream when exiting the narrow die of an extruder. Knowing the viscoelastic properties of a polymeric material is therefore essential to optimize formulations and blends as well as to adapt a process to the properties of a given material.

Rheology has proven to be an excellent tool to analyze the mechanical properties of polymers in their different states. Various testing methods are available for a full rheological characterization of polymeric materials. Though rotational steady state shear experiments allow for measuring the non-Newtonian viscosity of dilute and semi-dilute polymer solutions, the preferred testing methods for polymer melts (and solids) utilize the application of an oscillatory shear deformation. This is due to their high elasticity and the consequential occurrence of edge failures when they are exposed to large deformation in the measuring geometry of a rotational rheometer.

The information gained from rheological tests in oscillation mode is manifold. Shear rate depending viscosity data derived from oscillatory frequency sweep experiments together with the utilization of the Cox Merz rule for instance, allow for quantifying the flow resistance of a material during different high shear processing applications. The low frequency (shear) data on the other hand can be used to calculate the average molecular weight of a polymer melt. Fig. 1 shows a typical viscosity curve of a polymer melt and the shear rate ranges that occur in typical applications.

Viscosity data of a polystyrene melt (master curve at 190 °C)

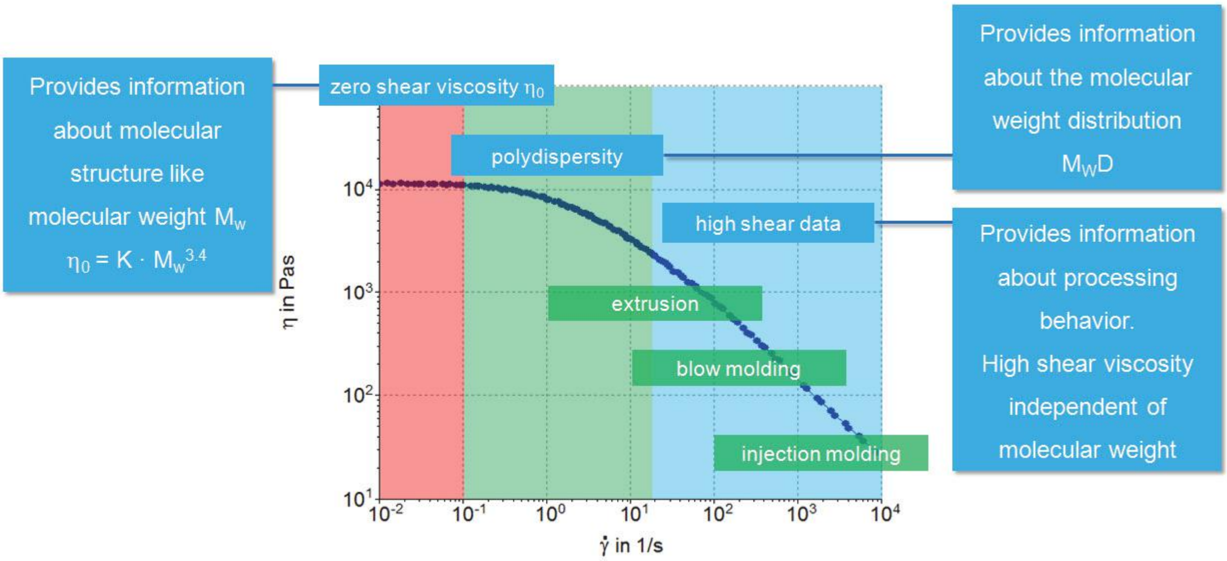

Fig. 1: Shear rate depending viscosity of a polymer melt and typical applications.

Besides information about the overall flow resistance, frequency sweep data also provide a direct measure of the viscous and elastic properties of a polymer. These are represented by the storage and the loss moduli (G' & G") measured at different frequencies / time scales. The data reveals the general structure of a material and also provides information of the molecular weight MW and the molecular weight distribution MWD. Fig. 2 shows how the crossover modulus (G' = G") shifts when the MW or the MWD change for an otherwise identical polymer melt:

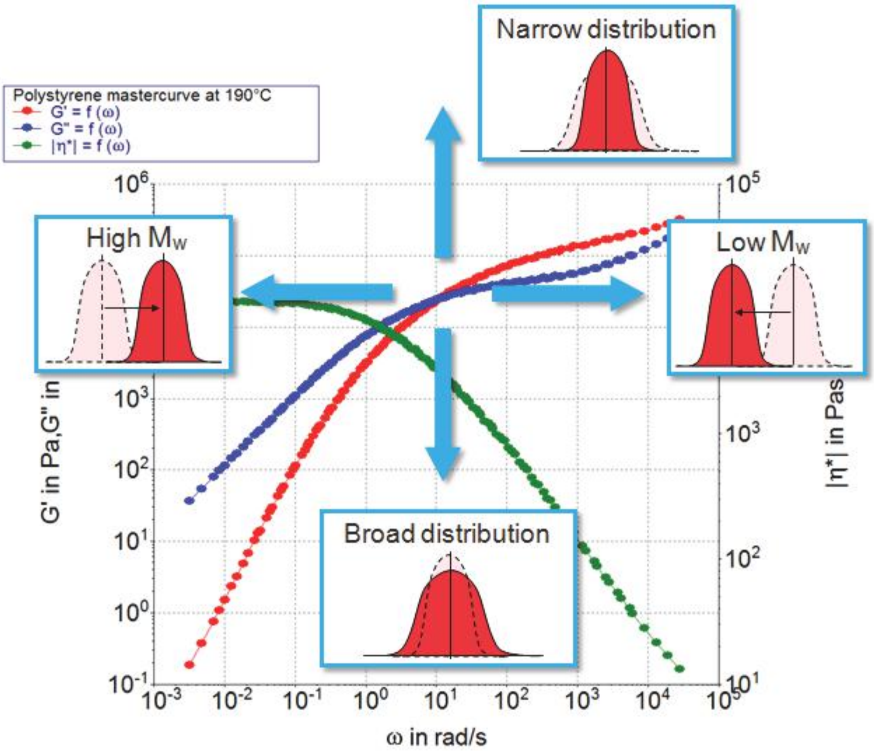

Fig. 2: Storage modulus G', loss modulus G" and the complex viscosity Iη*I as a function of the angular frequency ω for a polystyrene melt at 190°C.

Rotational rheometers can be utilized also to perform Dynamic Mechanical Thermal Analysis (DMTA) where a material is exposed to an oscillatory excitation while the temperature is changing continuously. The obtained data are used to identify characteristic phase transitions such as the glass transition or the occurring of melting and crystallization. In addition to this DMTA is used to determine the final product performance and important application related properties such as stiffness, brittleness, damping or impact resistance. Fig. 3 shows the example of a DMTA test with a semi crystalline polyethertetherketone (PEEK), tested from below its glass transition close to the melting temperature. The glass transition can be identified using different methods. The most common for rheological tests uses the maximum of the loss modulus G". The onset of the decrease of the storage modulus G' or the maximum in the tanδ (G"/G') are two other methods. As can be seen in Fig. 3, the maximum in G" is located more in the middle of a wider transition range, while the onset of the G' decrease is right at the beginning and the maximum in tanδ more at the end of this range.

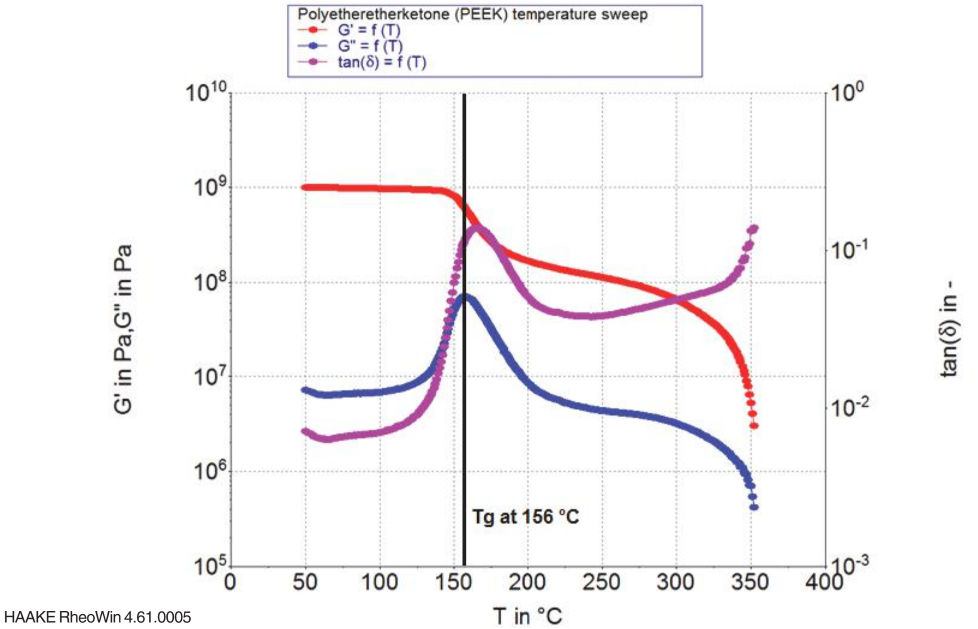

Fig. 3: Storage modulus G', loss modulus G" and tanδ as a function of temperature for a polyether-etherketone at 156 °C.

Application Packages for Polymer Analysis Thermo Scientific HAAKE MARS

Order-No. 379-0670, 379-0610, 379-0630

Application

If you are working on product improvement or new developments in the polymer industry, the Thermo Scientific™ HAAKE™ MARS™ rheometer platform is designed to meet the most demanding requirements in advanced quality control as well as applied in research and development.

Polymers are ubiquitous in our day-to-day life and play an important role in the production of many consumer goods. Polymer melts exhibit a complex flow and deformation behavior. Understanding the viscoelastic properties of a polymer in its molten state is essential to define and improve processing conditions and design final products for specific applications. Rheological tests with solid specimen help to understand the properties of final products under application conditions.

The HAAKE MARS is designed to perform rheological tests in Controlled Rate (CR), Controlled Stress (CS) and Controlled Deformation (CD) mode. The sensitive and precise normal force sensor can be used for reproducible gap setting and for compensating or investigating thermal expansion of the tested material.

Several HAAKE MARS application packages are available for comprehensive polymer analysis and to support you in every phase of your multi-layered processes.

The first package consists of the HAAKE MARS rheometer equipped with a lower electrical temperature module and an active upper heating system for tests with cone & plate and parallel plate measuring geometries up to temperatures of 400 °C. The package includes a 25 mm parallel plate measuring geometry.

For an extended temperature range up to 600 °C two additional HAAKE MARS packages with the Controlled Test Chamber (CTC) are available. Besides polymer melt testing with cone & plate and parallel plate measuring geometries, these configurations also allow for Dynamic Mechanical Thermal Analysis (DMTA) [1] or testing the extensional properties [2] when using optional sample fixtures. The extended CTC package includes accessories for low temperature testing down to -150 °C.

Typical samples, recommended measuring routines and material properties

- Amorphous and partly crystalline thermoplastics, thermosets, elastomers
- Oscillatory measurements including amplitude, frequency, time and temperature sweeps

Fig. 1: HAAKE MARS Rheometer with electrical temperature modules for plate and cone geometries.

- Storage and loss modulus, complex viscosity, glass transition temperature, melting temperature, crystallinity, molecular weight (distribution), extensional properties

Features

- High-end rheometer platform for individual demands
- Easy-to-operate, multilingual Thermo Scientific™ HAAKE™ RheoWin™ software for beginners and experts, with optional software-module: TTS, spectra and MWD
- Connect Assist quick coupling and automatic recognition of measuring geometries and temperature control modules
- Pneumatic release of the rotor to fulfill highest safety standards
- Normal force sensor for measurements of positive and negative normal forces

Fig. 2: Polymer workflow (from right to left) Mini compounder, injection molding system to produce test specimens and HAAKE MARS 60 rheometer with controlled test chamber for polymer tests in a temperature range between -150 °C up to 600 °C.

Order information

Order no.	Description
379-0670	HAAKE MARS 40 for polymer melts includes:
	379-0340 HAAKE MARS 40 with HAAKE RheoWin software
	222-1211 Filter unit
	222-1897 Power Supplies (2x)
	222-1860 Electrical Temperature Module (TM-EL-P)
	222-2172 Electrical Temperature Module for upper geometries (TM-EL-H) incl. holder 222-1902
	222-1928 Lower plate TMP25
	222-2195 Plate P25/Ti with "Connect Assist" and ceramic shaft
379-0610	HAAKE MARS 60 for polymer solids and melts up to 600 °C:
	379-0600 HAAKE MARS 60 with mounting rods and HAAKE RheoWin software
	222-1211 Standard filter unit
	222-1913 Controlled Test Chamber
	222-2251 Lower holder for exchangeable plates (incl. temp sensor)
	222-2143 P20 lower plate
	222-2223 Rotor P20-CTC/Ti with "Connect Assist" and ceramic shaft
379-0630	HAAKE MARS 60 for polymer solids and melts from -150 °C up to 600 °C:
	379-0600 HAAKE MARS 60 with mounting rods and HAAKE RheoWin software
	222-1211 Standard filter unit
	222-1913 Controlled Test Chamber
	222-1720 Low Temperature Option
	222-2251 Lower holder for exchangeable plates (incl. temp. sensor)
	222-2143 P20 lower plate
	222-2223 Rotor P20-CTC/Ti with "Connect Assist" and ceramic shaft

Necessary accessories

- Compressed air with standard filter unit or compressor

Optional polymer-specific accessories

- Self-centering and self-adjusting solids clamping tool for Dynamic Mechanical Thermal Analysis (DMTA) of solid specimens and measurements according to DIN/ ISO 6721-1 [1]
- Sentmanat Extensional Rheometer (SER) tool from Xpansion Instruments for extensional rheological measurements of polymer films [2]
- Additional HAAKE RheoWin Software-modules for Polymer Analysis (Time Temperature Superposition TTS, Spectra and Molecular Weight Distribution MWD)
- Disposable pellet filling aid for optimal gap filling
- RheoScope module for the measurement of the melting and crystallization behavior of polymers [3]

References

[1] Thermo Scientific Application Note V220 "Measurements on selected (semi)-solids in a wide temperature range using new solid clamps" Klaus Oldörp, Jint Nijman and Cornelia Küchenmeister

[2] Thermo Scientific Application Note V261 "Characterizing long-chain Branching in Polyethylene with Extensional Rheology" Jan Philip Plog, Oliver Arnolds and Ulrich Schulz

[3] Thermo Scientific Product information P040 "Thermo Scientific HAAKE RheoScope module: image acquisition at (very) high shear rates using a stroboscope light source" Cornelia Küchenmeister and Fritz Soergel

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Controlled Test Chamber (CTC) for Thermo Scientific HAAKE MARS Rheometers

Cornelia Küchenmeister-Lehrheuer and Fabian Meyer, Thermo Fisher Scientific, Karlsruhe, Germany

The Controlled Test Chamber (CTC) is a temperature control module for Thermo Scientific™ HAAKE™ MARS™ rheometers for performing measurements on both fluids and solids in the temperature range from -150 °C* up to 600 °C. The CTC consists of two temperature chamber half-shells that can be moved individually on a rail system. For sample loading, cleaning or changing the measuring geometry, the CTC half-shells can be moved into the so called parking position at the rear left side of the rheometer (Fig. 2). In the parking position the operator has full access to the sample and the measuring geometry without the danger of touching the hot (or very cold) inner part of the CTC. Since the CTC is fully closed when in parking position, the internal temperature can be controlled and maintained during cleaning, sample loading or geometry change. When in the measurement (front) position, the two half-shells of the CTC enclose the measuring geometry completely, what allows for a homogeneous and gradient free temperature control of the sample (Fig. 2). As a hybrid system, the CTC combines the advantages of convection heat transfer (homogeneous temperature distribution) with those of radiation heat transfer (rapid temperature changes). Both heat transfer systems are controlled by means of a digital control circuit. During a measurement the sample can be observed through the windows on both CTC half-shells.

The parking position also allows for using the HAAKE MARS rheometer with other temperature control modules (like Peltier temperature control modules for parallel plates and cone & plate or for coaxial cylinder measuring geometries) or with the RheoScope module without demounting the CTC (Fig. 3).

For measurements below ambient temperature, the CTC can be equipped with a low temperature option for cooling with liquid nitrogen. The low temperature option consists of an evaporation unit to be used with used a standard 50 l Dewar vessel (optionally available). The evaporation unit is connected to the CTC with flexible double-wall vacuum insulated metal hoses to prevent ice formation on the outside of the hoses.

For the HAAKE CTC various standard parallel plates and cone & plate measuring geometries are available (Fig. 3). The lower part of the measuring geometry is mounted on a lower holder with an integrated temperature sensor. The lower plates are designed to collect surplus material during sample loading or when a material is expanding during a measurement. Upper plate and cone rotors made of titanium (rotor shaft made of ceramic material) are available with different diameters (8, 20, 25 and 35 mm) and cone angles. All rotors are equipped with a quick fit coupling as well as auto-recognition functionality.

Fig.1: HAAKE MARS with Controlled Test Chamber (CTC).

Disposable geometries made of aluminum with diameters from 8 to 35 mm are also available. For this type of geometry a separate collection device is available which protects the temperature chamber against fouling (Fig.3).

Customized measuring geometries with different dimensions, with special surfaces (e.g. sandblasted) or made from another material (e.g. Hastelloy) are available on request.

Other measuring geometries available for the CTC include:

- Solids clamping tool for dynamic mechanical thermal analysis in torsion
- SER tool for measuring extensional viscosity of films or fibers
- DEA probe for simultaneous rheological and dielectric analysis
- Coaxial cylinder measuring geometry for testing low viscous fluids at very high temperatures

These geometries are described in detail in the corresponding product information.

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*with low temperature option

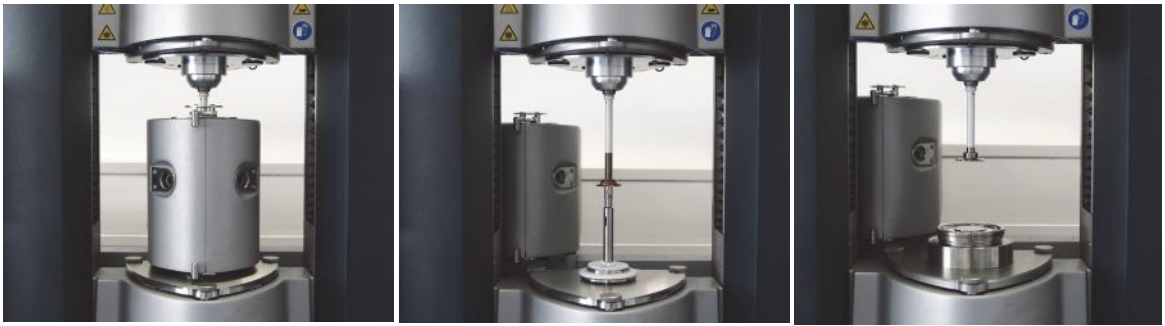

Fig. 2: HAAKE MARS with Controlled Test Chamber (CTC) in measurement position (left); in parking position (middle); in parking position and Peltier temperature control modules for parallel plates and cone & plate mounted (right).

Fig.3: HAAKE MARS with Controlled Tests Chamber (CTC) half-open (left); Standard measuring geometry for CTC consisting of lower shaft with exchangeable plate and upper rotor with ceramic shaft (middle); Disposable measuring geometry for CTC with collection device to prevent chamber fouling (right).

