

HAAKE MARS Rheometers for polymer analysis

APPLICATION COMPENDIUM

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Introduction

A broad variety of products used on a daily base are either made entirely of plastics or contain at least some polymer-based components. Numerous processing techniques are available for blending raw materials and / or for creating the final product shape. All these techniques have in common that the raw polymer material has to be converted from solid-state (e.g. granulate or powder) into a molten state. This can be done by using an extruder.

For an effective dimensioning and modeling of an extruder, the adequate shear rate range as well as the temperature-dependent properties of the extruded material have to be considered and therefore be tested in advance.

To understand these processing properties, rheology is the method of choice to characterize polymeric materials. Due to its high elasticity, edge failure in a polymer melt can occur due to the large deformation applied during a rheological shear experiment. Hence rotational measurements are not preferred, and oscillatory measurements are used instead.

Frequency sweep experiments can be used to gain information about the flow resistance during the extrusion process at high shear rates utilizing the so-called Cox-Merz rule. Additionally, the viscous and elastic properties represented by the storage modulus G' and loss modulus G'' can be determined. These parameters are directly related to the polymer structure, its molecular weight, and molecular weight distribution. All these factors influence the processing behavior of a material tremendously. Thus, knowing the rheological properties of material before setting up a new extrusion process can be a time and cost-saving advantage, not only for new formulations but also for recycled samples.

During the extrusion process, the main energy input is mechanical and generated by the rotation of the screw(s). In a rheometer, on the contrary, the energy input is mainly due to heating, when performing oscillatory testing. Hence, rheology cannot simulate the whole extrusion process but can be used to evaluate the processing conditions to run trials at a small-scale extruder and scale-up afterward.

Furthermore testing polymers in the molten state, rotational rheometers can also be used to perform Dynamic Mechanical Thermal Analysis (DMTA) with solid specimens. For this type of test, the sample is exposed to an oscillatory excitation while the temperature changes continuously. The obtained data is used to identify characteristic phase transitions such as the glass transition or the occurring of melting and crystallization. Besides, DMTA is used to determine the final product performance as well as important application-related properties such as stiffness, brittleness, damping or impact resistance.

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

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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.



Figure 1: Typical flow anomalies of viscoelastic polymer fluids

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.

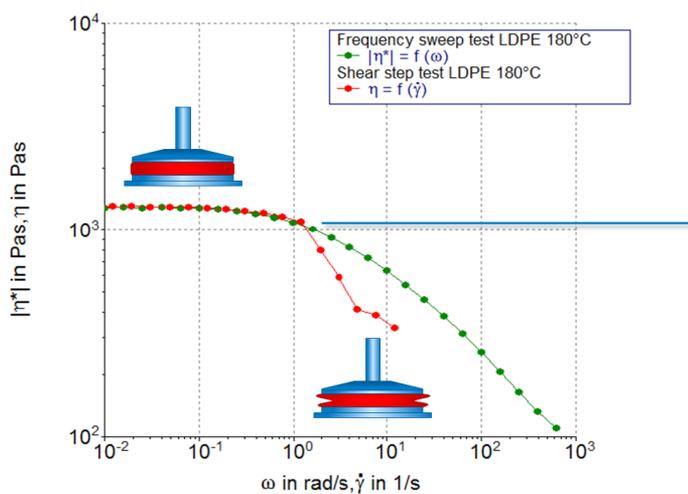


Figure 2: Comparison of viscosity data obtained from a steady state shear (red symbols) and an oscillation frequency sweep test (green symbols)

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.

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.

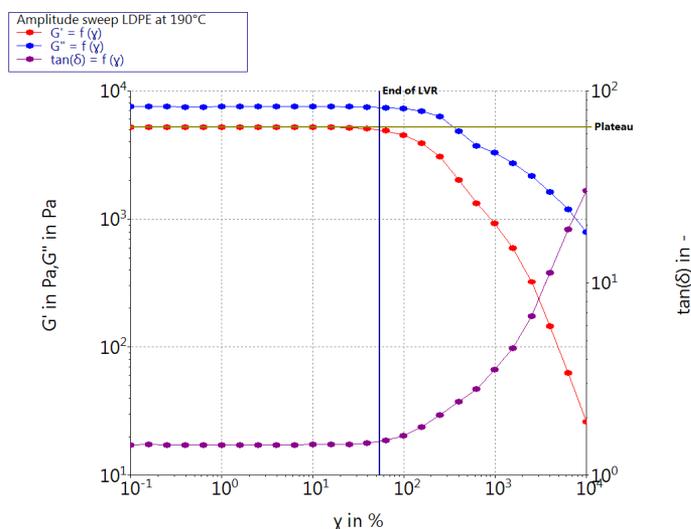


Figure 3: Storage modulus G' , loss modulus G'' and the complex viscosity $|\eta^*|$ as a function of the deformation γ for a LDPE melt at 1 Hz and 190°C.

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:

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

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.

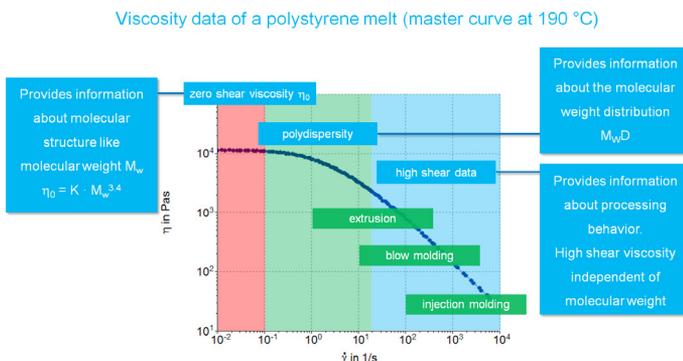


Figure 4: Shear rate depending viscosity of a polystyrene melt and typical applications

Besides information about the overall flow resistance, frequency sweep data also provides 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 MW 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 the 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.

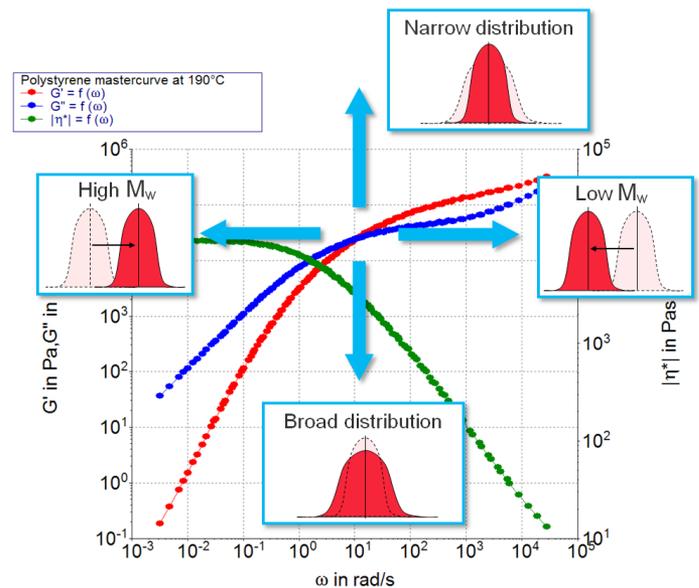


Figure 5: Storage modulus G' , loss modulus G'' and the complex viscosity $|\eta^*|$ as a function of the angular frequency ω for a polystyrene melt at 190°C.

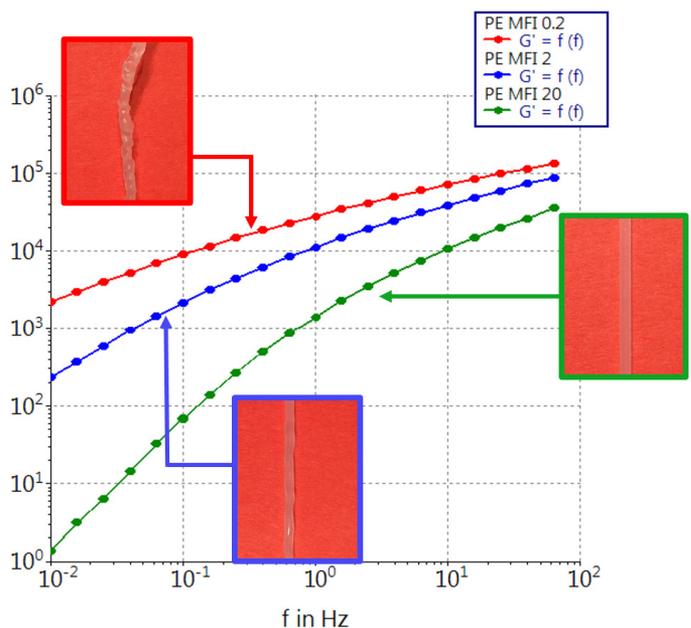


Figure 6: Storage modulus G' as a function of the angular frequency ω for polyethylene melts with different MFI at 190°C. The images show the extrusion strands that were prepared with the melts in a twin screw extrusion process.

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 orders 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.

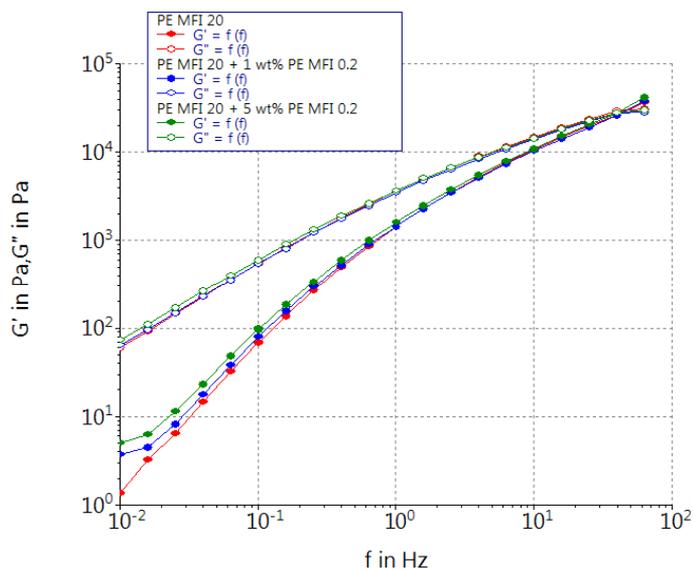


Figure 7: Storage modulus G' and loss modulus G'' as a function of the angular frequency ω for a low molecular weight polyethylene melt and two blends at 190°C .

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, with 190°C chosen 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'' . Here 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.