Order information

379-0600 Controlled Test Chamber for temperature range 30 °C up to 600 °C, if input voltage is not 230 V transformer is needed (222-1768)
222-1914 Mounting rods (needs to be ordered for HAAKE MARS 40, in HAAKE MARS 60 included)
222-1730 Option ”low temperature” with low energy consumption for temperatures down to -150 °C
222-1733 Dewar vessel (50 l)

Standard measuring geometries

Lower plates:
222-2251 Lower holder for exchangeable measuring geometries incl. temperature sensor 222-1769
222-2141 P35-CTC/St
222-2142 P25-CTC/St
222-2143 P20-CTC/St
222-2144 P8-CTC/S

Upper rotors with ”Connect Assist” and ceramic shaft:
222-2221 Plate P35-CTC/Ti (CS)
222-2225 Cone C35 4°-CTC/Ti (CS)
222-2226 Cone C35 1°-CTC/Ti (CS)
222-2222 Plate P25-CTC/Ti (CS)
222-2223 Plate P20-CTC/Ti (CS)
222-2227 Cone C20 1°-CTC/Ti (CS)
222-2224 Plate P8-CTC/Ti (CS)

Disposable measuring geometries

222-2251 Lower holder for exchangeable measuring geometries incl. temperature sensor 222-1769
222-2151 Adapter P2 (CS) Adapter for disposable plates D PXX /Al (upper adapter for CTC) with ”Connect Assist” and ceramic shaft

222-2152 D P8 /Al Plates D P8 /Al (40 pcs., as lower or upper plate)
222-2153 D P10 /Al Plates D P10 /Al (40 pcs., as lower or upper plate)
222-2154 D P20 /Al Plates D P20 /Al (40 pcs., as lower or upper plate)
222-2155 D P25 /Al Plates D P25 /Al (40 pcs., as lower or upper plate)
222-2156 D P35 /Al Plates D P35 /Al (40 pcs., as lower or upper plate)

Recommended accessory:
Collection device for disposable plates
222-1778 for P20 mm Al Ex
222-1779 for 25 mm Al Ex
222-1787 for 35 mm Al Ex

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Solids clamping tool for Dynamic Mechanical Thermal Analysis (DMTA) with HAAKE MARS rheometers

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Key words
Dynamic Mechanical Thermal Analysis (DMTA), Solids clamping tool, Thermo Scientific HAAKE MARS, Controlled Test Chamber, DIN/ISO 6721-1

A solids clamping tool for measurements according to DIN/ISO 6721-1 is available for the Thermo Scientific™ HAAKE™ MARS™ rheometers in combination with controlled test chamber (CTC) (Figure 1). It consists of an upper and a lower clamp, each equipped with two moving jaws, which guarantee an automatic centering of the sample relative to the rheometer motor axis (Figure 2).

The automatic clamping force adjustment and a simple semi-automatic gap adjustment for a wide range of sample thicknesses allow to measure over a wide temperature range in one run without ever loosing the grip on the sample.

The jaws are easy to remove for cleaning and exchange. Jaws with different profiles for different sample stiffness (soft, medium, hard) are available.

Rectangular specimen with a width from 5.0 to 12.7 mm, a thickness from 0.15 to 4.0 mm and a maximum length of 68 mm can be tested with the solids clamping tool.

In order to position differently dimensioned specimens in the center of test chamber, the bottom clamp can be adjusted in height. Thus all samples are always exposed to the same extremely low temperature gradient within the tests chamber. During the measurement the temperature is measured close to the sample center by a flexible temperature sensor.

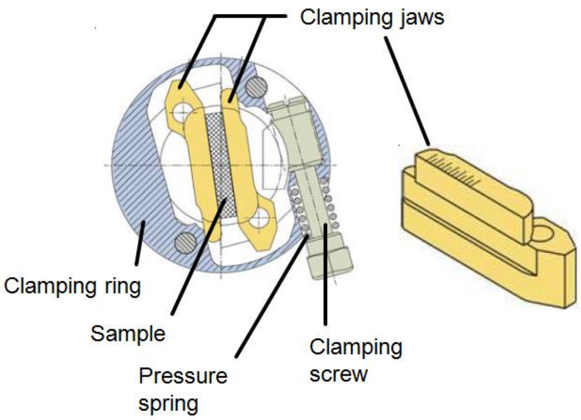

Fig.2: Technical drawing of solids clamping tool.

Fig.1: HAAKE MARS rheometer with controlled test chamber and solids clamping tool.

Figure 3 shows the results of a dynamic mechanical thermal analysis of a polyether ether ketone (PEEK) performed with the solids clamping tool. One method to determine the glass transition of a material is to use the maximum value in G” of a dynamic mechanical thermal analysis. For the PEEK this method gives a glass transition of 158 °C.

The solids clamps are available in two versions. On the hand with a threaded coupling for the previous HAAKE MARS models and on the other hand with quick fit coupling and automatic recognition for HAAKE MARS models 40 and 60. For an easier handling an additional triangular base plate is recommended on which the lower holder of the solids clamping tool is adapted. This additional plate saves time for changing from the solids clamping tool to regular cone & plate or parallel plate geometries.

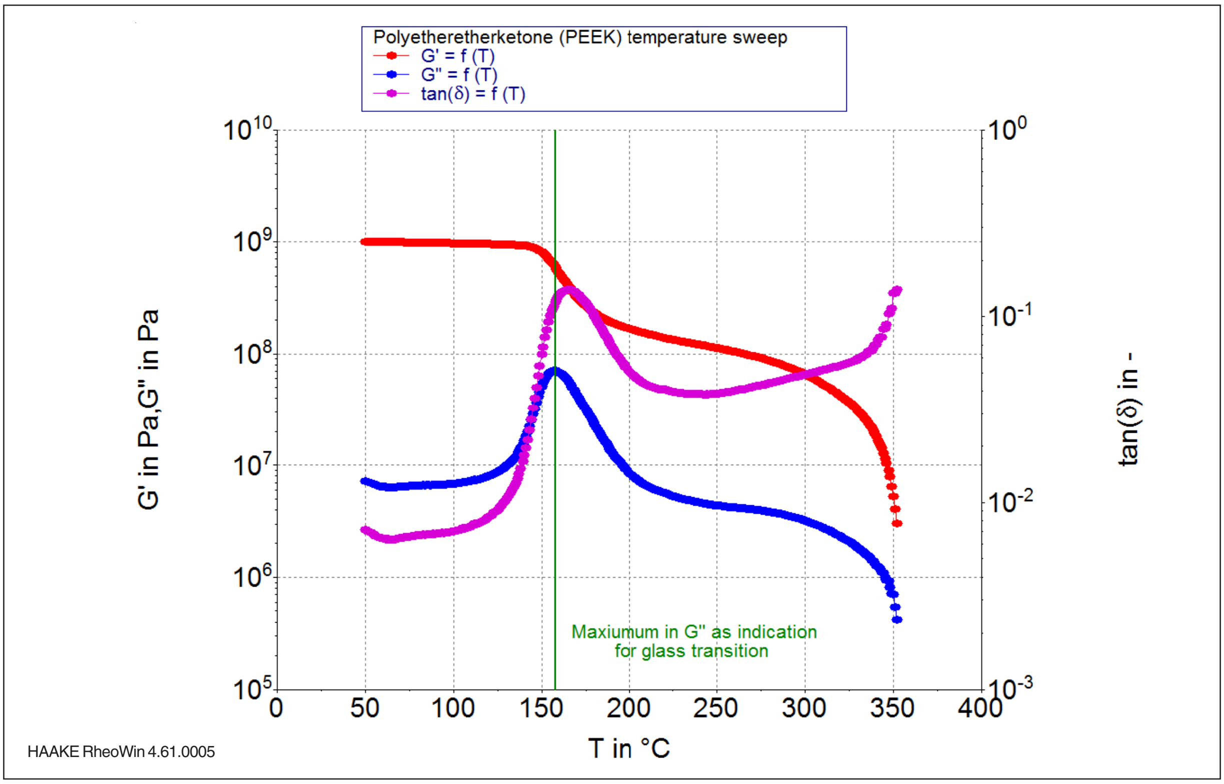

Fig. 3: Dynamic mechanical analysis with Polyether ether ketone (PEEK).

Fig.4: Solids clamping tool with temperature sensor, spacer and tool.

Order information

Solids clamp consisting of an upper and a lower holder, incl. temperature sensor, set of jaws for medium samples (4 pcs.), spacers and screw drivers (Figure 4).

222-1734 for HAAKE MARS models I, II, III
222-2231 for HAAKE MARS models 40 & 60 with “Connect Assist“

Optional accessories

222-1781 Jaws for soft samples (4 pcs.)
222-1782 Jaws for medium samples (4 pcs.)
222-1783 Jaws for hard samples (4 pcs.)
222-1856 Triangular adapter plate for CTC measuring geometries

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Dynamic Mechanical Thermal Analysis (DMTA) on Polymer Nanocomposites

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Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Key words
DMTA, Composites, Solids clamping tool, Glass transition

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. Especially the higher mechanical strength, combined with the low weight of polymeric materials is a desired property. 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 industry, as well as 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 pre-dispersed in a carrier liquid and feeding 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 will exhibit the desired properties.

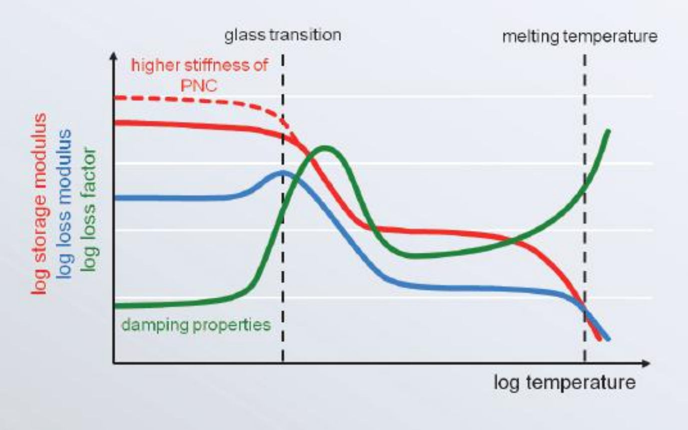

Fig. 1: Schematic drawing of dynamic mechanical thermal analysis results of a semi-crystalline polymer.

For testing the mechanical properties of a polymer nanocomposite, 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 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 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 higher mechanical strength. 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 fibre enforced composite sample.

Materials and Methods

To extend its range of testing methods into the field of composites and other solids, the Thermo Scientific™ HAAKE™ MARS™ 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 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 ones they are even able to fix hard composite materials with smooth surfaces during oscillatory testing. Due to their unique design with 2 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, Controlled Test Chamber and the solids clamping tool. The first sample was a light weight carbon fiber enforced material, like its being used for instance in airplane construction. The second sample was a glass fiber enforced polyphenylene-sulfids (PPS). Such materials are used for applications where a high mechanical and thermal stability are required.

Dynamic mechanical thermal analysis (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 3×10^9 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 any thermal expansion or contraction (see black curve in Fig. 4). Thus, the distance between the upper and the lower clamping fixture followed 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 clamps’ 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 3×10^9 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 went over inter 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 $\alpha = 3.3 \times 10^{-6}\ \mathrm{K}^{-1}$ can be calculated.

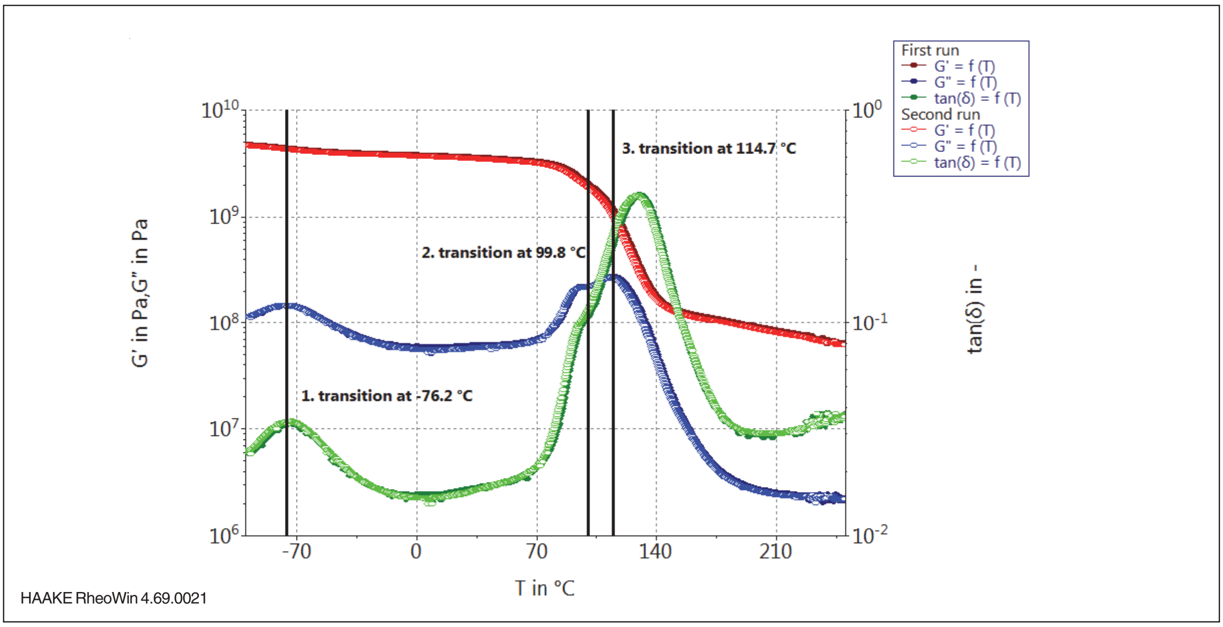

Fig. 3: Storage Modulus G' (red), Loss Modulus G" (blue) and tan(δ) (green) as a function of temperature for the carbon based sample. The glass transition temperature T_G is indicated by the green line. The results of 2 independent tests (open and filled symbols) run on fresh samples each show the excellent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

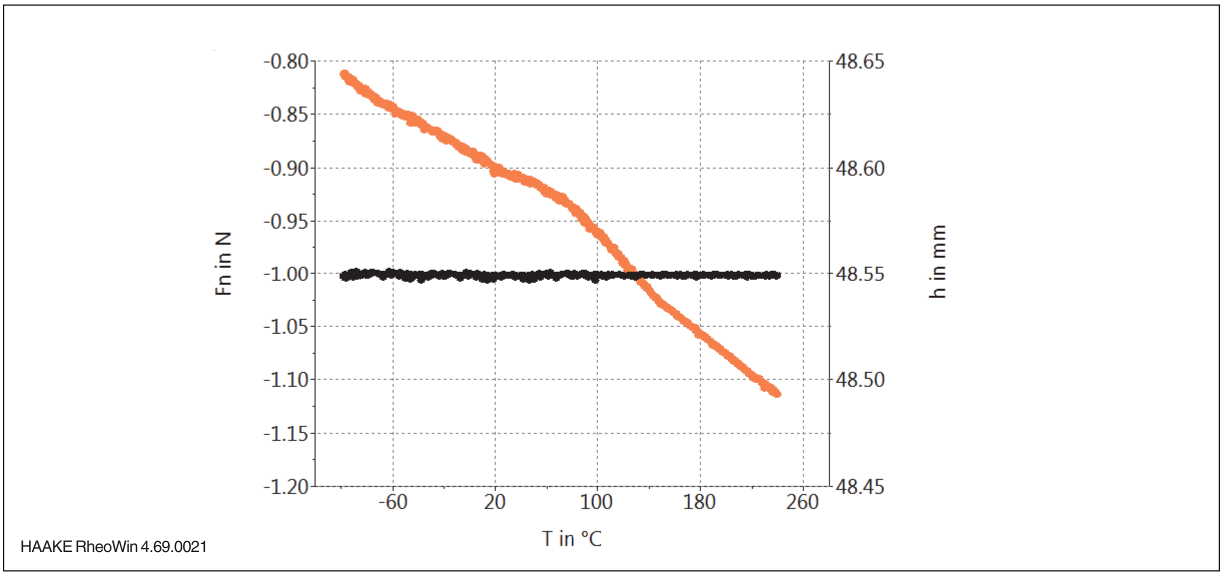

Fig. 4: Constant normal force (black) and decreasing sample length (orange) during a temperature increase from -100 °C to 240 °C on the carbon fibre enforced sample.

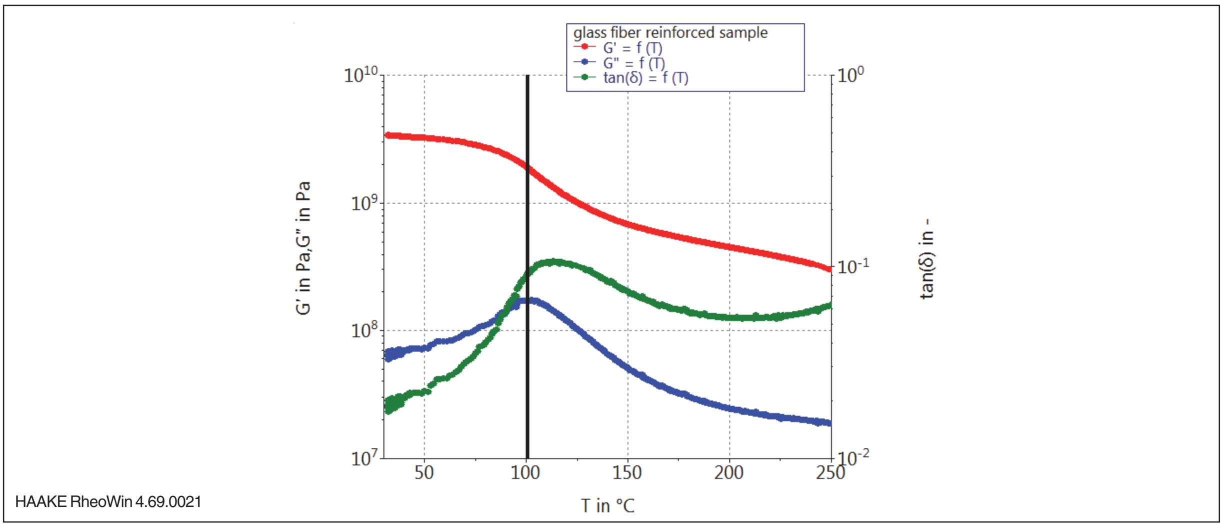

Fig. 5: Storage Modulus G' (red), Loss Modulus G" (blue) and tan(δ) (green) as a function of temperature for a glass fibre enforced PPS sample. The glass transition temperature TG is indicated by the black line.

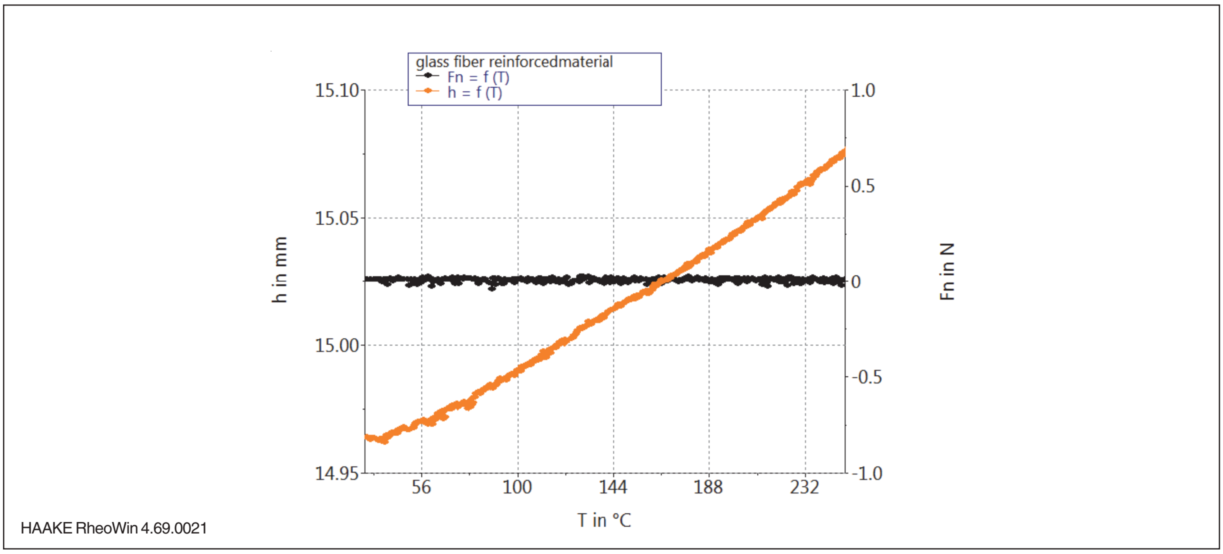

Fig. 6: Constant normal force (black) and increasing sample length (orange) during a temperature increase from 30 °C to 250 °C on one of the glass fibre enforced PPS samples.