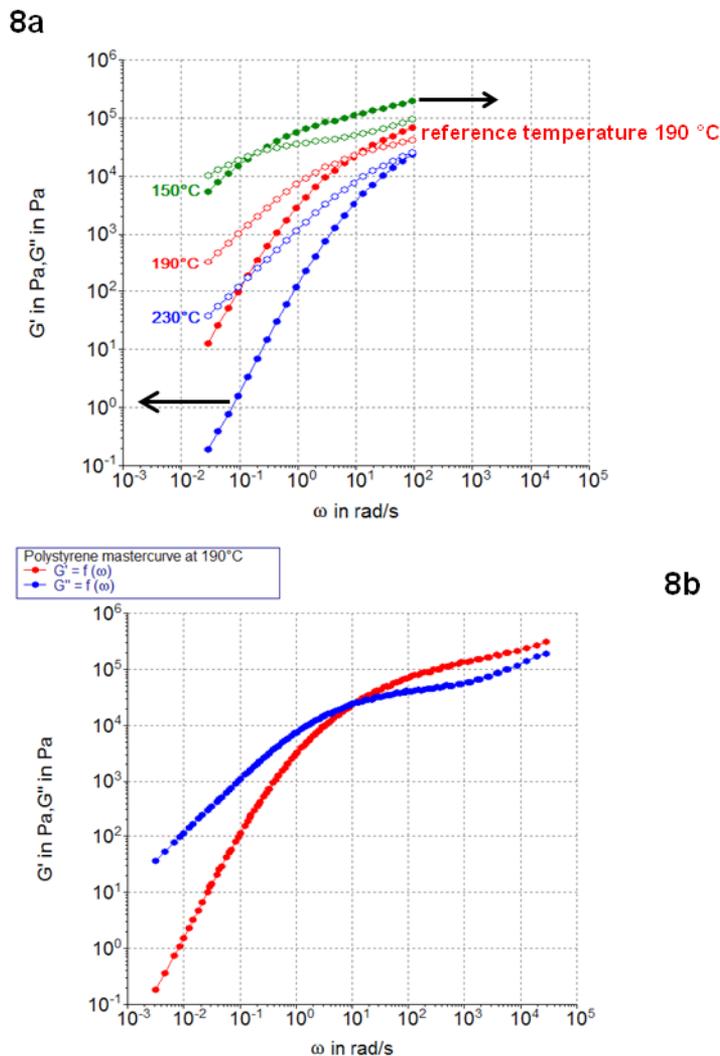


Figure 8: Application of the Time-Temperature-Superposition principle with a polystyrene melt

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 is 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 $\tan\delta$ (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 $\tan\delta$ closer to the end of this range.

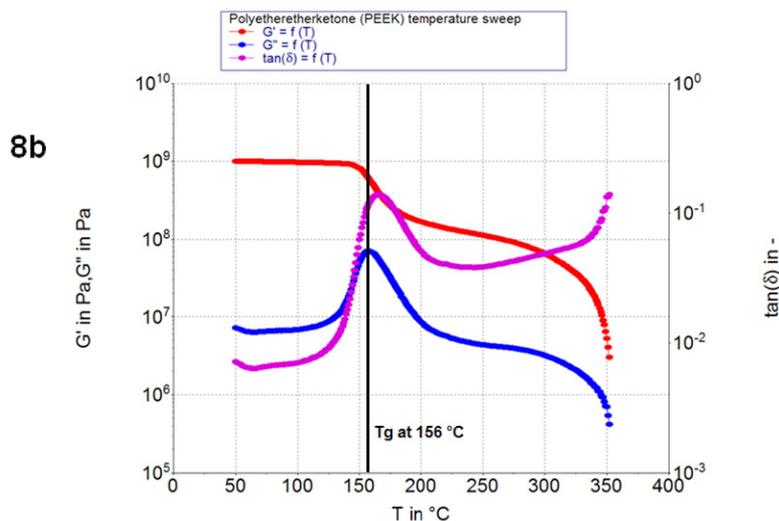


Figure 9: Storage modulus G' , loss modulus G'' and $\tan\delta$ as a function of temperature for a polyetheretherketone.

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.

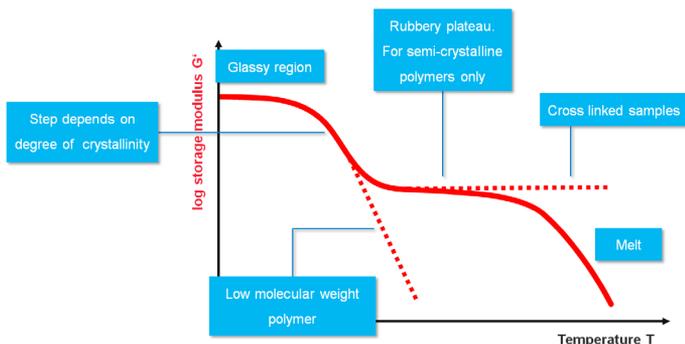


Figure 10: Generalized behavior of polymer sample in a DMTA test

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).

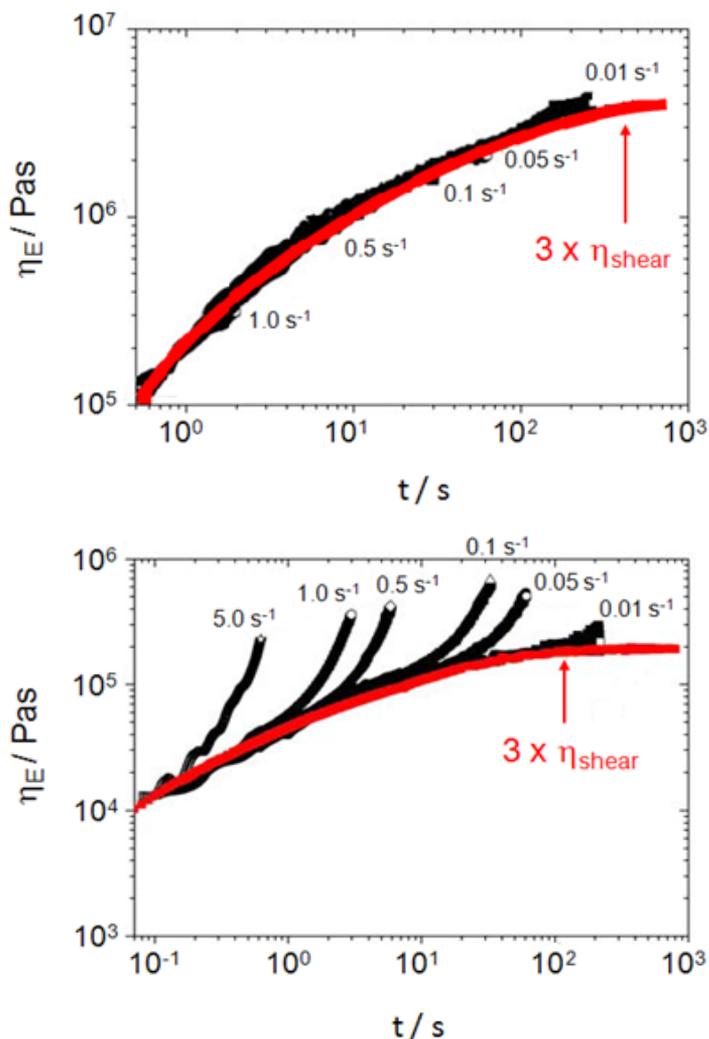


Figure 11. Extensional viscosity as a function of strain rate for a non-branched HDPE (top) and highly branched LDPE (bottom). All tests were performed at 150 °C.