Summary

The special design of the HAAKE MARS' solids clamping tool 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 for example the calculation of the sample's thermal expansion coefficient.

With its Controlled Test Chamber and its solids clamping tool, 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 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.

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

Sentmanat Extensional Rheometer (SER) for the Thermo Scientific HAAKE MARS

Cornelia Küchenmeister-Lehrheuer and Fabian Meyer Thermo Fisher Scientific, Karlsruhe, Germany

Product information P019

Key words
Thermo Scientific HAAKE MARS, Controlled Test Chamber, Extensional Rheology, Solid Tensile Testing

The SER3 fixture is available for the Thermo Scientific™ HAAKE™ MARS™ rheometers in combination with the controlled test chamber (CTC). It transforms the (rotational) shear rheometer in an extensional rheometer for melts and semi-solids.

The measuring principle of the SER fixture, which was developed by Dr. Martin Sentmanat (Xpansion Instruments), is based on two counter rotating windup drums, which are applying an extensional deformation to an attached specimen. With the SER system a uniform uniaxial extensional deformation of the sample is achieved. In additional to the measurement of extensional viscosity, the SER tool can be used for solid tensile testing, tear and peel testing, as well as friction testing.

The drums are removable for easy cleaning or drum exchange. Different drums are available on request. The operating temperature range of the SER tool covers 0 °C to 315 °C. The combination of convection and radiation heating in the CTC guarantees fast temperature changes and an even temperature distribution within the sample. During sample loading the CTC can be moved into a closed parking position where the test temperature is maintained. After closing the heated CTC around the loaded SER tool, the sample reaches the test temperature more rapidly.

The SER system is fully integrated in the Thermo Scientific™ HAAKE™ RheoWin™ measuring and evaluation software.

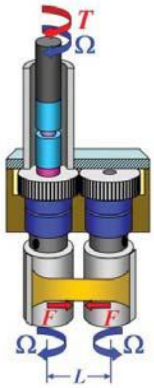

Fig.2: Schematic setup of the SER tool (image taken from: http://www.xinst.com/products_specs.htm).

Fig.1: SER3 tool with HAAKE MARS rheometer and Controlled Test Chamber (CTC).

Measurements can be made in both controlled extensional rate and controlled tensile stress mode. The extensional properties of the sample are calculated automatically and presented directly in the software.

Figure 3 shows the results of measurements on branched LDPE performed with a MARS rheometer and the SER tool. All tests were performed at 150 °C. Depending on the extensional rate strain hardening occurs at different times. The data is compared with the transient shear viscosity obtain from a shear experiment with a cone & plate geometry (red curve).

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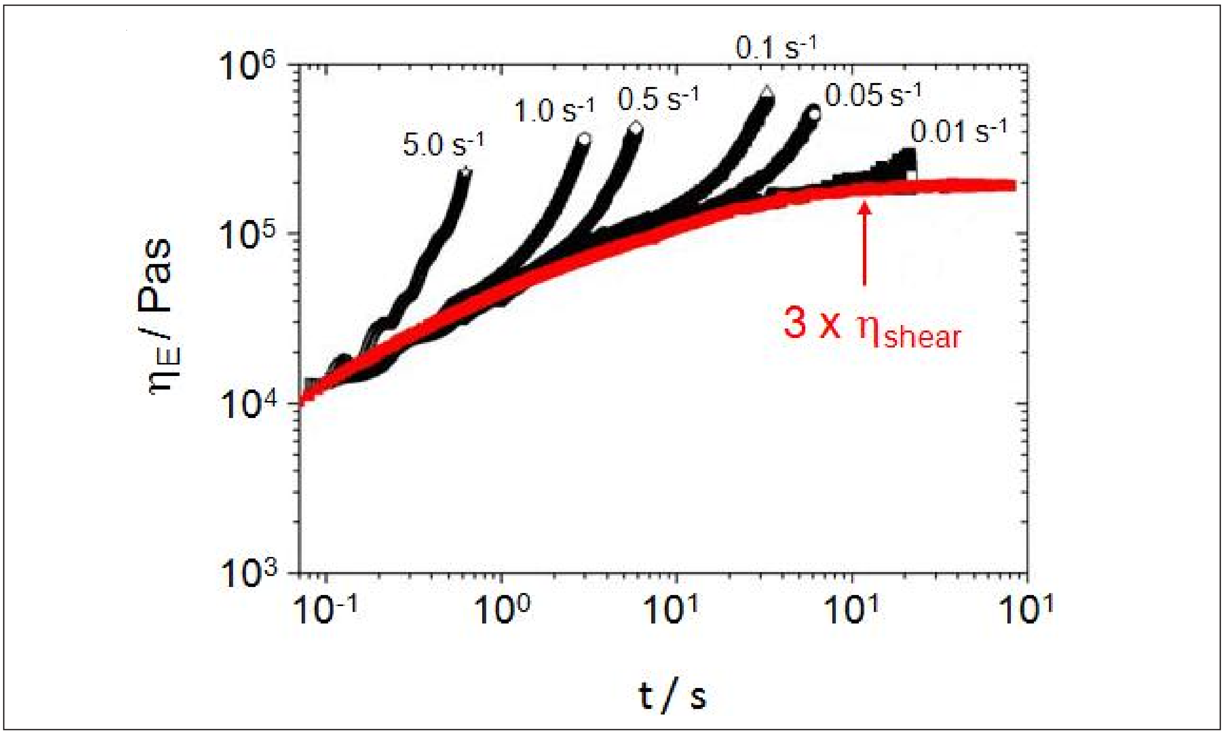

Fig. 3: Extensional viscosity as a function of time for branched LDPE at different extensional rates.

Order information

The extensional rheology fixtures for the HAAKE MARS rheometers are consisting of the SER system from Xpansion Instruments with a corresponding adapter for the following models:

222-1935 for HAAKE MARS II
222-1803 for HAAKE MARS I/III
222-1803 for HAAKE MARS 40/60 with “Connect Assist“
603-1205 Triangular base plate with lower holder and Pt100 sensor as accessory for SER tool (for all HAAKE MARS models)

Specification SER - Extensional Rheology System	
Max. recommended Hencky strain rate	20 s^{-1}
Max. Hencky strain per drum revolution	4
Operating temperature	0 °C - 300 °C
Wind-up drum diameter	10.31 mm
Stretch zone gage length	12.72 mm
Specification sample	
Min. shear viscosity in extension mode	10000 Pas
Sample mass	5 mg - 200 mg
Recommended sample width	1 mm - 12.7 mm
Recommended sample thickness	0.05 mm - 1 mm

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Characterizing long-chain Branching in Polyethylene with Extensional Rheology

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Key words
Extensional viscosity, SER tool, polyethylene, branching

Introduction

Polyethylene is a partly crystalline thermoplastic polymer frequently used for packaging such as plastic bags or films. Polyethylene exists in different structural types that differ mainly in terms of their branching structure. The degree of branching along the main chain determines the mechanical properties significantly, since the degree of crystallization, amongst others, depends strongly on it. The branching structure can also affect the melt viscosity of a polyehtylene usually leading to higher values for materials with more long side chains.

Polyethylene melts are usually characterized by means of small amplitude oscillatory shear (SAOS), as this mode of deformation can be applied easily on a rotational rheometer like the Thermo Scientific™ HAAKE™ MARS™ instruments. However, many technical processes such as blow molding or fiber spinning are dominated by extensional rather than shear deformation.

Thus measuring the extensional behavior of a polymer melt yields important information not only for optimizing processing steps, but also for establishing structure property relationships. This information is usually not available from the results of SAOS or steady shear measurements. Experiments with extensional deformation are needed together with SAOS and steady shear to obtain a complete picture of a samples rheological behavior.

One of the main goals of extensional testing is to probe for the strain hardening behavior, or in other words the increase of the extensional viscosity in dependence of the applied extensional strain rate. This strain hardening is mainly dominated by long-chain branching, where a higher degree of branching usually leads to a more pronounced increase in extensional viscosity.

In this application note the results of extensional tests performed on a highly branched low density polyethylene (LDPE) and a weakly branched high density polyethylene (HDPE) are presented and discussed. Furthermore details of the measurement procedure are provided.

Materials and Methods

To characterize the extensional behavior of two differently branched polyethylene samples the HAAKE MARS rotational rheometer was used together with the SER (Sentmanat Extensional Rheometer) tool for extensional testing of films.

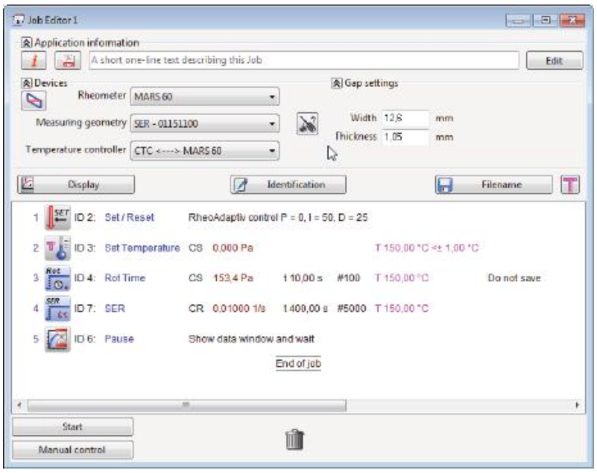
Fig. 1: Controlled Temperature Chamber (CTC) of the HAAKE MARS with the SER.

The testing principle of the SER tool is based on two counter rotating drums to which a rectangular specimen is attached by a clamping mechanism [1]. As both drums rotate with the same speed in inverse directions, the deformation field applied is a purely uniaxial one. More information about the SER tool for the HAAKE MARS rheometers can be found in Reference [2]. Fig. 1 shows the SER tool mounted to a HAAKE MARS rheometer.

For temperature control the rheometer was equipped with a controlled tests chamber (CTC) which combines forced convection and heat radiation techniques and therefore enables fast temperature changes and a homogeneous temperature distribution within the chamber. More information about the CTC can be found in Reference [3] .

All tests were performed at a temperature of 150 °C. The temperature was measured with a Pt100 sensor that is located close to the sample. The melting process and the general state of the sample can be monitored visually via two glass windows in the respective CTC halves.

Before one can start with the extensional experiments, it is important to determine the internal friction of the SER tool itself with a rotational test procedure. Details about the exact setup of the calibration procedure can be found in the SER tool instruction manual. The so determined torque needs to be subtracted from the torque signal during the experiment to obtain correct results. This is achieved by implementing this torque in the torque correction factor of the SER in the Device Manager of the Thermo Scientific™ HAAKE™ RheoWin™ software. The polyethylene specimens were deformed with the SER tool at different extensional rates. To do this, the sample has to be attached carefully to the drums of the SER tool using a clamp mechanism. The test itself was then conducted with HAAKE RheoWin via the routine that can be seen in Fig. 2. After the sample has reached 150 °C and the temperature was held constant for 5 minutes, the sample was pre-stretched at a constant stress (153 Pa for LDPE) for 10 seconds to counteract any gravitation induced sagging as well as ensure that the gearbox of the SER tool is in a pre-stressed state at the beginning of the test. In the actual extensional experiment (element 4 in Fig. 2) the drums rotated at a defined strain rate until the deflection angle reached a value of 230 °. At higher deflection angle the clamps may touch if the tested specimen exceeds a certain thickness. The experiments were conducted at strain rates of 0.01 s^{-1}, 0.05 s^{-1}, 0.1 s^{-1}, 0.5 s^{-1}, 1.0 s^{-1} and 5.0 s^{-1}.



A short one-line text describing this Job

Rheometer: MARS 60
Measuring geometry: SER - 01151100
Temperature controller: CTC <---> MARS 60
Width: 12,6 mm
Thickness: 1,05 mm

```
1  ID 2:  Set / Reset        RheoAdaptiv control P = 0, I = 50, D = 25
2  ID 3:  Set Temperature    CS  0,000 Pa                              T 150,00 °C <± 1,00 °C
3  ID 4:  Rot Time           CS  153,4 Pa     t 10,00 s    #100    T 150,00 °C       Do not save
4  ID 7:  SER                CR  0,01000 1/s  t 400,00 s   #5000   T 150,00 °C
5  ID 6:  Pause              Show data window and wait
                             End of job
```

Fig. 2: Measuring routine to characterize the extensional behavior of Polyethylene, comprised of the following elements:
1. RheoAdaptiv-Control, 2. Temperature Control, 3. Pre-stretch of the sample, 4. Extensional Test.

Results and Discussion

Fig. 3 shows the results of several extensional experiments with HDPE performed at different extensional strain rates. The extensional viscosity η_E is plotted versus the experimental time. For comparison the linear viscoelastic response, represented by three times the shear viscosity is also displayed in the same plot. The transient shear viscosity was obtained by rotational experiments using a cone & plate setup. The factor three derives from the Trouton ratio for uniaxial flow [4]. As can be seen in Fig. 3, the linear HDPE does not show any deviation from the linear viscoelastic response and therefore no strain hardening, even at highest extensional strain rates. The branches, if any are present, are so small that they don't influence the result, meaning that only the molecular weight effect can be monitored. In contrast to that the LDPE (Fig. 4) shows a clear deviation from the linear viscoelastic behavior and dramatic strain hardening effects. The onset of strain hardening is shifted towards longer experimental times with decreasing extensional rate. However, when comparing the results for both polyethylenes, it can also be observed, that the overall extensional viscosity before the onset of strain hardening, is lower for a HDPE of the same molecular weight. This is due to the decreased coil size in the melt, resulting in a lower number of entanglements. The characteristics seen in extensional tests can be used to model certain processing steps like for instance blow-molding or foil production. In addition to that, the extensional viscosity can be used for sample identification and thus for quality control applications.

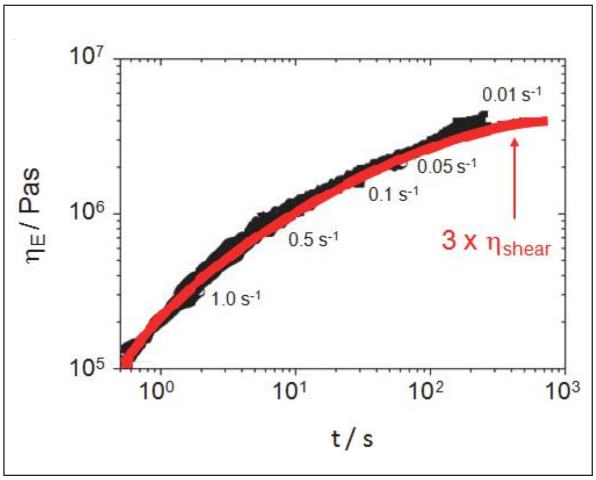


Fig. 3: Extensional viscosity as a function of strain rate for non-branched HDPE.

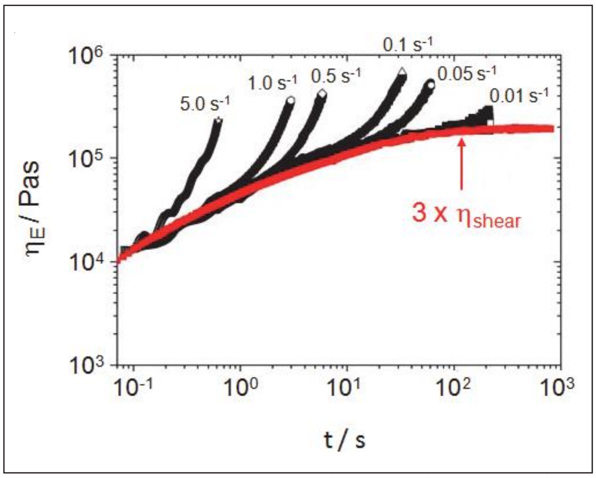


Fig. 4: Extensional viscosity as a function of strain rate for highly branched LDPE.

References

[1] Sentmanat, M. L., Miniature universal testing platform from extensional melt rheology to solid state deformation behavior, Reol. Acta43, 657-669, 2004

[2] Küchenmeister-Lehrheuer, C., Meyer F., Sentmanat Extensional Rheometer (SER) for Thermo Scientific HAAKE MARS,
Thermo Scientific Product information P019

[3] Küchenmeister-Lehrheuer, C., Meyer F., Controlled Test Chamber (CTC) for Thermo Scientific HAAKE MARS Rheometers,
Thermo Scientific Product information P057

[4] Trouton, F.T., On the coefficient of viscous traction and its relation to that of viscosity Proc. Roy. Soc., A77 426-440, 1906

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Material Characterization

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Rheological Measurements with the new Thermo Scientific HAAKE MiniLab 3 and their correlation with dynamic oscillation data

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Thermo Fisher Scientific, Karlsruhe, Material Characterization, Germany

Introduction

The Thermo Scientific™ HAAKE™ MiniLab Series is well known for being the ideal equipment, if it comes to compounding and processing of very small sample quantities of just about 7 ml.

The HAAKE MiniLab 3 is a small conical twin screw extruder, equipped with a back flow channel and a bypass valve, which allows to control the residence time of the sample in the compounder.

The patented design of the back flow channel has a slit-capillary flow channel and two pressure transducers, which are used to measure the pressure drop in the capillary. From the pressure drop and the geometry of the slit capillary, a shear stress can be calculated. From the selected screw speed and the measured back pressure, a shear rate is correlated. The shear stress and the shear rate values are used to calculate the relative sample viscosity at different screw speeds.

This lab report shows the correlation between the relative viscosity measurements done on the new HAAKE MiniLab 3, with results of absolute rheological measurements performed with a Thermo Scientific™ HAAKE™ MARS™ 60 rotational rheometer.

Materials & Sample Preparation

For this study two different LDPE grades (Lupolen 1800H and Lupolen 1800S from LyondellBasell) have been mixed in different ratios.

To have a consistent sample preparation and homogenous product, all samples have been pre-compounded on a Thermo Scientific™ Process 11 Twin-Screw Extruder.

Table 1: Compounding of the samples.

No.	Sample	Compounding
Sample 1	"LDPE1800 H"	100% Lupolen 1800H
Sample 2	"LDPE1800 H2S1"	66% Lupolen 1800H + 34% Lupolen 1800S
Sample 3	"LDPE1800 H1S1"	50% Lupolen 1800H + 50% Lupolen 1800S
Sample 4	"LDPE1800 H1S2"	34% Lupolen 1800H + 66% Lupolen 1800S
Sample 5	"LDPE1800 S"	100% Lupolen 1800S

Testing Equipment

a) HAAKE MiniLab 3 with pneumatic ram feeder
Set of co- rotating screws
Software: Thermo Scientific™ HAAKE™ PolySoft OS for MiniLab
N_2 purge

Fig. 1: The Thermo Scientific HAAKE MiniLab 3.

b) HAAKE MARS 60 rotational rheometer
20 mm parallel plates measuring geometry
Controlled Test Chamber (CTC) for temperature control
N_2 purge

Test Conditions & Test Procedure

Extruder

Sample Weight: 6.5 g
Testing Temperature: 190°C
Inert Gas: N_2 purge
Feeding Speed: 50 rpm
Testing Speed: Speed program from 50 rpm to 350 rpm (controlled via the HAAKE PolySoft OS Software)

Rheometer

Testing temperature: 190 °C
Testing mode: Frequency sweep in controlled deformation (CD) mode
Frequency range: 0.1 - 628 rad/s
Deformation: 1%

After a preheating time of about 10 minutes the pressure transducers of the MiniLab have to be calibrated at the selected measuring temperature, to avoid any temperature effect on the pressure measurement.