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.

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Dynamic mechanical thermal analysis (DMTA) on polymer nanocomposites

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Keywords

DMTA, 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. In particular, the greater mechanical strength of polymeric materials combined with low weight are desired properties. Additionally the incorporation of nanocomponents can lead to an improved heat and chemical resistance as well as electric conductivity. Nowadays, polymer nanocomposites are frequently used in the automotive and aviation industries, as well as in construction materials for windmill blades.

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

For testing the mechanical properties of a polymer 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



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

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 ($\tan \delta$) are obtained from DMTA. The storage modulus represents the elastic, and the loss modulus represents the viscous properties of a material. For solids, the storage modulus is larger than the loss modulus and vice versa for fluids. The loss factor is the ratio of G'' and G' and is also a measure for the damping properties of a material. Figure 1 shows the schematic diagram for DMTA on a semi-crystalline polymer. The glass transition can be identified using different

approaches. The most common approach for rheological tests uses the maximum of the loss modulus (Figure 1). The onset of the decrease of the storage modulus or the maximum in the $\tan \delta$ (G''/G') are two alternative methods. At room temperature, polymer nanocomposites are usually in the glassy state and show high values for G' , indicating the high stiffness of the material. Compared to the unfilled polymers, polymer nanocomposites show higher G' values in the glassy state indicating their greater mechanical strength.

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.



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

Material and methods

To extend its range of testing methods into the field of composites and other solids, the Thermo Scientific™ HAAKE™ MARS™ Rheometer can be equipped with a solids clamping tool [1]. The temperature control for this setup is provided by the Controlled Test Chamber (CTC) (Figure 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 Figure 2) thus allowing testing of larger samples under uniform temperature conditions. The solids clamping tool can be equipped with special jaws for soft, medium or hard samples.

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

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

DMTA was performed with both samples. The carbon fiber enforced material was tested in a temperature range between $-100\text{ }^{\circ}\text{C}$ and $+240\text{ }^{\circ}\text{C}$. 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 $30\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$. 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 $2\text{ }^{\circ}\text{C}/\text{min}$.

Results and discussion

Figure 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 $3 \times 10^9\text{ Pa}$. 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 $150\text{ }^{\circ}\text{C}$. The two maxima of G'' at $99\text{ }^{\circ}\text{C}$ and $115\text{ }^{\circ}\text{C}$ 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 Figure 3 are almost perfectly identical.

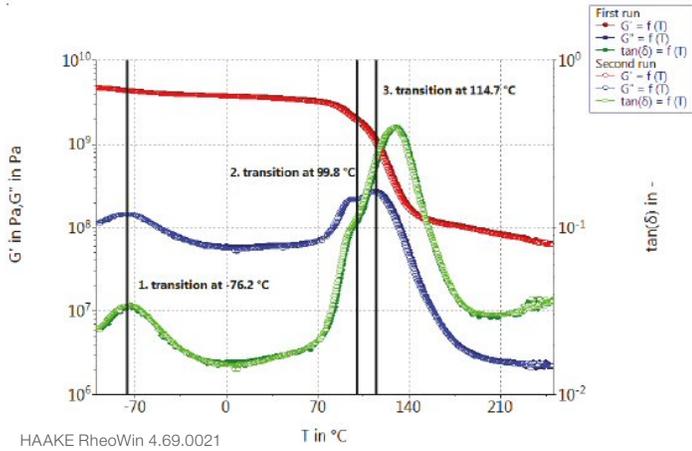


Figure 3: Storage modulus G' (red), loss modulus G'' (blue) and $\tan(\delta)$ (green) as a function of temperature for the carbon based sample. The glass transition temperature T_g is indicated by the green line. The results of 2 independent tests (open and filled symbols) run on fresh samples each,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

During the measurement, the rheometer applied a constant small pulling force on the sample to compensate for any thermal expansion or contraction (see black curve in Figure 4). This results in a lift motion of the rheometer, that reacts to any change in sample length. This information can be used to check whether the clamps were able to hold the sample or might have lost their grip. In a plot of the sample length as a function of temperature, any slipping of the sample between the jaws of the clamps would show as a step-change. The smooth progression of the orange curve in Figure 4 documents the clamp's steady grip even on such a hard material.

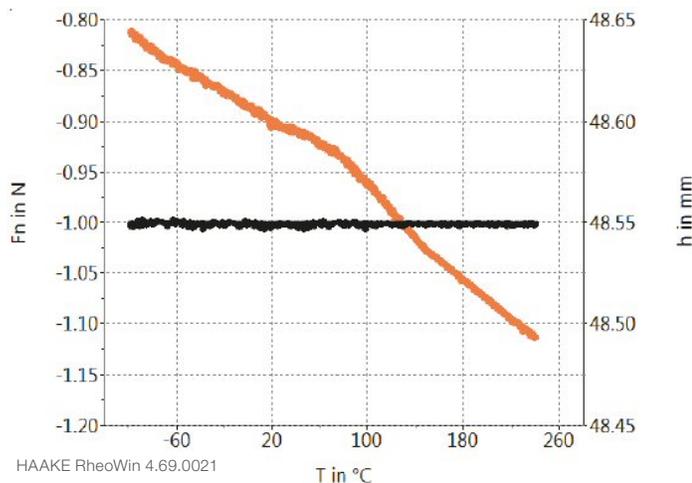


Figure 4: Constant normal force (black) and decreasing sample length (orange) during a temperature increase from -100 °C to 240 °C on the carbon fiber enforced sample.

Apart from its diagnostic value, the data shown in Figure 4 contains valuable information about the sample itself.

The length decrease with increasing temperature reflects the negative temperature expansion coefficient (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°.

Figure 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 transformed into a rubber elastic condition, where the moduli data changed less with increasing temperature.

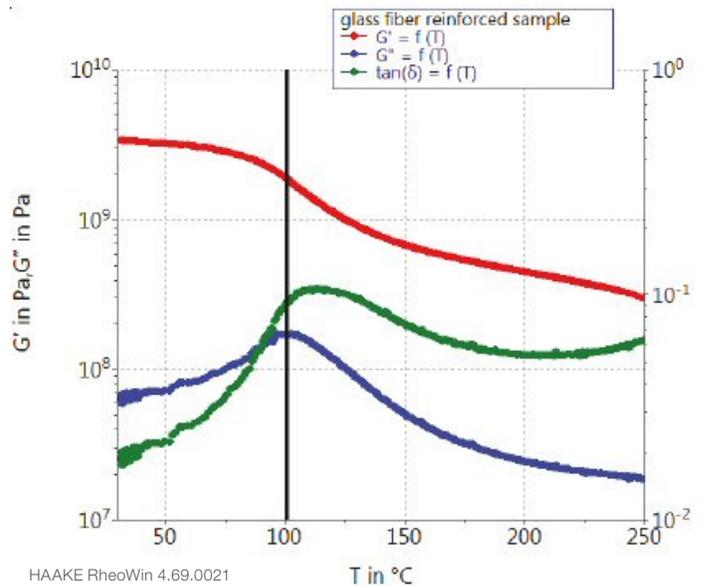


Figure 5: Storage modulus G' (red), loss modulus G'' (blue) and $\tan(\delta)$ (green) as a function of temperature for a glass fiber enforced PPS sample. The glass transition temperature T_g is indicated by the black line.

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 Figure 5, a constant coefficient of approximately $\alpha = 3.3 \times 10^{-6} \text{ K}^{-1}$ can be calculated.

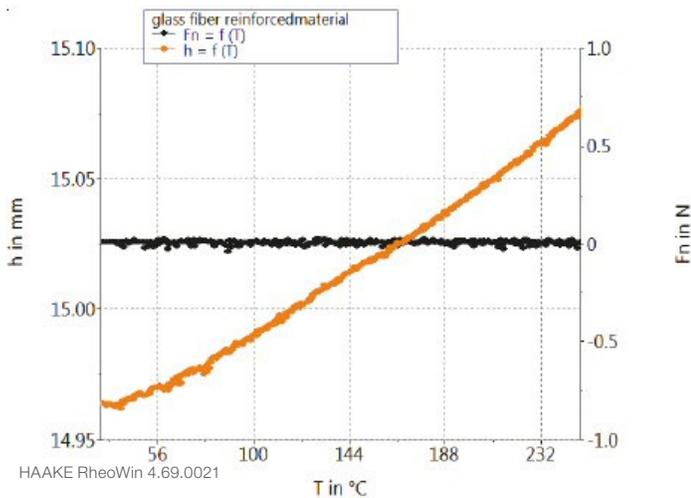


Figure 6: Constant normal force (black) and increasing sample length (orange) during a temperature increase from 30 °C to 250 °C on one of the glass fiber enforced PPS samples.

Summary

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

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

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

Reference

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

Find out more at thermofisher.com/rheometers

Characterizing long-chain branching in polyethylene with extensional rheology

Authors: Jan Philip Plog, Fabian Meyer and Ulrich Schulz

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 polyethylene 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 sample 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



Figure 1: Controlled Temperature Chamber (CTC) of the HAAKE MARS Rheometer with the SER tool.

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.

Methods and materials

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 film. 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]. Figure 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 Software via the routine that can be seen in Figure 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 Figure 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.

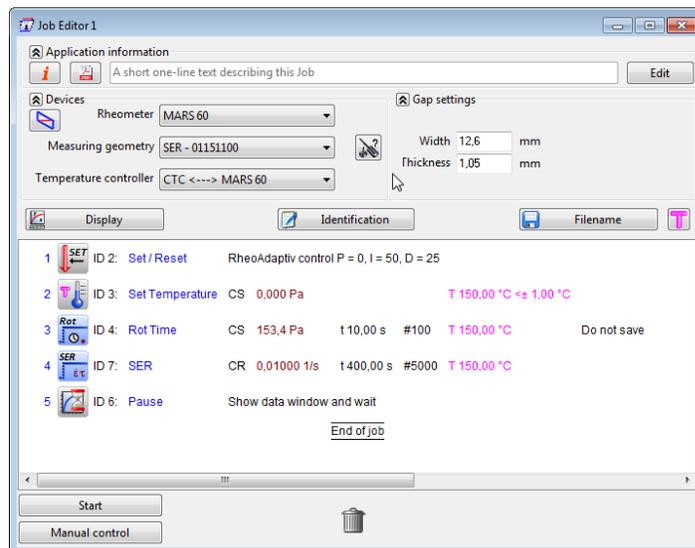


Figure 2: Measuring routine to characterize the extensional behavior of Polyethylene, comprised of the following elements: 1. RheoAdaptiv-Control, 2. Temperature control, 3. Pre-stretch of the sample, 4. Extensional test.

Results and discussion

Figure 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 Figure 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 (Figure 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.

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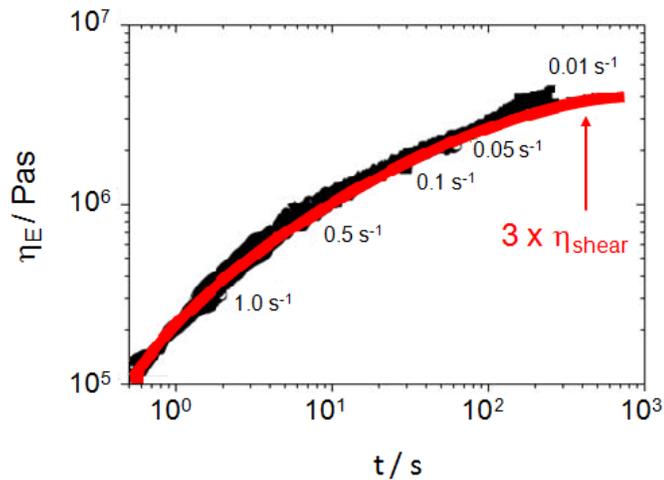


Figure 3: Extensional viscosity as a function of strain rate for non- branched LDPE.