The pneumatic feeding piston and the extruder barrel are constantly purged by a constant Nitrogen flow, to avoid the presence of oxygen during the tests, and prevent degradation of the LDPE samples.

The sample is then feed into the running extruder by means of the pneumatic feeding piston.

After 1-2 minutes the extrusion pressure is getting equilibrated, what indicates that the sample is properly molten and ready for the rheological test.

The rheological test itself is performed and controlled by the HAAKE PolySoft OS Software. The software runs the pre-programmed measuring steps (Fig. 2), checks when steady state conditions are reached and then measures the pressure drop between the pressure transducers in the slit capillary channel to calculate the shear stress.

Results Rheological Tests - HAAKE MiniLab 3

The result of two rheological tests with Sample 1 („LDPE1800 H“) can be seen in Fig. 3.

Each measuring point of the flow curve corresponds to one screw speed on the MiniLab compounder. With increasing shear rate the viscosity is decreasing, due to the typical shear-thinning behavior of polymer melts.

It can also be observed, that the viscosity curves of two independent tests are nearly identical, which proves the very good repeatability of the test method.

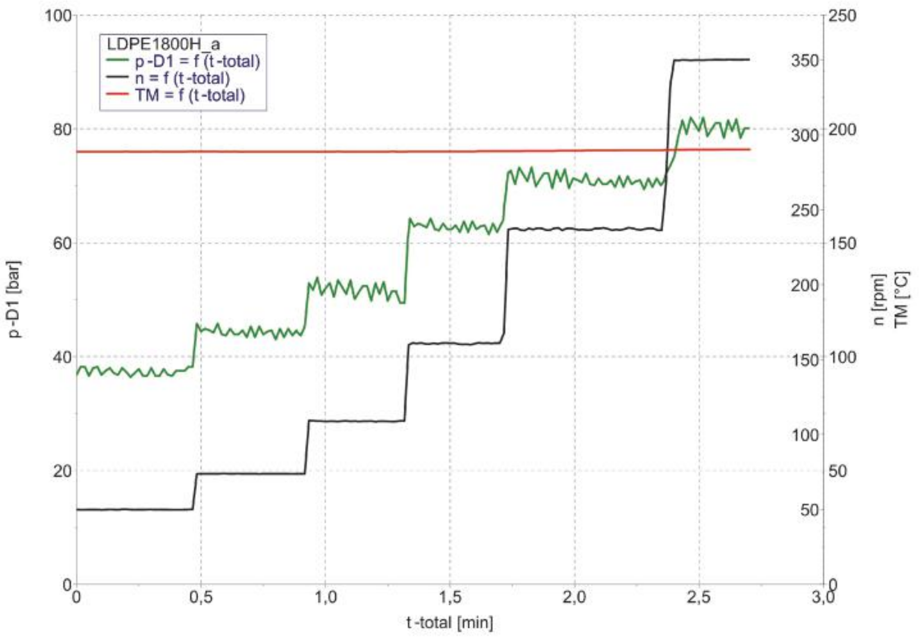

Fig. 2: Pressure drops in slit capillary of HAAKE MiniLab 3 at different rotational speeds.

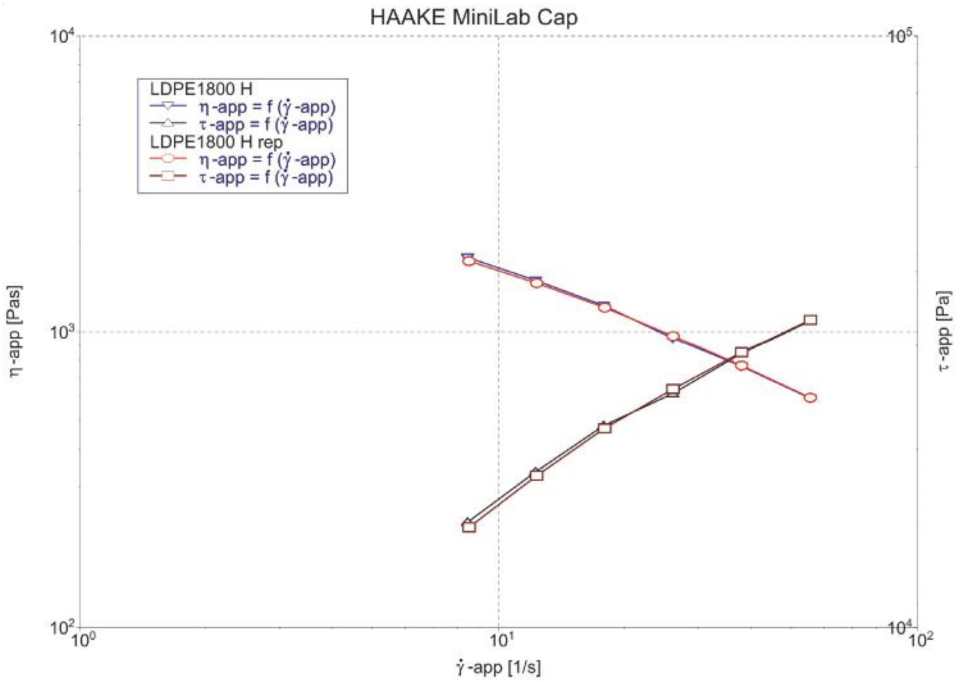

Fig. 3: Apparent viscosity $\eta_{\alpha\pi\pi}$ and apparent shear stress $\tau_{\alpha\pi\pi}$ as a function of the apparent shear rate for low density polyethylene. The results of two independent runs with the same polymer are presented.

Fig. 4 shows the results of the rheological measurements performed with all five compounded samples in one diagram. It nicely can be seen how the sample viscosity is dropping with the increasing content of LDPE1800S and the decreasing amount of LDPE1800H in the compound.

Relative Measurement vs. absolute Measurement

Of course it is very interesting how the relative tests results generated on the HAAKE MiniLab 3 correlate with the results obtained an absolute rotational rheometer.
To check this, one of the compounds (Sample 3 “LDPE1800 H1S1“) was tested in an oscillatory frequency sweep experiment on a HAAKE MARS 60 rheometer.
For the comparison of the tests with the HAAKE MiniLab and the HAAKE MARS Rheometer the rule of Cox-Merz relation is applied.

Empirically the two scientists who gave this relation their name found that the steady-shear viscosity measured as function of shear rate could be directly compared to the dynamic complex viscosity measured as a function of angular velocity:

$$|\eta*|\,(\omega) = \eta(\dot{\gamma}) \rightarrow \omega = \dot{\gamma}$$

This relationship was found to be valid for many polymer melts and polymer solutions, but it rarely gives reasonable results for suspensions. The advantage of this Cox-Merz relation is that it is technically simpler to work with frequencies than with shear rates. Most of the time polymer melts cannot be measured at shear rates not higher than 50 1/s in a rotational rheometer with open systems such as cone & plate or parallel plate due to the elastic effects encountered. Thus instead of measuring a flow curve in steady-state shear, one can more easily use the complex viscosity of dynamic testing [1].

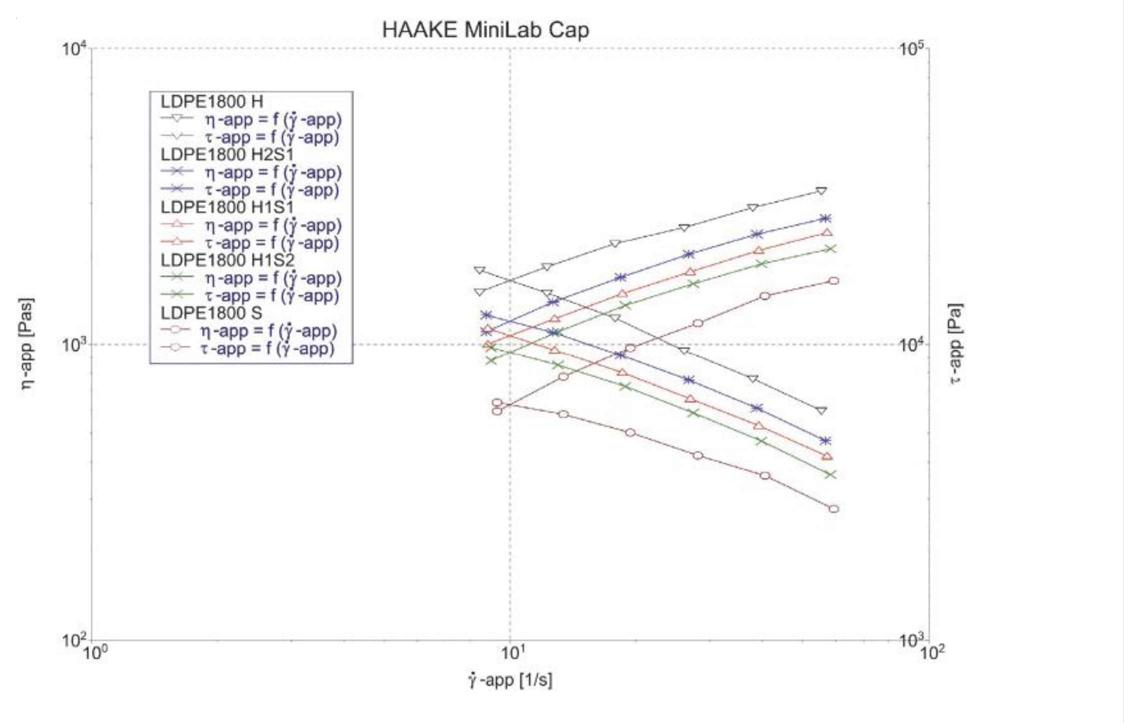

Fig. 4: Flow and viscosity curves for all compounds.

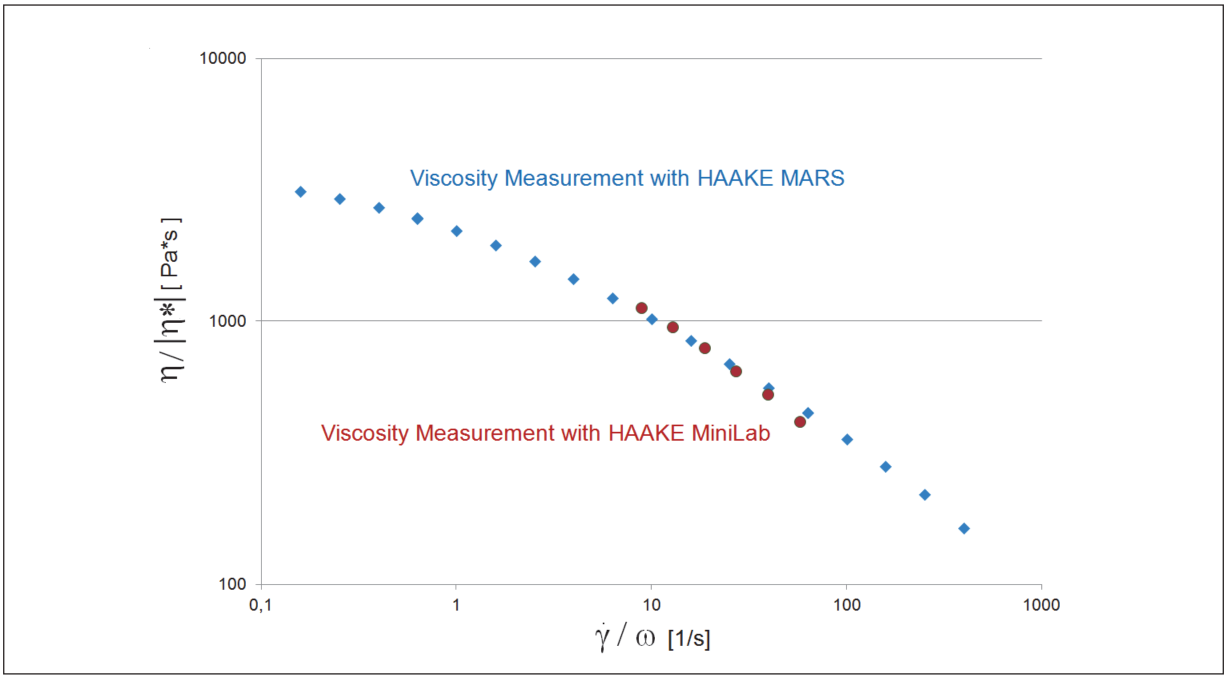

Fig. 5: Comparison of viscosity data obtained from measurement with HAAKE MiniLab 3 extruder and HAAKE MARS rheometer.

Conclusion

Fig. 5 shows nicely how the relative viscosity measurement performed on a HAAKE MiniLab compounder correlates with the absolute data obtained from a high end rotational rheometer.

As the experiment could prove, measuring the change in flow behavior using pressure sensors in the slit capillary channel eliminates possible influences from screw forces and thus delivers reliable rheological information.

Measuring the rheological data directly during compounding has a two-fold advantage to the researcher. First of all it safes time when the measuring takes place directly in the extruder and also sample preparation can be neglected. But also structural changes within the sample that occur during compounding can be observed directly and thus delivers valuable process information on the spot.

The HAAKE MiniLab 3 is collecting the rheological data under process conditions. When a broader measuring range is required the HAAKE MARS rheometer is a perfect complementary extension of the experimental setup.

Fig. 6: The Thermo Scientific HAAKE MiniLab 3.

Literature

[1] Schramm, Gebhard / A Practical Approach to Rheology and Rheometry, 2nd Edition, Karlsruhe 2004, p. 124.

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Spectroscopical insight into rheology with the Rheonaut module for Thermo Scientific HAAKE MARS Rheometers

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Manfred Feustel, Resultec Analytic Equipment, Illerkirchberg, Germany

Key words
Rheonaut, Thermo Scientific HAAKE MARS, Parallel plates and cone & plate measuring geometries, FT-IR spectroscopy, ATR principle, Hyphenated methods

The Rheonaut[*] is a compact module to investigate structural changes on a molecular level by FT-IR spectroscopy available exclusively for the Thermo Scientific™ HAAKE™ MARS™ rheometers. The patented[**] module couples a standard FT-IR spectrometer with a rotational rheometer and allows for simultaneous spectroscopic and rheological experiments. Suitable spectrometer models are e.g. the Thermo Scientific™ Nicolet™ iS™ 10 or iS™ 50.
The Rheonaut module is designed for parallel plates and cone & plate measuring geometries and allows for performing all rheological testing methods available for the HAAKE MARS rheometers. The Rheonaut module provides the lower stationary plate for the rheological experiments and includes a monolithic diamond that serves as the optical element using the ATR (attenuated total reflection) principle. Compared to standard infrared transmission or specular reflection spectroscopy, with the ATR technique, the sample thickness can be adjusted to the rheological needs and is independent from any IR requirements. Accordingly, all available plate or cone rotors up to a diameter of 60 mm can be used with the Rheonaut module.

The Rheonaut module can be operated at two different temperature ranges to guarantee a homogeneous temperature distribution as well as for temperature-dependent tests such as thermal curing reactions. A Peltier temperature control unit (0 °C up to 120 °C, optional extendable down to -20 °C, Fig. 3) and an electrical unit for temperatures from ambient up to 400 °C are available. For higher temperatures an electrical upper temperature module TM-EL-H is recommended.

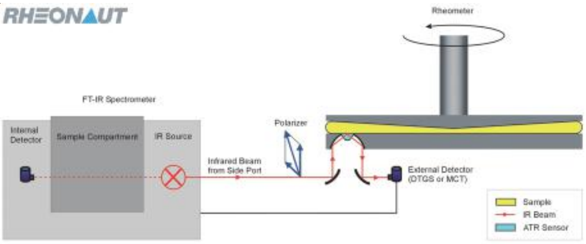

Fig. 2: Scheme of the Rheonaut module.

Fig. 1: Setup with HAAKE MARS rheometer, Rheonaut module and FT-IR spectrometer.

For spectrometer control during the experiment as well as spectra evaluation the corresponding spectrometer software is used. For selected spectrometer models[***] the Thermo Scientific™ HAAKE™ Rheowin™ software allows for triggering the spectrometer software to guarantee a simultaneous start of spectroscopic and rheological data acquisition and for measuring an equal number of FT-IR spectra and rheological data points in synchrony. Furthermore the lower plate can be moved via software control.
Several wire grid polarizers are optionally available (Fig. 4) to set the polarization direction for the infrared radiation both parallel and perpendicular to a fixed reference direction.
One of the main uses of infrared polarizers is to monitor molecular orientation in polymer samples. To accomplish this, polarizing devices split unpolarized (natural) light into two orthogonal components; one of the linearly polarized components is transmitted, the other is reflected, redirected or absorbed. The polarized light component coinciding with the dipole of the infrared active moiety increases in absorption intensity, thereby revealing the band assignment and the orientation of the molecular group.

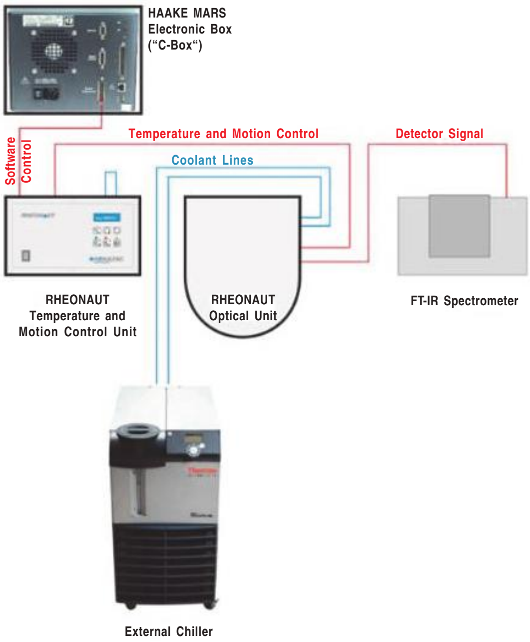

Fig. 3: Peltier temperature module for Rheonaut with extended temperature range down to -20 °C.

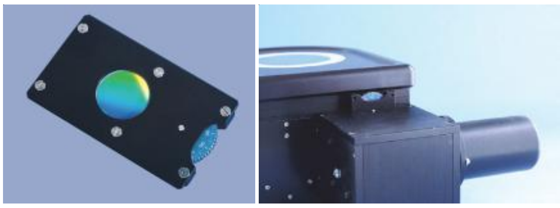

Fig. 4: Example of a manual polarizer, left: content of delivery, right: build-in.

The Rheonaut technology enables a new level of understanding of rheological properties and processes, which depend on changes on the molecular structure. On the one hand, deformations and orientations of molecules as function of shear can be monitored. On the other hand the in-situ-spectroscopy enables the investigation of chemical reactions in the measuring gap such as chemical or thermal curing of polyurethane (PU)- or epoxy- adhesives.

Order information

The Rheonaut module consists of an optical unit (ready to enable purging) with integrated detector with preamplifier, temperature control unit and a HAKE MARS frame extension for connecting a commercially FT-IR spectrometer.

Necessary accessories

- Rheonaut unit with support chassis for FT-IR spectrometer****
- FT-IR detector (DTGS or MCT, preinstalled in Rheonaut module)
- Temperature Controller
- Lower plate with Peltier or electrical heating
- HAAKE Rheowin FT-IR control software module (for Rheonaut control and spectrometer software trigger)
- FT-IR spectrometer with side port (e.g. Thermo Schientific Nicolet iS10 or iS50)
- HAAKE MARS 40 or 60 rotational rheometer
- Cone or plate rotor for HAAKE MARS

603-0600 Rheonaut module incl. frame extension for e.g. Nicolet iS10 (603-0751) or iS50 (603-0754)
603-0601 Lower ATR plate (exchangeable), electrical controlled heating
603-0604 Lower ATR plate (exchangeable), Peltier controlled heating and cooling
222-2172 Electrical temperature module TM-EL-H for upper geometries for HAAKE MARS 40 & 60 for temperatures up to 400 °C, holder 222-1902 and safety ring 222-2271 required
603-0607 DTGS detector
603-0606 MCT detector, for fast spectra acquisition trigger box 603-0886 required
098-5061 FT-IR spectroscopy tool for HAAKE RheoWin software

Manual Polarizers
603-2130 ZnSe: Spectral range cutoff at 450 Wavenumber. For standard applications.
603-2131 KRS-5: Spectral range cutoff at 200 Wavenumber. For applications which require an extended spectral range, e.g. inorganics.
603-2132 Ge: Spectral range cutoff at 570 Wavenumber. For precision applications which require a very high polarization efficiency.

Rotors with "Connect Assist" and ceramic shaft, e.g.
222-2063 Rotor P60/Ti
222-2089 P35/Ti

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*Developed by Resultec Analytic Equipment
**Patent numbers: DE 10140711, EP 02762251, US 6988393, JP 4028484
***Thermo Scientific spectrometer models Nicolet iS10, iS50 and 6700; Bruker spectrometer models Vector, Vertex and Tensor
****Depending on spectrometer model and manufacturer

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Curing of an Acrylate Glue – Rheology with Simultaneous FT-IR Spectroscopy

Klaus Oldörp, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Introduction

Everybody who has ever worked with glues knows that timing is one of the crucial issues. Subsequently technical leaflets for glues sometimes look like timetables. Terms like pot life, open time, time for minor adjustments, curing time or time to reach maximum bonding strength, are used to describe the properties of glues and to give guidance for their successful application.

For the development of new glues all these times have to fit the application to create a product the market targeted will accept. For example, depending on the method to apply the glue the open time needs to be adjusted to avoid curing before the parts have been joined.

A rheometer is an essential tool to characterise not only the uncured glue but especially the curing process itself. No matter if a drying glue, a 2 component system, a thermally curing glue, or a UV-curing glue is investigated, due to their wide range of accessories the Thermo Scientific™ HAAKE™ MARS™ rheometers are the perfect tools to characterize curing behaviours.

Still, the classical limitation of rheological methods remains: a rheometer can only tell us what happens during the curing but it does not tell us why. The “why“ becomes especially important when we want to understand why a batch of the glue shows other properties than the expected ones or when we want to develop glue for a new application. To overcome this limitation, the rheological data needs to be combined with data from another analytical method able to detect what happens on the molecular scale. A perfect match is the FT-IR spectroscopy, a method, which is able to identify and quantify different chemical groups in a substance or in a mixture of substances.

The disadvantage of running tests on two separate instruments is the extra effort it takes to prepare two different samples following different procedures for each method. Plus, as a consequence, this approach makes it virtually impossible to collect both sets of data on two identical samples under exactly the same conditions.

To combine rheological tests with FT-IR spectroscopy avoiding the aforementioned disadvantages, the Rheonaut module has been developed; a unique combination of a temperature control module for the HAAKE MARS rheometers and an Attenuated Total Reflection (ATR) cell with its own IR detector. With the Rheonaut module the HAAKE MARS can be combined with an FT-IR spectrometer to one analytical setup (Fig. 1). Only with this unique combination it is possible to record the mechanical changes of the curing glue while at the same time and, even more important, on the same sample IR spectra can be collected to track the chemical changes inside the sample.


Fig 1: Setup with HAAKE MARS rheometer, Rheonaut module* and FT-IR spectrometer.

Experimental

A consumer-grade 2 component acrylate glue was prepared by mixing both components outside the rheometer according to its technical leaflet. Part of this mixture was transferred into the rheometer.

When designing the test method, two important facts about curing materials have to be kept in mind:

1. The curing reaction starts already outside the rheometer. To be able to compare different datasets, the test method contains an element to reset the internal time at the moment the 2 components are started to be mixed (Fig. 2, step 3 and 4). Otherwise,any deviation in the loading procedure would lead to an undefined offset on the time axis.

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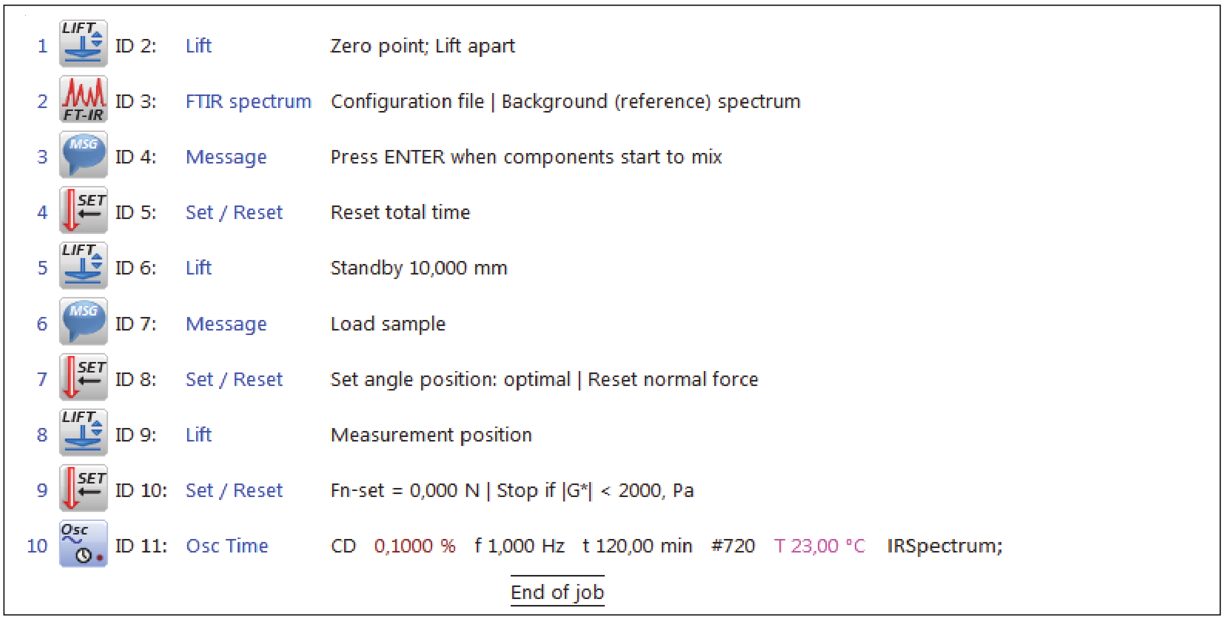
*Resultec developed the Rheonaut module for exclusive resale by Thermo Fisher Scientific.



1 ID 2: Lift Zero point; Lift apart
2 ID 3: FTIR spectrum Configuration file | Background (reference) spectrum
3 ID 4: Message Press ENTER when components start to mix
4 ID 5: Set / Reset Reset total time
5 ID 6: Lift Standby 10,000 mm
6 ID 7: Message Load sample
7 ID 8: Set / Reset Set angle position: optimal | Reset normal force
8 ID 9: Lift Measurement position
9 ID 10: Set / Reset Fn-set = 0,000 N | Stop if |G*| < 2000, Pa
10 ID 11: Osc Time CD 0,1000 % f 1,000 Hz t 120,00 min #720 T 23,00 °C IRSpectrum;
End of job

Fig. 2: Test method for 2 component glues in Thermo Scientific HAAKE RheoWin measuring and evaluation software. In step 3 and 4 the time is reset when the 2 components mix outside the rheometer. In step 5 the upper geometry moves to a 10 mm gap to minimize lift travel after the sample is put onto the lower plate. Step 8 moves the upper geometry to the measuring gap and step 10 starts the test without waiting for temperature equilibration.

2. The biggest changes happen during the first moments of the curing process. The test method has been optimized to start the test as quickly as possible after the sample was put onto the lower plate. The upper geometry is lowered to 10 mm before loading the sample to shorten the time to reach the measuring gap (Fig. 2, step 6). The test itself starts immediately after the measuring gap has been reached without any time for thermal or mechanical equilibration.

The rheological part of the test method is an oscillation time curve (Fig. 2, step 10) where the oscillation parameters are kept constant to detect only changes in the sample due to the curing. Since drastic changes of the moduli are expected during the test, the rheometer's controlled deformation (CD)-mode is used to ensure optimum signal quality throughout the whole test. A small amplitude within the sample's linear viscoelastic range (LVR) is selected, which still yields data with a good signal-to-noise-ratio from the uncured glue.

The evaluation can be based on the storage modulus G' representing the elastic part of the viscoelastic properties and the loss modulus G" representing the viscous part (Fig. 3).

The freshly prepared glue is mainly viscous, G" dominates over G' with phase angle (δ) values around 70° (purely viscous: δ = 90°, purely elastic: δ = 0°). The curing reaction proceeds quickly, after 3.2 min the crossover point where G" = G' or δ = 45° is reached. From this so-called gel time on, the glue behaves mainly elastic because a widemeshed network has developed throughout the sample. Joining and fixing the two parts to be glued together has to be done well before the gel time is reached. Otherwise any movement in the glue line is either not possible any more or would reduce the final bonding strength. After 10 min δ drops to 3° and G' reaches an almost constant value when the glue reaches its final strength. Although, strictly speaking, acrylate glues continue to cure at a slow rate, reaching their final strength after 12 – 24 h.

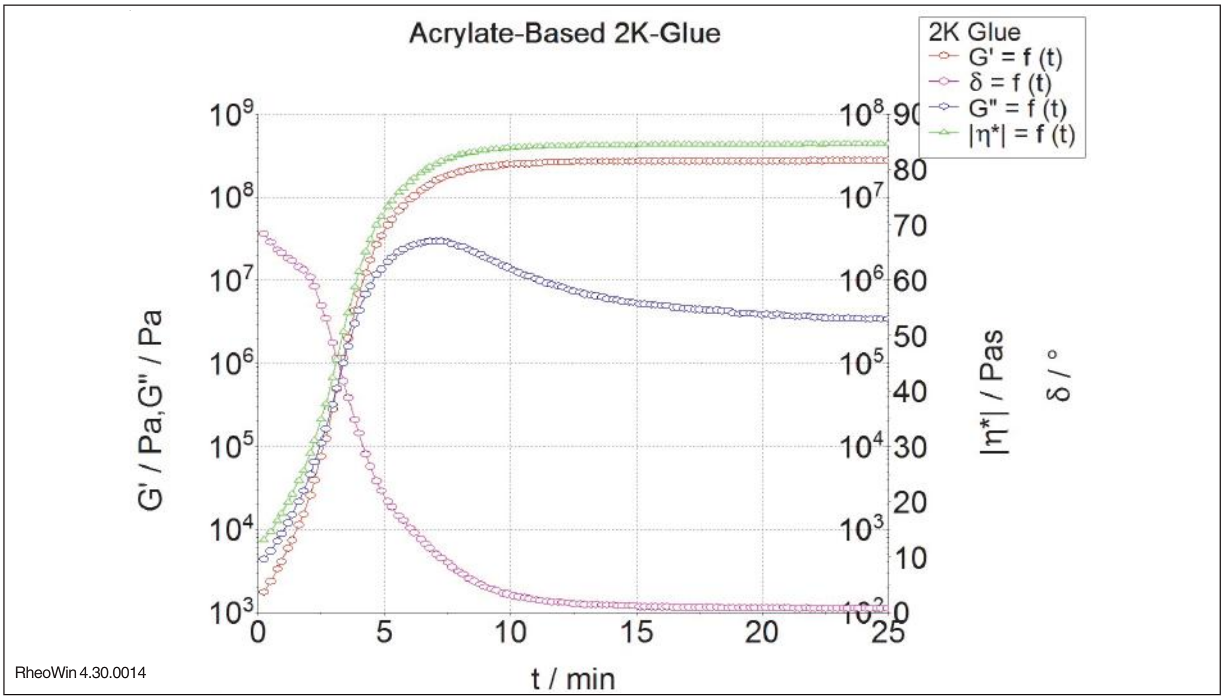


Fig. 3: Curing of an acrylate glue: development of the moduli G' and G", the complex viscosity |η*| and the phase angel d over time.

Simultaneously with the rheological data FT-IR spectra have been collected about every 13 s yielding 115 IR-spectra during the 25 min the rheological test lasted. The spectra show several characteristic signals, which can be correlated with the progress of the chemical reaction (Fig. 4). The signal at 1637 cm^{-1} for example is characteristic for the C=C-bond of the acrylate monomer. Its decrease over time illustrates the consummation of the monomer during the curing reaction. The signal at 1241 cm^{-1} on the other hand is, amongst others, characteristic for the O=C-O-C ester bond in the polymeric acrylate formed during the curing of the glue (Fig. 5).

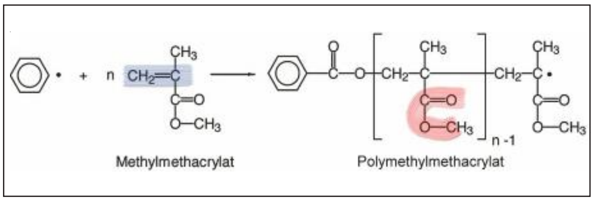


Fig. 4: Radical polymerization of Methylmethacrylate (MMA) to Polymethylmethacrylate (PMMA). Marked in blue: C=C-bond of the monomer, marked in red: ester bond in the polymer.

When G' reaches its plateau value after 10 min the decrease of the monomer slows down significantly due to the reduced mobility of the monomer in the solidifying glue. The increase of the ester bond in the polymer is also reduced but still continues with twice the speed of the monomer's decrease. This indicates that intramolecular processes are more important for the final curing stage compared to reactions of the free monomer, which dominated the initial part of the curing.

With this information it is possible to understand why the curing process runs the way it does. Subsequently a targeted approach to optimize a glue or to design a completely new formulation is now possible, knowing for example if it would be better to add more monomer or to increase the temperature to increase the mobility of the existing monomer.

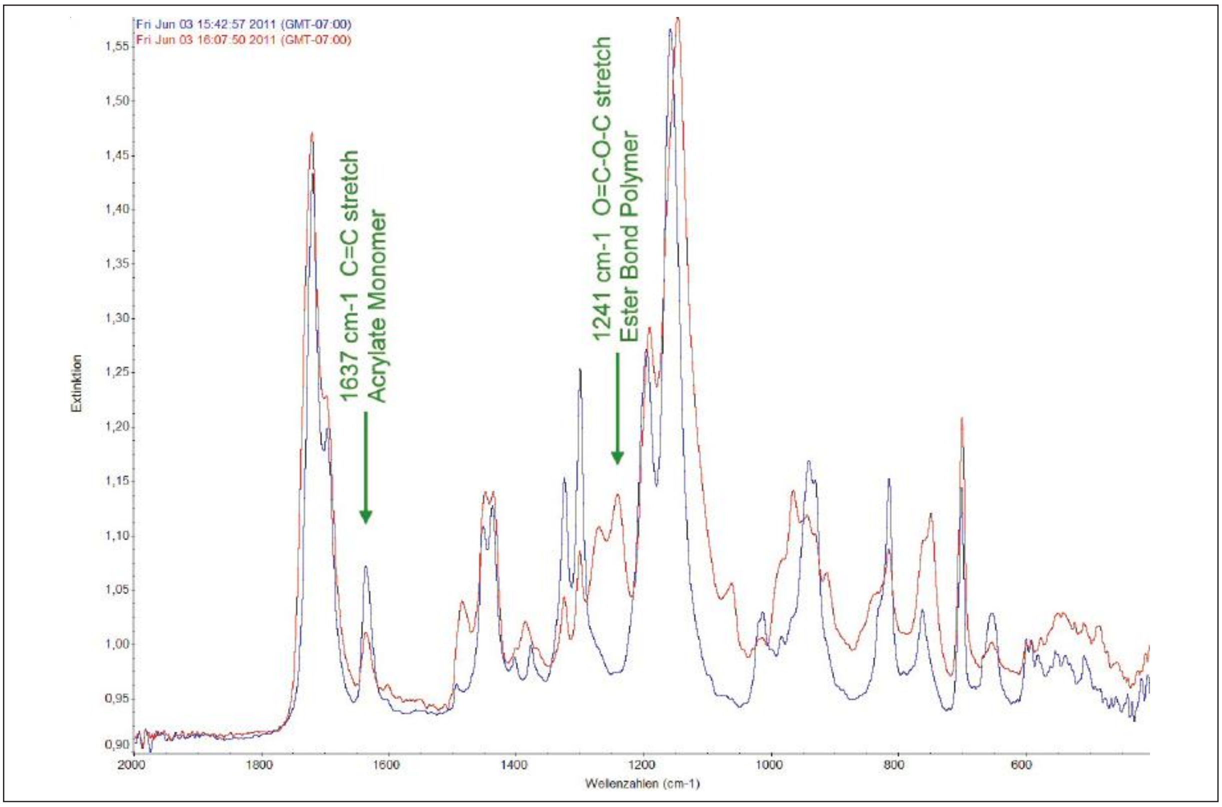


Fig. 5: First IR-spectrum (blue) and last IR-spectrum after 25 min (red) collected during the curing of an acrylate glue at 23 °C. The signal at 1637 cm^{-1} decreases over time while the signal at 1241 cm^{-1} increases.

The Thermo Scientific OMNIC software with its optional OMNIC Series add-on allows to line-up the spectra in chronological order in a 3D-graph and to evaluate how characteristic signals change during the time of the test (Fig. 6).

Cutting through the data set along the characteristic wavenumbers results in absorbance profiles, which show the changing amounts of the corresponding chemical groups in the sample.

Combining the rheological data with the spectroscopic profiles shows that the initial increase of the moduli corresponds with the decreasing amount of monomer (Fig. 7).

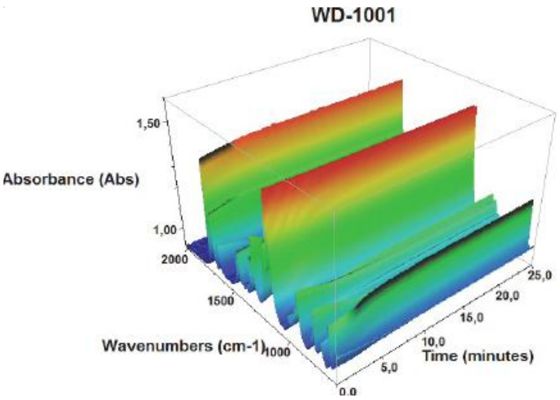


Fig. 6: 3D-Profile illustrating the time-dependant change of the IR-spectra collected during the curing of the sample in the rheometer, created with the OMNIC Series add-on.