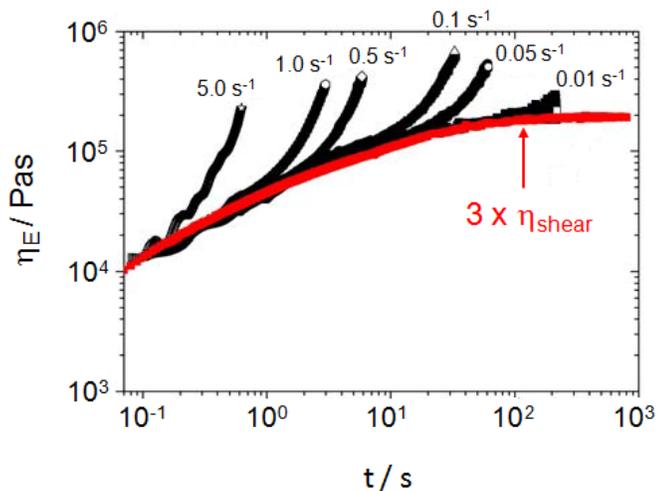


Figure 4: Extensional viscosity as a function of strain rate for highly branched LDPE.

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Curing of an acrylate - Rheology with simultaneous FTIR spectroscopy

Author: Klaus Oldörp

Introduction

Anybody 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 such times have to fit the application to create a product that the target market 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 characterize not only the uncured glue but especially the curing process itself. Regardless of whether a drying glue, a 2-component system, a thermally curing glue or a UV curing glue is investigated, the Thermo Scientific™ HAAKE™ MARS™ Rheometer and its wide range of accessories are the perfect tools to characterize curing behaviors.

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 glue shows properties other than those expected 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. The molecular data provides the complementary „why“ information to the rheological measurements. A perfect



Figure 1: Setup with the HAAKE MARS Rheometer, Rheonaut module* and FTIR spectrometer.

match is FTIR spectroscopy, a technique that can identify and quantify different chemical groups in a substance or in a mixture of substances.

Rheometers and spectrometers are two different types of analysis, each often with its own instrument. 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 FTIR spectroscopy without the aforementioned disadvantages, the Rheonaut module has been developed. This module is a unique combination of a temperature control module and an attenuated total reflection (ATR) cell with its own IR detector. With the Rheonaut module, the HAAKE MARS Rheometer can be combined with an FTIR spectrometer to one analytical setup (Figure 1). Only with this unique combination is it possible to record the mechanical changes of the curing glue while simultaneously and, even more importantly, collecting IR spectra on the same sample to track the chemical changes inside the sample.

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 start to be mixed (Figure 2, steps 3 and 4). Otherwise, any deviation in the loading procedure would lead to an undefined offset on the time axis.
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 is 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 (Figure 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 (Figure 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 (Figure 3).

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

Figure 2: Test method for 2-component glues shown in Thermo Scientific™ HAAKE™ RheoWin™ Measuring and Evaluation Software. In steps 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.

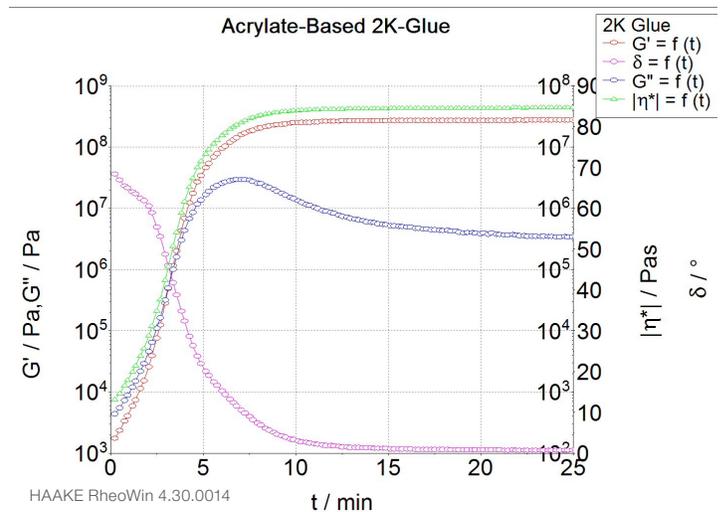


Figure 3: Curing of an acrylate glue; development of the moduli G' and G'' , the complex viscosity $|\eta^*|$ and the phase angle δ over time.

The freshly prepared glue is mainly viscous; G'' dominates over G' with phase angle (δ) values around 70° (purely viscous: $\delta = 90^\circ$, purely elastic: $\delta = 0^\circ$). The curing reaction proceeds quickly; after 3.2 min the crossover point where $G'' = G'$ or $\delta = 45^\circ$ is reached. From this so-called gel time on, the glue behaves as mainly elastic because a wide meshed 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 no longer possible 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.

Simultaneously with the rheological data, FTIR spectra have been collected about every 13 s yielding 115 IR spectra during the 25 min of the rheological test. The spectra show several characteristic signals, which can be correlated with the progress of the chemical reaction (Figure 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 (Figure 5).

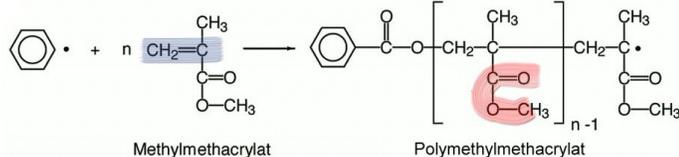


Figure 4: Radical polymerization of Methylmethacrylate (MMA) to Polymethylmethacrylate (PMMA). Marked in blue: C=C-bond of the monomer. Marked in red: ester bond in the polymer.