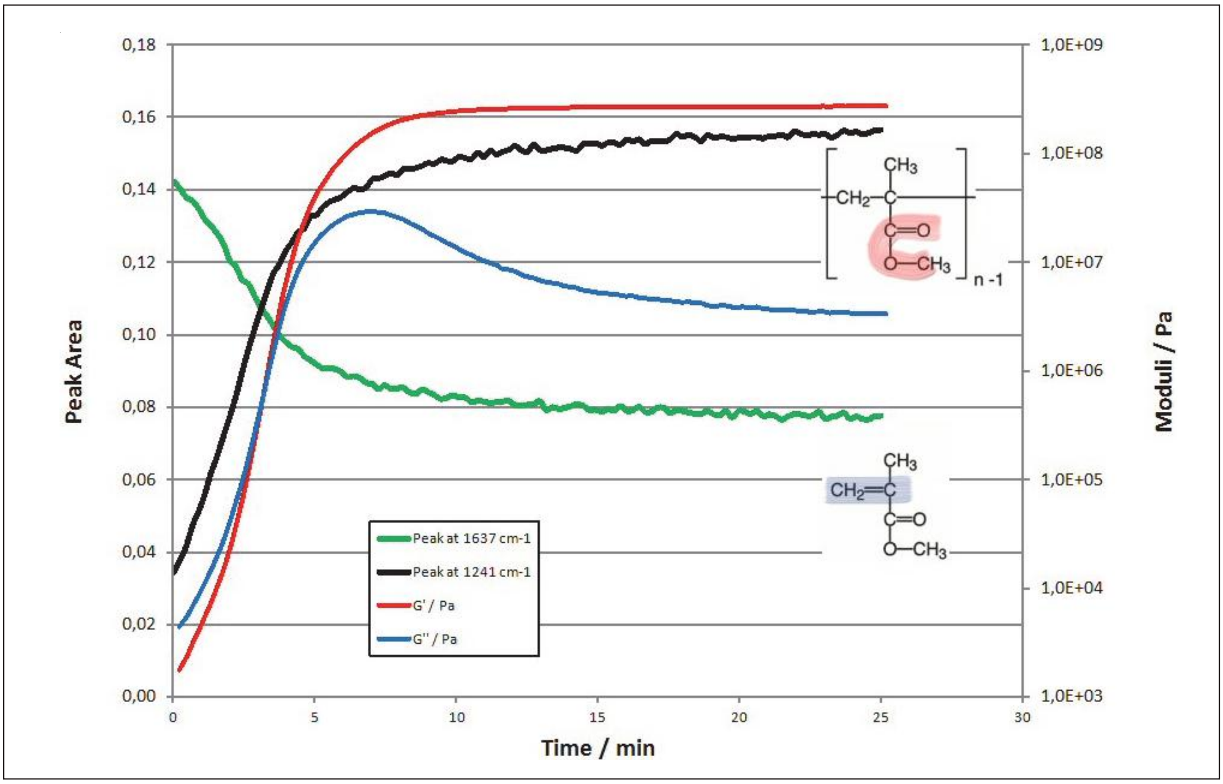


Fig. 7: Curing of the acrylate glue monitored with rheology and simultaneous FTIR. The increase of the sample's moduli (red and blue) corresponds with the decreasing signal of the monomer (green) and the increasing signal of the polymer's ester bond (black).

Summary

An oscillation time sweep is a well established method to characterize the curing of glues and similar curing materials. It shows the transition from the liquid to the solid state based on the mechanical properties of the glue. The rheological results can answer questions about the dosing and application properties of the liquid glue as well as the toughness of glue bond. The evaluation of the changing rheological properties gives the characteristic time spans like the pot life, the curing speed and the time to reach maximum strength of the bond.

Using the Rheonaut module the HAAKE MARS rheometer can be combined with an FT-IR spectrometer to simultaneously record on the same sample what happens during the curing process and why it happens on a molecular level. This reduces significantly the time for sample preparation and analysis and excludes any uncertainties due to different sample composition or sample treatment when running both analysis separately.

This unique combination of methods not only increases the quality of the data collected but also increases the time efficiency and cost efficiency of an analysis like the one described in this report.

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Simultaneous Rheology and Raman Spectroscopy: Tracking Molecular Structures as a Function of Stress, Strain and Temperature

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Key words
Thermo Scientific HAAKE MARS rheometer platform, Thermo Scientific Nicolet DXR Raman microscope, Hyphenated measuring method, RheoRaman module

The result of a rheological test tells us, how a substance behaves under a given stress or strain. What it does not tell us is the reason why, as rheology is a bulk method, only looking at the sample as a whole. However, to be able to fully understand the rheological behaviour of a given fluid, one needs additional information about the sample's micro- and/or molecular structure. This information can be supplied by an additional analytical method like i.e. microscopy, dielectrical analysis (DEA) as well as FT-IR and Raman spectroscopy.

Using the traditional approach, running two independent tests on two different samples bears the risk that due to the different ways of sample preparation or sample history in general, the test results are not comparable. This risk can be avoided by running both test methods on the same sample simultaneously using a combination of two analytical methods in one setup. Subsequently, the two resulting data sets can be correlated without any doubt, since they have been collected at the same time on the same sample. As an additional benefit, this approach saves a significant amount of time since only one sample has to be prepared and both tests run at the same time.

This product note focuses on the newly available coupling of a Thermo Scientific™ HAAKE™ MARS™ rheometer and a Thermo Scientific™ Nicolet™ DXR Raman microscope.

Rheometer: The Thermo Scientific™ HAAKE™ MARS™ rheometer can be equipped with a RheoRaman module for cone or plate geometries with a diameter up to 60 mm. This module is equipped with an integrated temperature module which can be used in a temperature range from -5 °C up to 300 °C. For temperatures above ambient, an active upper temperature control module is recommended (Fig. 1, 3).

Raman Microscope: The Thermo Scientific™ Nicolet™ DXR Raman microscope is used to collect Raman spectra with an excitation source of a depolarized 532 nm laser with 6 mW laser power at the sample (or 785 nm laser with 100 mW power at the sample). Exposure times varied between five and thirty seconds with three replicates.

Fig.1: Combination of a HAAKE MARS rheometer with RheoRaman module and adapted Nicolet DXR Raman microscope.

A 20x ultra long working distance Olympus lens integrated in the RheoRaman module is used to collect the 180° Raman back scattering.

Coupling: The Nicolet DXR Raman microscope is coupled with the HAAKE MARS rheometer by sending the external Raman beam from the microscope to the RheoRaman module. The 45° degree mirror placed inside the RheoRaman module directs the beam through the objective. The focus of the laser spot is controlled through the Thermo Scientific™ HAAKE™ RheoWin™ software. The rheological and Raman data collection are started simultaneously through the respective software (HAAKE Rheowin and Nicolet Omnic). The test results can then be exported to Excel to allow for a simultaneous display and subsequent analysis via the time stamps for each rheological data point and the corresponding spectrum (Fig. 2).

Typical applications for this kind of *in-situ* Raman and rheological measurements are the chemical analysis of polymers which allows for deep insights of molecular changes in real-time. These molecular changes include e.g. the formation or breaking of bonds and increase/decrease in crystalinity and ultimately add specificity capabilities to rheological measurements.

The technique can be applied to temperature dependent phenomena of emulsions as well as to gels, pastes and any given polymeric material.

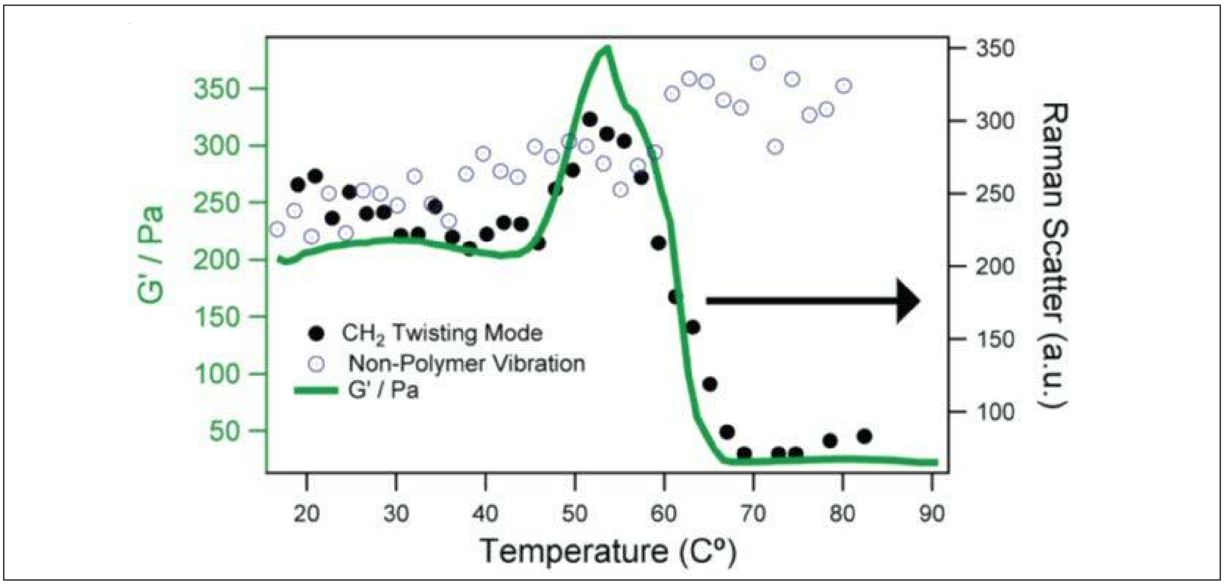

Fig. 2: Example of a RheoRaman data curve: Temperature-dependency of a polystearate described with the rheological moduli (storage modulus G' in green) as well as the simultaneously measured Raman intensity (CH2 twisting mode in black). Polystearate serves as an emulsifier in the polymer emulsion sample (hand cream). The stabilizing effect is most likely due to the strong adsorption on the interface which results from its amphiphilic, polymeric structure. The non-polymer vibration represents a component in the lotion with a Raman band at 450 cm^{-1}.

Fig.3: Detail view of HAAKE MARS Rheometer with RheoRaman module and upper temperature module TM-EL-H for high temperature application.

Order information

379-0600 HAAKE MARS Rheometer 60 (or alternative MARS model)*
222-2313 RheoRaman Module
222-1817 Lense with 20 time magnification
222-1812 Lower measuring plate with glass
222-2113 Cone C35/2° with ceramic shaft and “connect assist“ (or alternative rotor)

For high temperatures:
222-2172 Electrical temperature module TM-EL-H for upper geometries
222-1902 Holder for TM-EL-H
*Compressed air needed.

Necessary accessories

Nicolet DXR Raman microscope and related accessories

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Application Notes V-283

Tracking Polymer Crystallization with the Combination of a Rheometer and a Raman-Microscope

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Key words
Rheology, Raman Spectroscopy, Polymer Crystallization, Combined Methods

Introduction

The use of a coupled rheometer and Raman spectrometer for obtaining comprehensive insight into a materials behavior is presented in this application report.
Rheology is the analytical method of choice to correlate the absolute flow and deformation characteristics of a given product with its behavior towards a certain processing or application step. However, Rheology as an integral method only yields answers on the bulk of the investigated sample. It does not give any insights into what is actually happening on the molecular level during a certain processing step.
Raman spectroscopy has shown its ability as a powerful, effective and non-invasive method for chemical analysis. Coupling a rheometer with a Raman spectrometer provides direct information about the molecular structure and the mechanical properties. This is extremely useful for studying the crystallization behavior of polymer melts during processing. It can also provide insight for in-situ characterization and monitoring which can be challenging when working with on-line techniques as only relative flow fields are characterized.
In this application note, we present results obtained with the brand new combination of a Thermo Scientific™ HAAKE™ MARS™ rheometer with a Thermo Scientific™ DXR™ Raman spectrometer as shown in Fig. 1.

Results and Discussion

Melting and crystallization are two common phase transitions that are critical to the flow properties of various complex fluids. These temperature-sensitive transitions are often indicated via changes in molecular conformation, while optical measurements provide direct observation of structural characteristics. However, measurements performed on separate instruments are often challenging to correlate due to variations between samples, processing history, and temperature control. To demonstrate the capabilities of the RheoRaman microscope we provide simultaneous Raman, rheological, and optical measurements on high density polyethylene (SRM 1475, National Institute of Standards and Technology, Gaithersburg, MD) during crystallization.

Fig. 1: Combination of a Thermo Scientific HAAKE MARS with a Thermo Scientific DXR Raman Microscope.

The experimental setup shown in Fig. 1 represents a novel integration of commercial instrumentation: a Raman microscope (Thermo Scientific DXR Raman Microscope) and rotational rheometer (Thermo Scientific HAAKE MARS) are coupled through an optically transparent base modified from the Thermo Scientific™ RheoScope Module.
To monitor crystallinity one has to have a look at the Raman spectra for HDPE as shown in Fig. 2.

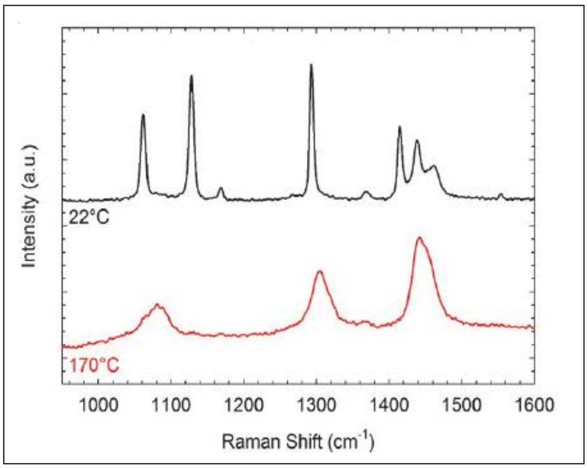

Fig. 2: Raman spectra of polyethylene at temperatures corresponding to the semi-crystalline state (22 °C) and the amorphous state (170 °C).

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The spectrum at room temperature shows sharp peaks corresponding to the C-C stretch, CH_2 twist, and CH_2 bend. At 170 °C HDPE is in the melt state, and the sharp peaks are replaced with broader spectral features.

The Raman spectra of HDPE can be analyzed to quantify the crystallinity of the sample. Specifically, the area under the peak at 1416 cm^{-1} in the HDPE spectra is directly proportional to the mass fraction of crystallinity in the sample. In order to calculate the crystallinity, the integrated peak area I_{1416} is normalized by the total area under the peaks in the CH_2 twist region and a scale factor N_c

$$\alpha_{cr} = \frac{I_{1416}}{\left(I_{1296} + I_{1303}\right) N_c} \quad . \tag{1}$$

The scale factor N_c is a ratio of $I_{1416}/(I_{1296} + I_{1303})$ for an HDPE sample to the crystallinity of that sample measured via DSC.

For HDPE on the RheoRaman microscope, the measured scale factor is $N_c = 0.80 \pm 0.03$. Although this is larger than calculated values of N_c from prior measurements [1] the Raman peak intensities of HDPE (and therefore the scale factor values) are strongly dependent upon the polarization state of the incoming and collected light as well as the scattering angle [2]. The crystallinity for the room temperature sample in Fig. 2 is (73 ± 4) % which agrees with the crystallinity value of (74 ± 5) % measured via DSC.

The structure-property relationships during polymer crystallization are of critical interest and can be studied simultaneously using the RheoRaman microscope. An HDPE sample of thickness 750 µm was heated for 5 minutes at 155 °C, cooled at 10 °C/min to 134 °C, and then cooled at a slower rate of 2 °C/min to 124 °C and held at temperature to crystallize.

Fig. 3 shows simultaneous rheology, Raman, and polarized optical measurements during HDPE crystallization. The complex modulus is measured during small-amplitude oscillatory shear using a fixed strain amplitude of 0.01 and oscillation frequency of 2π rad/s. Fig. 3a shows that early times in the crystallization process are characterized by G'< G" , but over time a crossover occurs in the modulus as the values of G' and G" increase over 2 orders of magnitude. The plateau in G' and G" at later times indicates the cessation of crystallization as measured by the complex modulus.

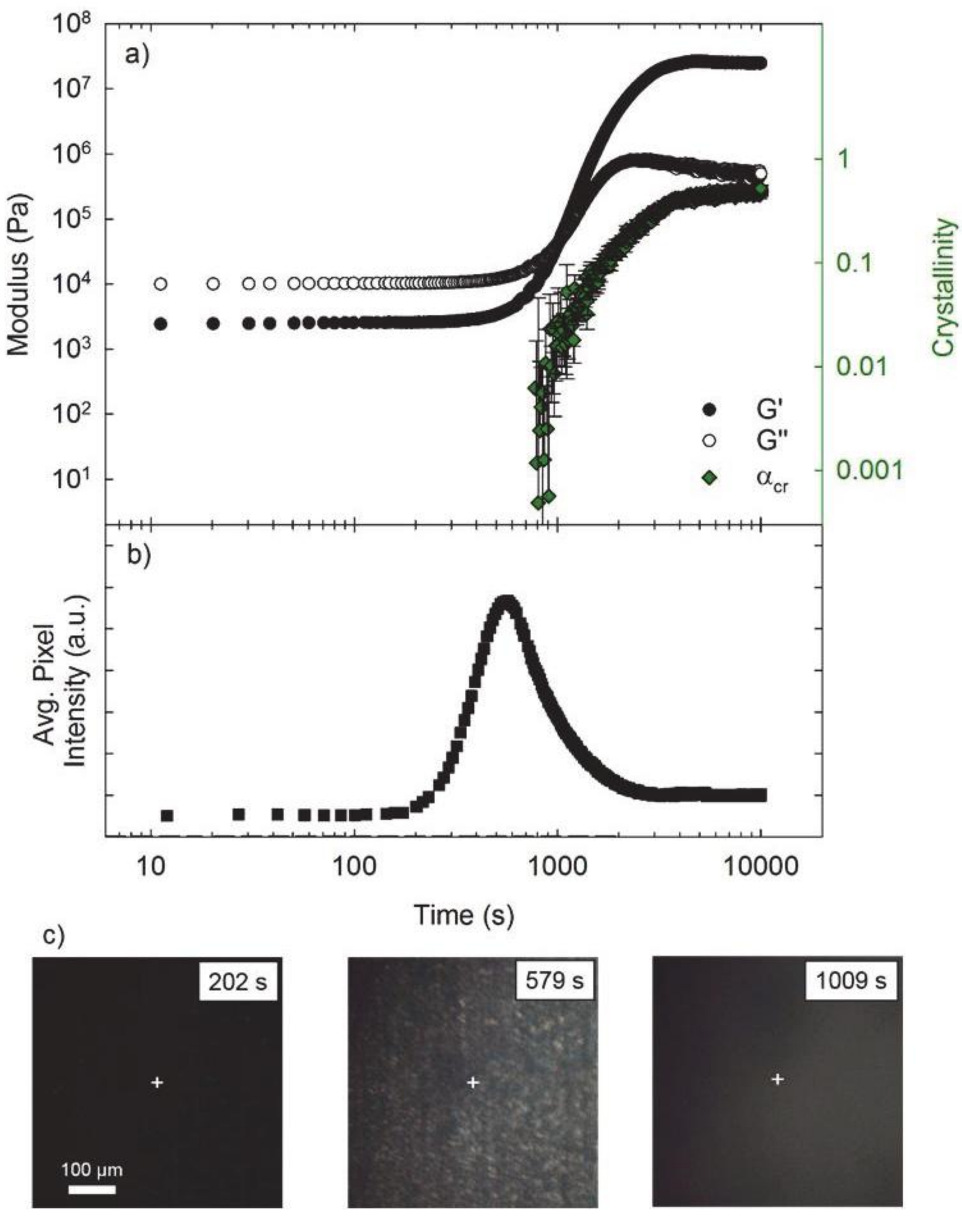

Fig. 3: a) Complex modulus and crystallinity of PE versus time during isothermal crystallization at 124 °C. b) Average pixel intensity of images taken during crystallization versus time. c) Images of the crystallization process at indicated times. The white cross marks the position of the laser spot for Raman spectroscopy.

We can correlate the Raman spectroscopy and optical imaging with the rheology. For these measurements the objective is focused approximately 100 µm below the rotor. Raman spectra measured during the crystallization process are used to calculate the crystallinity of the sample via Equation 1. Fig. 3a shows the instantaneous mass fraction of crystalline material, which first exceeds the measurement noise at approximately 800 s and increases over time. The appearance and increase in crystallinity as measured by Raman spectroscopy correlates with the increase in the complex modulus near the crossover point. The average pixel intensity of the raw images taken during the crystallization process are shown in Fig. 3b with specific images shown in Fig. 3c. The average pixel intensity is initially constant with time and the images show no structural features under crossed polarizers. At approximately 200 s the intensity increases due to the appearance of birefringent structures growing near the rotor surface shown in the middle image of Fig. 3c. The average pixel intensity increases until the sample becomes more turbid due to the large amount of light-scattering structures growing in the bulk of the sample. We note that the increase in average pixel intensity appears prior to any observable conformational change via Raman or modulus change via rheology. However, the decreasing pixel intensity correlates well with the increase in crystallinity and complex modulus.