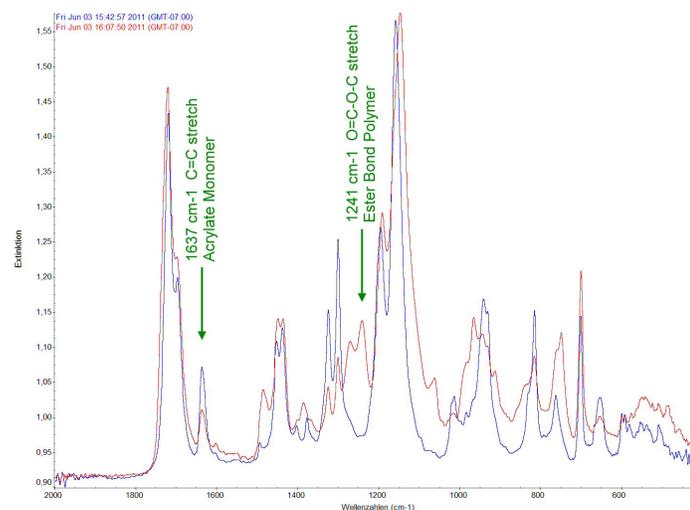


Figure 5: First IR spectrum (blue) and last IR spectrum after 25 min (red) collected during the curing of an acrylate glue at 23 °C. The signal at 1637 cm^{-1} decreases over time while the signal at 1241 cm^{-1} increases.

The Thermo Scientific™ OMNIC™ Spectroscopy Software with its optional OMNIC Series add-on allows the spectra to be lined up in chronological order in a 3D-graph and characteristic signals changes to be evaluated during the time of the test (Figure 6).

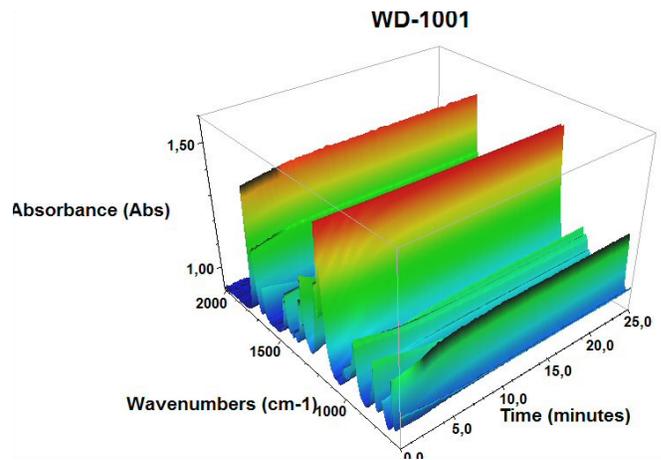


Figure 6: 3D profile illustrating the time-dependent change of the IR spectra collected during the curing of the sample in the rheometer, created with the OMNIC Series add-on.

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 (Figure 7).

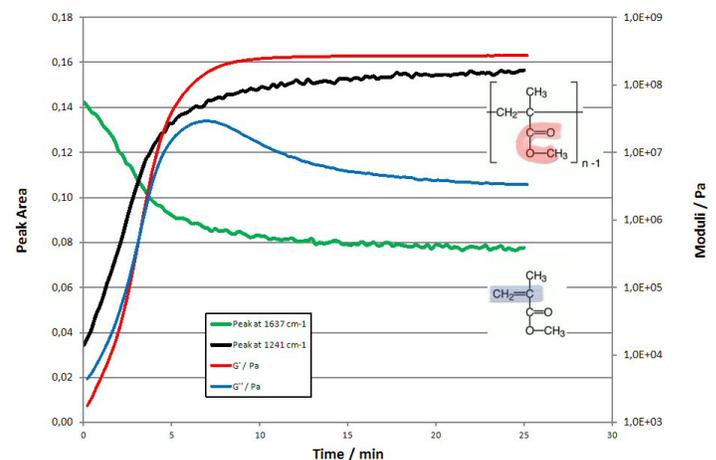


Figure 7: Curing of the acrylate glue monitored with rheology and simultaneous FTIR. The increase of the sample's moduli (red and blue) corresponds with the decreasing signal of the monomer (green) and the increasing signal of the polymer's ester bond (black).

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. For example, it's known whether it would be better to add more monomer or to increase the temperature to increase the mobility of the existing monomer.

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 FTIR spectrometer to simultaneously record on the same sample what happens during the curing process and why it happens on a molecular level. This significantly reduces the time for sample preparation and analyses and excludes any uncertainties due to different sample composition or sample treatment when running both analyses separately.

The unique combination of rheological and spectroscopic 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

Melting and recrystallization of polypropylene

Authors: Nathan C. Crawford and David Drapcho

Introduction

Rheology is the study of the flow and deformation of matter, including fluids to solid-like materials (and anything in between). Rheological measurements are commonly used to examine or induce bulk physical material changes, such as melting, crystallization, gelation, and/or polymerization etc. Raman spectroscopy, on the other hand, is a vibrational spectroscopic technique that can provide insights to these processes at the molecular level, both chemically and morphologically. However, until very recently¹, Raman studies are often conducted *ex-situ*, whereby Raman spectra are acquired prior to and after the observed physical transformation. The true chemical/morphological changes driving these processes are largely left uncaptured, leaving much room for data interpretation and speculation surrounding these dynamic physicochemical relationships.

The Thermo Scientific™ HAAKE™ MARSxR (Figure 1) is a fully integrated RheoRaman system that enables simultaneous rheology and Raman spectroscopy measurements. The seamless hyphenation of these two techniques allows for real-time, *in-situ* measurements of both physical and chemical/morphological properties with great ease. This multimodal analytical tool offers several advantages compared to the traditional *ex-situ* approach. First, data collection efficiency is greatly improved by combining multiple one dimensional experiments into a single multifaceted experiment. Secondly, because both techniques are employed simultaneously, sample fidelity is preserved and the transformation of the material is captured in real-time. And finally, sample consumption is reduced, which can be beneficial for new material/formulation development where sample quantities are limited and/or expensive.



Figure 1:
The Thermo Scientific HAAKE MARSxR RheoRaman system.

In this note, a MARSxR RheoRaman system was used to investigate the temperature-dependent melting and crystallization of polypropylene, as well as the isothermal crystallization process. The melt and crystalline phase transitions of polymeric materials are commonly correlated with variations in viscous and elastic behavior during rheological analysis. In addition, these phase transitions are often associated with spectral pattern changes in characteristic Raman peaks during spectroscopic investigation. Measurements performed *ex-situ* are often challenging to compare due to discrepancies in temperature control, slight deviations in sample composition, and differences in processing history. The *in-situ* RheoRaman system, on the other hand, completely eliminates these discrepancies, allowing for a more valid analysis of the melt and crystalline phase transitions from both the macroscopic and molecular levels.