The turbidity increase in the sample indicates spherulite growth in the sample bulk, although structure growth from the base plate obscures clear imaging. Despite this, we can observe spherulite growth when repeating the experiment focused in the sample bulk as shown in Fig. 4. The first image corresponds to when the crystallinity measured via Raman first exceeds $\alpha_{cr} > 0.001$. Spherulite growth is expected to increase the turbidity of the sample, which is evident in the loss of average pixel intensity in Fig. 3b.

Relating Raman, rheological, and optical measurements would be difficult on multiple instruments due to the sensitivity of the crystallization process on temperature, but using the RheoRaman microscope we can clearly correlate changes in the complex modulus with structural and conformational changes in the crystallizing HDPE melt.

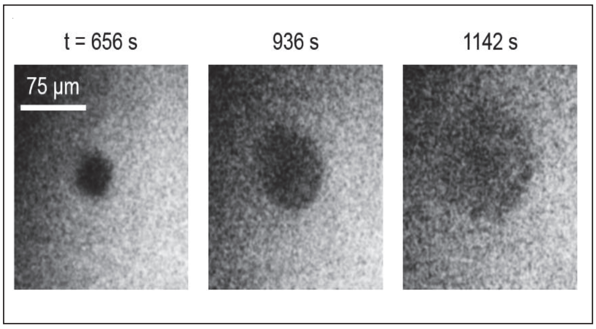

Fig. 4: Sequential images of spherulites generated during the crystallization of PE at 124 °C. Elapsed time t is indicated above each image. Images have been digitally enhanced for clarity.

Summary

Relating Raman, rheological, and optical measurements would be difficult on multiple instruments due to the sensitivity of the crystallization process on temperature, but using the rheo-Raman microscope we can clearly correlate changes in the complex modulus with structural and conformational changes in the crystallizing HDPE melt.

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Material Characterization

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Simultaneous Rheological-Dielectrical Characterization Using the HAAKE MARS Rheometer Platform

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Key words
Thermo Scientific HAAKE MARS, NETZSCH DEA 288 *Epsilon*, Hyphenated measuring method, Post-curing, Degree of curing

The result of a rheological test tells us how a substance behaves under a given stress or strain. What it does not tell us is the reason why, rheology is a macroscopic method and regards the sample as a homogeneous amount of substance. To be able to explain the rheological behaviour, we need additional information about the sample's microstructure, supplied by an additional "microscopic" method. Microscopy, FT(IR) spectroscopy, Raman spectroscopy or dielectrical analysis (DEA) are well established microscopic methods.

Using the traditional approach, running two independent test methods on two different samples, always bears the risk that due to the different ways of sample preparation or sample history in general, the tests happen under different conditions and the test results are not then really comparable. This risk can be avoided by running both test methods on the same sample simultaneously using a combination of two analytical methods in one setup. Subsequently, the two resulting data sets can be correlated without any doubt since they have been collected at the same time on the same sample. As an additional benefit, this approach saves a significant amount of time since only one sample has to be prepared and both test run at the same time.

The Thermo Scientific™ HAAKE™ MARS™ rheometer can be equipped with parallel plate geometries with an integrated DEA sensor for simultaneous investigations on rheological and DEA behaviour. This method combination can be used in temperature range up to 220 °C using a temperature chamber (Fig 1).

Typical applications, which can be investigated using this method combination, are the curing behaviour of reactive thermosets, composites, glues, inks, coatings and dental materials.

Depending on the viscosity range, plates with different diameters are available. The sample is loaded into a plate/plate geometry, like for classical rheological tests covering the DEA comb sensor on the lower plate. During the test, a sinusoidal voltage (excitation) is applied and the resulting current (response) is measured together with the phase shift between voltage and current. Both current and phase shift are used to determine the loss factor, based on which the ion mobility (ion conductivity) is calculated. For curing reactions, the inverse ion conductivity is used, the so-called ion viscosity.


Fig.1: Parallel plates geometry with integrated DEA comb sensor in a temperature chamber for the HAAKE MARS rheometer.

It is essential for simultaneous measurements and their evaluation to present both results in one data file. For this purpose the rheological results can be automatically exported into an ASCII file with the Thermo Scientific™ HAAKE™ RheoWin™ Software at the end of a measurement. This format allows the import into the *Proteus*® Software from NETZSCH. By this means both results can be displayed in one graph, as for example shown in Fig. 2.

Whilst with a rheometer the start and the progress of a curing reaction can be measured very well, the DEA delivers valuable additional information, e.g. if the curing reaction is completed or if there still is potential for post-curing. Based on the ion viscosity the progress of the reaction can be read from the data and the degree of curing can be determined (conversion curve). On top of that, the DEA is capable of expanding the frequency range from mHz to MHz.

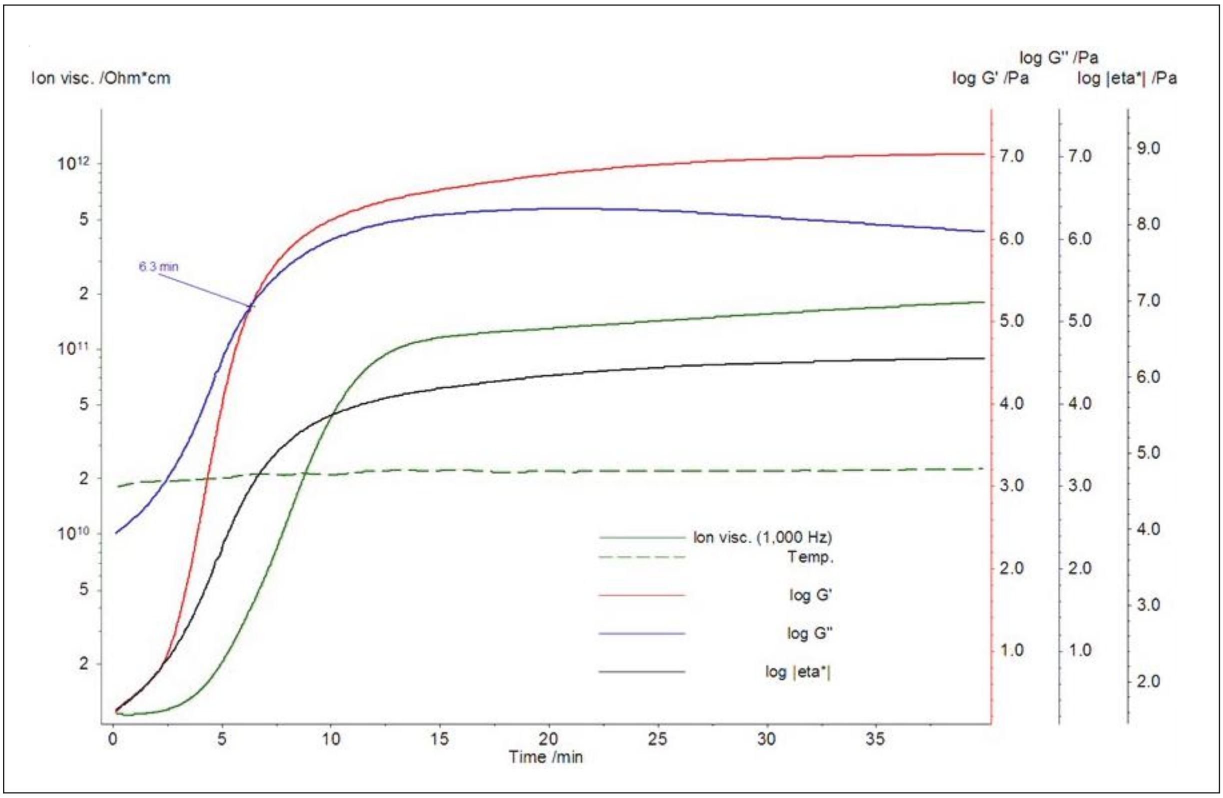

Fig. 2: Time-dependent curing reaction of a two component epoxy resin described with the rheological moduli (red and blue) and the dynamic viscosity (black) as well as the simultaneously measured ion viscosity (green) by DEA at room temperature and a measuring frequency of 1 Hz.

Fig.3: Detailed view - parallel plates geometry with integrated DEA comb sensor.

Order information

Triangular adapter plate for HAAKE MARS including lower holder with plate and integrated DEA sensor as well as thermocouple.

With different plate diameters available:
603-1200 20 mm*
603-1201 25 mm*
603-1230 35 mm*
*upper plate not included.

Necessary configuration

HAAKE MARS with controlled test chamber CTC,
NETZSCH DEA 288 *Epsilon*

thermofisher.com/mars

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Coaxial cylinder measuring geometry for HAAKE MARS rheometers with CTC-oven

Fabian Meyer, Thermo Fisher Scientific, Material Characterization, Karlsruhe, Germany

Key words
Coaxial cylinder, DIN 53019/ISO 3219, Thermo Scientific HAAKE MARS, Controlled Test Chamber (CTC)

The Z20 DIN measuring geometry for CTC is a coaxial cylinder system that can be used with the Thermo Scientific™ HAAKE™ MARS™ rheometers equipped with the CTC (Controlled Test Chamber). It allows for testing of low and medium viscous fluids over a wide temperature range. The design and dimensions of the Z20 DIN for CTC are according to the DIN 53019/ISO 3219 standard. The setup consists of a rotor, a cup with lid, a solvent trap container and a lower shaft (Figure 1). The dimensions of rotor and cup are shown in Table 1. The Z20 DIN for CTC is mounted on a triangular base plate and used with a separate temperature sensor. The temperature sensor is guided through the hollow shaft and the tip of the probe is placed in close distance to the measuring cup (Figure 2). The measuring range of the Z20 DIN for CTC with a HAAKE MARS III rheometer for viscosity and shear stress vs. shear rate is shown in Figure 3. Figure 4 shows the results of a viscosity measurement for silicon oil from 30 °C to 300 °C with the Z20 DIN for CTC measuring geometry. For the performed test the temperature was increased in steps of 20 °C at a constant shear rate of 100 s^{-1}.

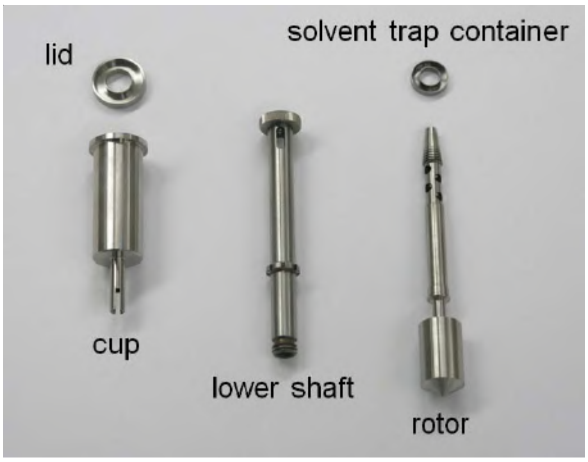


Fig. 1: Individual parts of Z20 DIN for CTC measuring geometry.

Fig. 2: Z20 DIN for CTC geometry in measuring position with temperature sensor.

Order information

603-0429	Z20 DIN for CTC
222-1856	Triangular adapter plate for HAAKE MARS for CTC measuring geometries
222-1769	Temperature sensor for lower shaft (CTC)

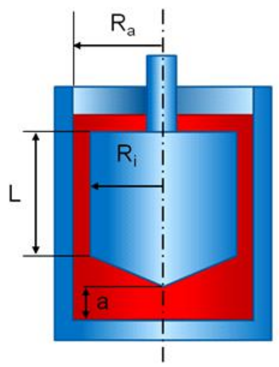
		Z20 DIN for CTC
	**Rotor**	
	Mass m (g)	118.8
	Material	Stainless steel 1.4401
	Inertia (kg m^2)	3.3 x 10^{-6}
	Radius R_i	10.00
	Length L	30.00
	Clearance to bottom (mm)	4.20
	Cup	
	Radius R_a (mm)	10.875
	Material	Stainless steel 1.4401
	Ratio of Radii R_a/R_i	1.0847
	Gap Ra-Ri (mm)	0.85
	Sample volume /cm^3)	8.2
	Calculation factors	
	A (Pa/Nm)	48230
	M (s^{-1}/rad^{-1})	12.29

Table 1: Dimensions and materials for Z20 DIN for CTC measuring geometry.

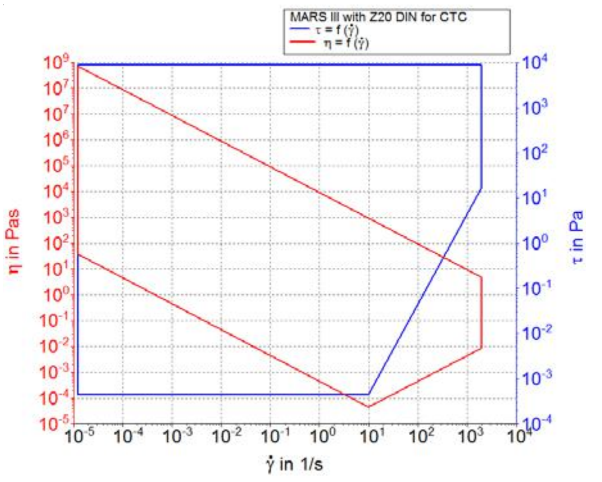


Fig. 3: Measurement range for viscosity η and shear stress τ vs. shear rate of the Z20 DIN geometry for CTC in combination with a HAAKE MARS III rheometer.

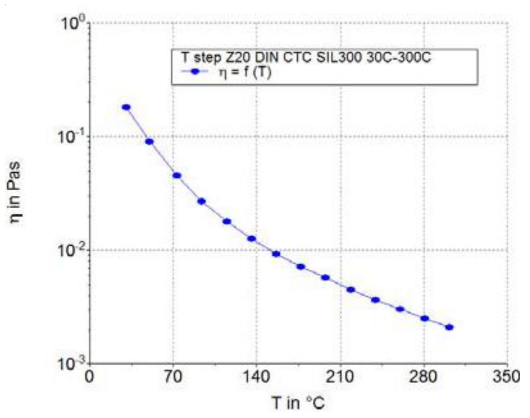


Fig. 4: Viscosity as a function of temperature for a silicon oil under a constant shear rate of 100 s^{-1}.

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Optimizing process conditions and ensuring end product requirements of plastics with rheological analysis

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Key words
Polymers, melt, viscoelasticity, molecular weight, processing, DMTA, extensional testing

Introduction

Plastics are polymeric materials that are used in a wide range of applications and for a broad variety of consumer products. In order to make these products, polymers are commonly processed at elevated temperatures in a molten state. Understanding how these melts deform and flow is key to knowing how to effectively process and transform them into the end products we readily consume.

Due to their chemical structure and high molecular weight, polymer melts exhibit a complex flow and deformation behavior. They are considered viscoelastic materials, showing both viscous (liquid-like) and elastic (solid-like) properties. A good knowledge of the viscoelastic properties of a polymeric material is essential to optimize formulations and blends as well as to adapt a process to the properties of a given material. The molecular structure as well as the testing or processing conditions of a polymer melt determine which behavior is dominant (viscous or elastic). Too much elasticity can lead to flow anomalies and unwanted effects during many common processing steps [1]. One example is the swelling of a melt stream exiting the narrow die of an extruder. Other examples of flow anomalies caused by elastic properties of polymeric fluids are shown in Figure 1.

Capillary viscometers and melt flow indexers are frequently used to measure the melt viscosity of polymers. However, these instruments will not provide any information about the viscoelastic properties of the tested sample. Rotational rheometers with the capability to perform rheological tests with small oscillatory mechanical excitations on the other hand, allow for a comprehensive investigation of these properties.

This report is intended to give an overview of the different rheological tests that can be performed with rotational rheometers and explain how the obtained results relate to different processing conditions as well as to the final product properties.

Rotational vs. oscillatory testing - The Cox-Merz rule

Rheology has proven to be an excellent tool to analyze the mechanical properties of polymers in their different physical states. Various testing methods can be utilized to fully characterize the rheological behavior of polymeric materials. Though rotational steady state shear experiments allow for measuring the non-Newtonian viscosity of dilute and semi-dilute polymer solutions, the preferred testing methods for polymer melts (and solids) utilize the application of an oscillatory shear deformation. This is due to their high elasticity and the consequential occurrence of edge failures when exposed to large deformations in a rotational rheometer. According to the Cox-Merz rule, the complex viscosity ($|\eta^*|$) derived from oscillatory frequency sweep measurements plotted against the angular frequency (ω) is identical to the steady-state shear viscosity from rotational testing plotted against the shear rate [2]. The Cox-Merz rule is an empirical rule that is valid for many polymer melts and polymer solutions. Figure 2 shows the comparison of viscosity data obtained from rheological tests in rotation and in oscillation mode.

Fig. 1: Typical flow anomalies of viscoelastic polymer fluids.

Once the end of the Newtonian (zero shear viscosity) plateau is reached and the viscosity starts to decrease, the shear viscosity (red symbols) drops abruptly and no longer displays a continuous, smooth progression. The observed drop is due to sample fracture at the edge of the measuring geometry caused by secondary flow fields [1]. The oscillation frequency sweep (green symbols), on the other hand, provides higher data quality across a broader frequency range.

The improved testing range of the oscillatory frequency sweep is due to the small amplitudes of the imposed oscillatory shear. As a result, performing an oscillatory frequency sweep and applying the Cox-Merz rule is the preferred method for obtaining shear viscosity data for polymeric materials.

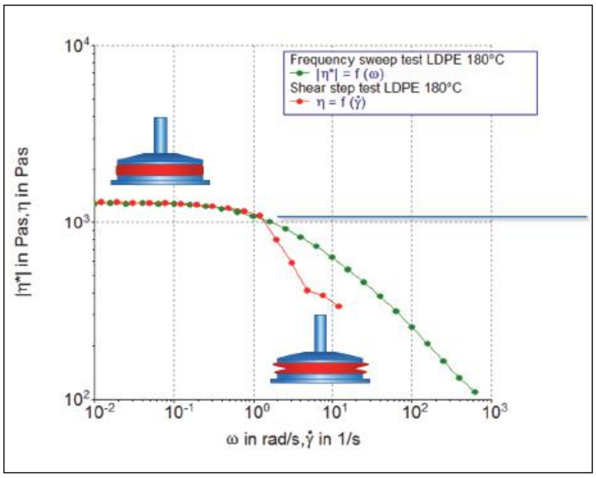

Fig. 2: Comparison of viscosity data obtained from a steady state shear (red symbols) and an oscillation frequency sweep test (green symbols).

Identifying the linear-viscoelastic range - The amplitude sweep tests

In order to obtain comparable viscosity data from a frequency sweep experiment (as discussed above), the applied sinusoidal oscillatory deformation must be relatively small and within a material's linear viscoelastic range (LVR). In this range, the material's microstructure remains unchanged and as a result, the rheological properties such as the storage and the loss modulus (G' and G", respectively) or the complex viscosity are constant and independent of the applied stress or deformation. Once a critical deformation or stress value is reached, the microstructure of the material begins to change and the rheological parameters start to change.
The linear viscoelastic range of a material is determined by performing an oscillation amplitude sweep test. During this test, which is performed at a constant frequency, the sinusoidal deformation or stress applied by the rheometer is gradually increased. Figure 2 shows the results of an amplitude sweep for LDPE at 190 °C. The end of the linear viscoelastic range of this LDPE melt was calculated automatically by the rheometer software and is equal to a deformation of 55 %. Further tests in oscillation mode, such as frequency, temperature, or time sweep tests, should be performed at a deformation below this critical value (unless the test is intended to be outside the LVR). When a frequency sweep test is performed over a wider frequency range (several orders of magnitude), it is recommended to perform several amplitude sweeps at different frequencies, in order to make sure that the selected deformation remains within the LVR across the entire frequency range.

Viscoelastic fingerprint of a material - The frequency sweep test

The information gained from the rheological tests in oscillation mode is manifold. For instance, shear rate dependent viscosity data derived from oscillatory frequency sweep experiments, together with the utilization of the Cox-Merz rule, allow for quantifying the flow resistance of a material during high shear processing applications such as extrusion or injection molding. The low frequency/shear data (zero shear viscosity, η_0), on the other hand, can be used to calculate the weight average molecular weight (M_w) of a polymer melt according to:

$$\eta_0 = k \cdot M_w^{3.4} \qquad (1)$$

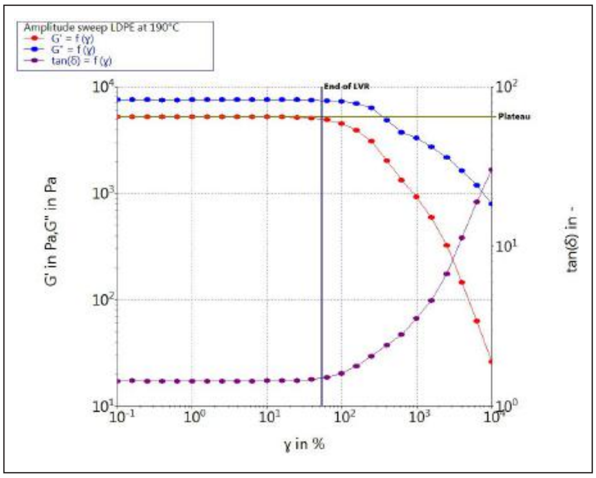

Fig. 3: Storage modulus G', loss modulus G" and the complex viscosity Iη*I as a function of the deformation γ for a LDPE melt at 1 Hz and 190°C.

The prefactor k depends on the molecular structure of the polymer [3]. Equation 1 is valid for polymers with a linear chain structure and a molecular weight above a critical value (M_c). Figure 4 shows a typical viscosity curve of a polystyrene melt and the corresponding shear rate ranges that occur in common processing applications.

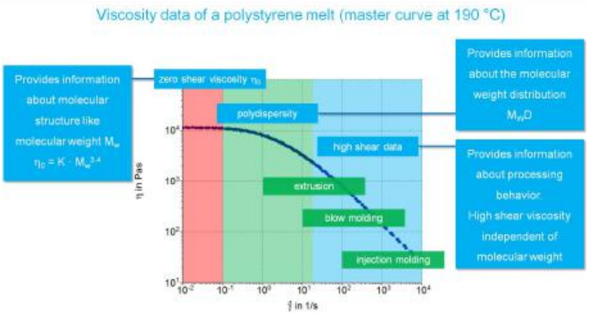

Fig. 4: Shear rate depending viscosity of a polystyrene melt and typical applications.

Besides information about the overall flow resistance, frequency sweep data also provide a direct measure of the viscous and elastic properties of a polymer. These are represented by the storage and the loss moduli (G' and G", respectively) measured at different frequencies/time scales. The data reveals the general structure of a material and also provides information of the molecular weight (M_w) and the molecular weight distribution (MWD). Repetitive frequency sweep measurements over a narrow frequency range that capture the crossover point can therefore be used to detect thermal degradation causing changes to the MW and MWD. Figure 5 shows how the crossover point (where G' = G") shifts when the M_W or the MWD change for an otherwise identical polymer melt.

As already mentioned, flow anomalies caused by the elasticity of polymer melts can lead to poor product quality in polymer processing applications such as extrusion. Figure 6 shows a comparison of storage modulus data as a function of the applied frequency for polyethylene samples with different Melt Flow Indices (MFI). The three PE samples were processed with a 16 mm parallel twin screw extruder under the same conditions. At the end of the extruder barrel the melts were forced through a vertical rod capillary die with a diameter of 1 mm and an L/D ratio of 10. Die swell of the extrudate was measured with a laser micrometer. A die-swell of 0.5 mm, resulting in a total strand diameter of 1.5 mm, could be found for t PE with the highest MFI (~20) and the lowest molecular weight. As can be seen in Figure 6 the strand came out of the extrusion line as an even strand with no signs of surface defects.

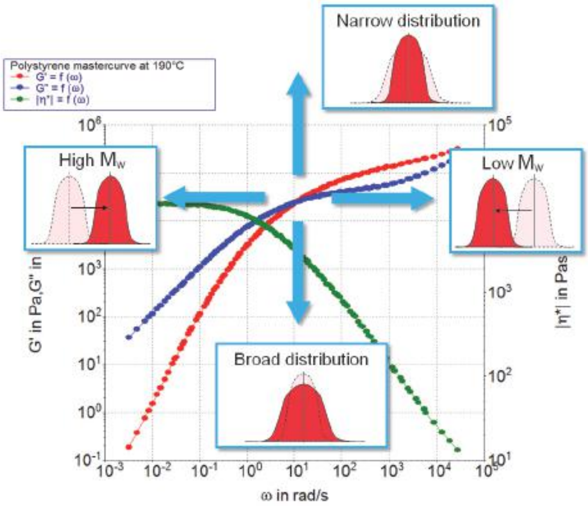

Fig. 5: Storage modulus G’, loss modulus G” and the complex viscosity Iη*I as a function of the angular frequency ω for a polystyrene melt at 190 °C.

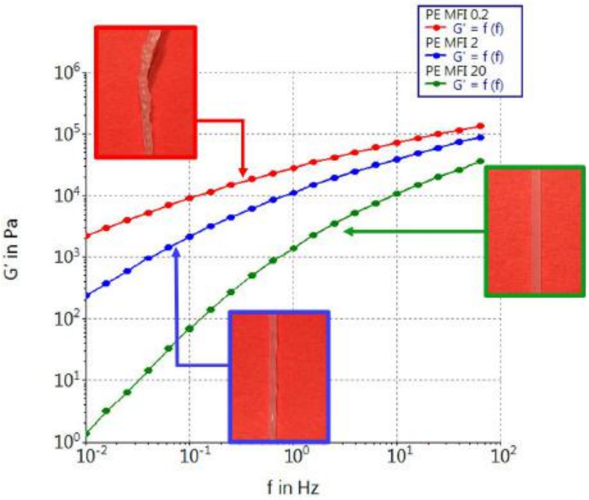

Fig. 6: Storage modulus G’ as a function of the angular frequency ω for polyethylene melts with different MFI at 190 °C. The images show the extrusion strands that were prepared with the melts in a twin screw extrusion process.

The PE sample with the medium MFI (~ 2) already showed an uneven surface structure with a changing diameter. The PE sample with lowest MFI (~ 0.2) and the highest molecular weight showed clear signs of melt fracture under the same extrusion conditions used for the other two samples. When looking at the rheological data, one can see that the three samples clearly differ in terms of their elasticity, as represented by G’. Especially at the lowest frequency (10^{-2} Hz), the values in G’ differ in one or more order of magnitude.

The storage modulus is a very sensitive indicator of the elasticity incorporated by a high molecular weight tail. Figure 7 shows the comparison of the results of three frequency sweeps performed on a low molecular weight LDPE and two blends of the same LDPE with a small weight fraction of a high molecular weight PE. In the low frequency range G’ shows clear differences for these three melts and even a small fraction of 1 wt% of high molecular weight PE can be detected. These small differences are usually not visible when performing Gel Permeation Chromatography (GPC) or similar techniques to determine the molecular weight distribution. Also the MFI results performed with a capillary viscometer would not reveal any differences between the three samples. The storage modulus data derived from oscillatory frequency sweep experiments is the most sensitive indicator of a high molecular weight tail in a polymer melt. Even small amounts of high molecular weight fraction can already cause flow anomalies that will lead to a poor quality of the final polymer strand.

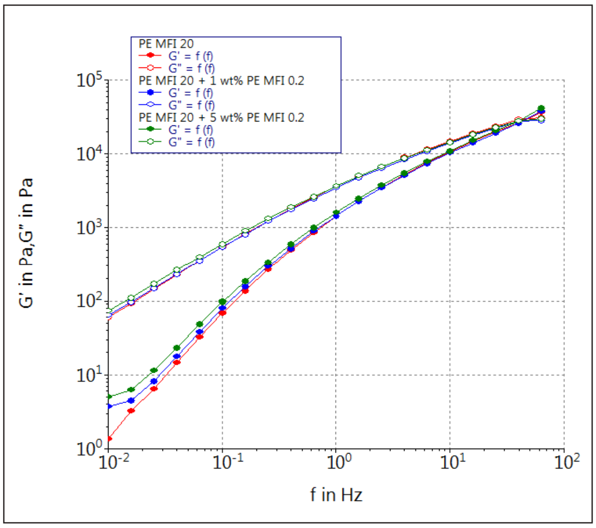

Fig. 7: Storage modulus G’ and loss modulus G” as a function of the angular frequency ω for a low molecular weight polyethylene melt and two blends at 190 °C.

Figure 5 shows rheological data acquired over an angular frequency range from below 10^{-2} rad/s to more than 10^4 rad/s. in order to obtain rheological data over such a wide range, more than a single frequency sweep test is necessary. The low and high frequency regions are restricted by either time concerns (duration of a single oscillation) or the rheometer specifications (maximum frequency). The time-temperature superposition principle is then used to overcome these limitations.

Extending the measuring range - The time-temperature superposition principle

Usually between 2 and 4 orders of magnitude in frequency are covered in a single frequency sweep test. In order to extend the data range beyond the low- and high-end frequencies, the Time-Temperature Superposition (TTS) principle can be applied. TTS uses the fact that temperature and frequency (time) have similar effects on the viscoelastic behavior of polymer melts [3]. As a result, one can perform several frequency sweeps over a smaller range at different temperatures. After selecting one set of data (at one temperature) as a reference, the other results can be shifted towards the reference curve in order to generate a master curve. Using the TTS-principle it is possible to obtain rheological data over a much wider frequency range compared to a single frequency sweep experiment. TTS works for many polymer melts and polymer blends but usually only over a limited temperature range [4].

Figure 8a shows the results of several frequency sweep tests performed at different temperatures. The TTS principle was then applied chosen 190 °C as a reference temperature. The resulting master curve (Figure 8b) contains viscoelastic data over almost 8 orders of magnitude in frequency.

The master curve can be divided in three regions. At low frequencies, the sample is in the terminal region and the polymer melt behaves predominantly viscous. In the terminal region, material behavior is governed by long molecule chain relaxation processes. Also, in the terminal region, G' and G" typically have slopes of 2 and 1 in a double logarithmic plot. At medium frequencies, a transition occurs with a crossover between G' and G". The viscoelastic behavior in this range is strongly driven by the molecular weight distribution of the polymer. At the highest frequencies, the sample behaves predominantly elastic, with G' larger than G". In the high frequency range, the polymer's behavior is governed by the fast relaxation motion of the shortest polymer chains.

In addition, G' and G" data acquired over a wide frequency range can be used to calculate the molecular weight and molecular weight distribution for many linear thermoplastic homopolymers. In order to perform this calculation, the tested frequency range must include data from the low frequency terminal region up to the end of the high frequency plateau region.

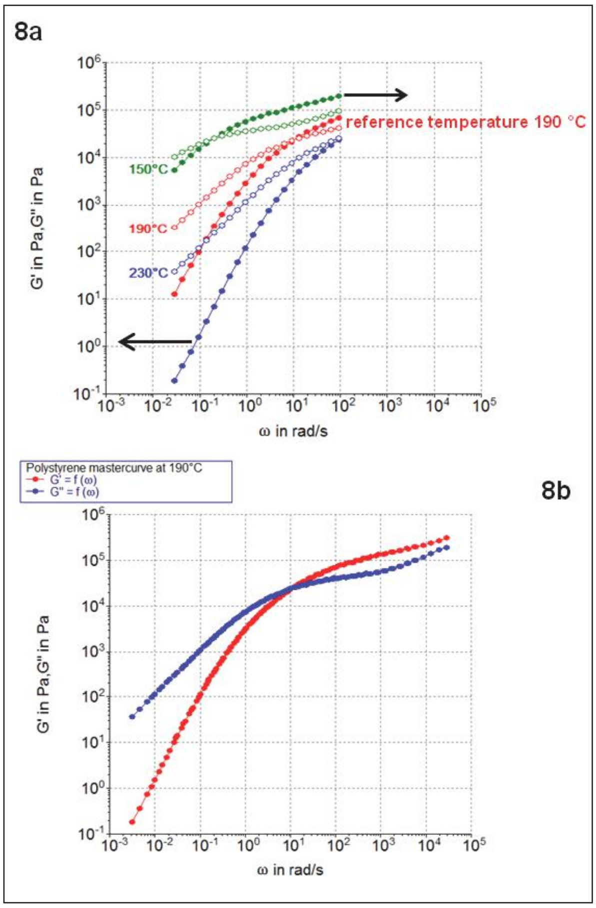

Fig. 8: Application of the Time-Temperature-Superposition principle with a polystyrene melt.

Investigating the final product properties - Dynamic Mechanical Thermal Analysis

Rotational rheometers can also be utilized to perform Dynamic Mechanical Thermal Analysis (DMTA) on solid, rectangular-shaped polymer specimens. During DMTA testing a material is exposed to an oscillatory mechanical excitation while the temperature is continuously changed. The obtained data are used to identify characteristic phase transitions, such as the glass transition or the occurrence of melting and/or crystallization within the polymer matrix. In addition, DMTA can be used to determine final product performance and to interrogate relevant application-based properties such as stiffness, brittleness, damping or impact resistance.

Figure 9 shows an example of a DMTA test with a semi-crystalline polyetheretherketone (PEEK) sample, tested from below its glass transition to just below its melting temperature. The test was performed using a special solids clamping tool for rotational rheometers [5]. The rectangular specimen was prepared with a lab scale injection molding system [6]. For rheological testing, the glass transition can be identified using different metrics. The most common metric uses the maximum in the loss modulus G", while the initial decrease in the storage modulus G' or the maximum in the tanδ (G"/G') are also readily used to indicate glass transition. As can be seen in Figure 9, the maximum in G" is located in the middle of a wider transition range, while the onset of the G' decrease is near the beginning of the transition and the maximum in tanδ closer to the end of this range.

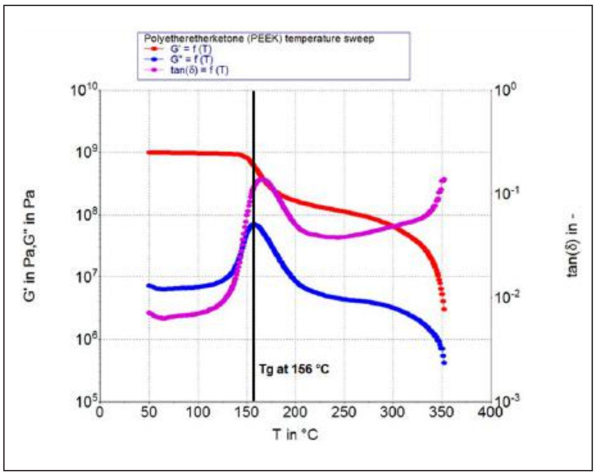

Fig. 9: Storage modulus G', loss modulus G" and tanδ as a function of temperature for a polyetheretherketone.

The generalized behavior of a polymeric sample during a temperature sweep test is presented in Figure 10. All semi-crystalline polymers transition from a glassy region at low temperatures to a rubbery plateau and eventually into the melt state at higher temperatures. The height of the step from the glassy region to the rubbery plateau depends on the degree of crystallinity of the polymer. As the degree of crystalline domains inside the polymer increases, the step height between the two regions will decrease.

Low molecular weight polymers do not exhibit a rubbery plateau. Once the glass transition is completed, the material becomes a soft melt and G' decreases with increasing temperature. Cross-linked polymers do not melt; instead they remain in a rubbery state until thermal decomposition occurs.

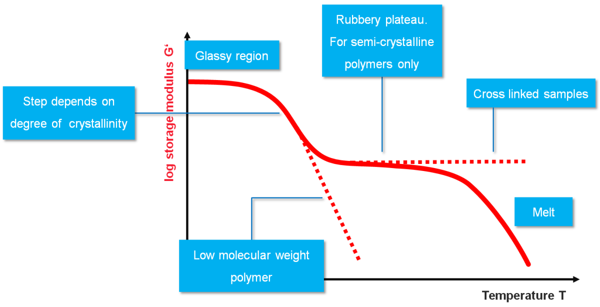

Fig. 10: Generalized behavior of polymer sample in a DMTA test.

Extensional testing

Besides rotation and oscillation, extension is the third main type of flow that can be investigated rheologically. Spraying and vessel filling are two examples of processes where extensional flows occur, however they are not very common for polymer melts. Examples of processes where extensional flows occur and that are more closely related to polymer melts are film blowing, injection molding, foam extrusion or fiber spinning. Figure 11 shows the transient extensional viscosity at different extensional deformation rates for two different polyethylene samples. The tests were performed with the Sentmanant Extensional Rheometer (SER) fixture for rotational rheometers [7]. The plot on the left presents the extensional behavior of a non-branched high density polyethylene (HDPE) sample. No strain hardening was observed for this type of material. The plot on the right, however, shows the results of the same experiments, performed with a highly branched low density polyethylene (LDPE) sample. For comparison, the red curves show the transient shear viscosities multiplied by three according to the Trouton ratio for uniaxial extension [8]. The shear viscosity data were obtained from rotational step experiments. Unlike the linear HDPE sample, the extensional behavior of the branched LDPE sample differed significantly from the behavior observed in shear flow. During extensional testing, the LDPE sample displayed shear hardening behavior, especially at higher deformation rates. Strain hardening behavior can be beneficial for many polymer processing techniques such as film blowing or fiber spinning. Therefore, having a good understanding of the extensional behavior of a polymeric material is crucial for optimizing its final product properties (behavior that is left uncaptured by standard rotational rheological measurements).

Conclusion

Understanding the viscoelastic properties of a polymeric material is essential to optimize formulations and blends as well as to adapt a process to the properties of a given material and avoid problems caused by flow anomalies. Rheological tests performed with rotational rheometers can be utilized to investigate the viscoelastic behavior of polymers from the melt-state to the solid-state and everywhere in between. The obtained data can be used not only to optimize processing conditions and the final product performance, but also to establish structure property relationships. This is the reason why rheological tests are commonly used in analytics for polymeric fluids in industry as well as academia.

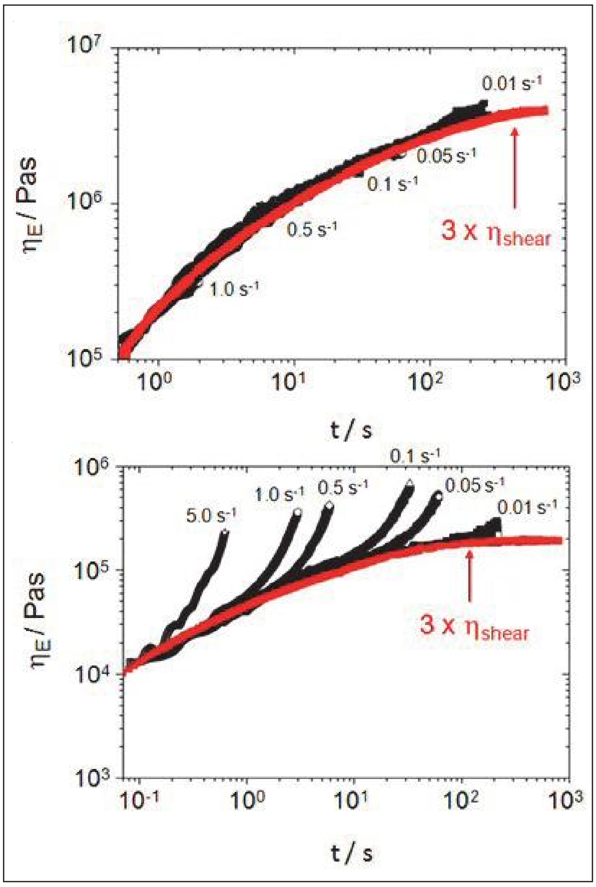

Fig. 11: Extensional viscosity as a function of strain rate for a non-branched HDPE (top) and highly branched LDPE (bottom). All tests were performed at 150 °C.

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