Materials and methods

Materials

Polypropylene (Ineos Olefins and Polymers, USA, R12C-00 random copolymer) pellets were used for this study. The pellets were melted at 190 °C on the rheometer to form a continuous, disk-shaped specimen for testing.

Rheometer

Rheological measurements were performed using the Thermo Scientific™ HAAKE™ MARS™ Rheometer, equipped with a 20 mm diameter stainless steel parallel-plate rotor. In order to extract viscoelastic behavior of the polypropylene, all measurements were conducted in the oscillatory mode. Oscillatory measurements were performed at 1 Hz with a constant strain of 0.1%, while data were collected every 5 s. To soften the polypropylene and help it conform to the measuring geometry, all samples were initially loaded at 190 °C. For the melt-to-crystallization phase transition study, the temperature was decreased from 190 °C to 30 °C, at a rate of 5 °C/min. For the isothermal crystallization studies at 138 °C and 150 °C, temperature was rapidly decreased from 190 °C to 10 °C above the target temperature. The temperature was then slowly decreased until it reached the test temperature (either 138 °C or 150 °C). The temperature was then held constant for a maximum of 1 h (3600 s), while the isothermal recrystallization process was observed.

Spectrometer

Raman spectroscopy measurements were performed using the Thermo Scientific™ iXR™ Raman Spectrometer. The iXR system employed a 532 nm, 10 mW laser, a triplet spectrograph providing Raman spectra over the range 3500 to 50 cm^{-1} Raman shift (Stokes) at 5 cm^{-1} resolution, and a CCD camera cooled to -50 °C. Alignment of the laser, Raman scatter, and aperture selection within the spectrometer were all software controlled. The minimum exposure collection time is 0.1 s. For the data presented here, the exposure collection time was 4 s and 2 sample exposures were averaged per spectra collection.

RheoRaman coupling

The Raman spectrometer (Thermo Scientific iXR Raman Spectrometer) and rheometer (Thermo Scientific HAAKE MARS) are coupled together using the Thermo Scientific™ HAAKE™ RheoScope module (Figure 2).

The iXR Raman spectrometer is free-space coupled to the rheometer with an optical train which uses two plane mirrors to direct the incident laser into the RheoScope module. Within the RheoScope, a series of mirrors directs the laser beam into a 20x objective, where the laser light is focused through a 2 mm thick fused silica window into the sample (perpendicularly to the flow or vorticity plane). Raman scattered light is collected in a 180° backscatter geometry using the 20x objective, and back into the spectrometer through the same optical train as the incident laser (eventually to the spectrograph inside the spectrometer). Free-space coupling of the laser to the rheometer, and the iXR spectrometer design, allow easy Raman excitation laser wavelength interchange to permit optimization of the laser wavelength to the sample (785 and 455 nm laser sets are also available).

The sample is positioned between the silica window and the rotor geometry attached to the rheometer measuring head (Figure 2). The objective can be adjusted for interrogation at different penetration depths within the sample, as well as positioned at various radial locations along the optical slit (from the true center to outer edge of the sample). An electrical heating element is positioned below the fused silica window to provide temperature control during testing. Cooling was provided from a temperature-controlled circulator with a 50:50 mixture of ethylene glycol and water. All instrumentation is controlled through the Thermo Scientific™ OMNIC™ and RheoWin software packages.

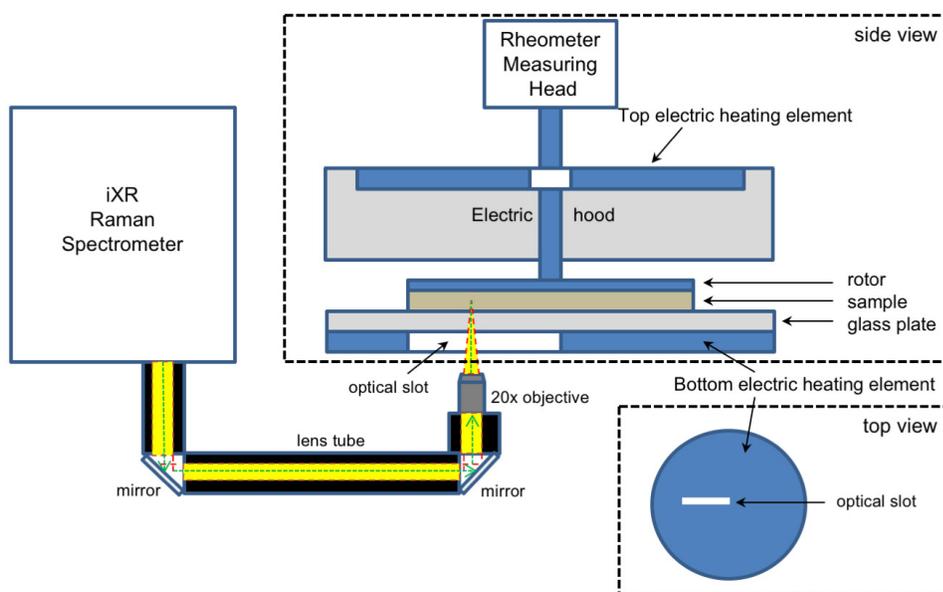


Figure 2: Schematic diagram of the MARS_{xR} RheoRaman system (showing side and top views of the rheometer sample stage). The iXR Raman spectrometer is free-space coupled to the MARS rheometer using plane mirrors that direct light into a 20x long-working-distance objective. The objective focuses the incoming laser (green dashed line) and collects the back-scattered Raman light (yellow) coming into and out of the sample (which sits atop the rheometer stage). The optical path from the spectrometer to the rheometer is enclosed in lens tubes (black). The optical slot in the bottom heating plate permits passage of the laser beam and scattered Raman light.

The electric heater allows for a maximum temperature of 300 °C and a minimum temperature of -5 °C, with a maximum heating/cooling rate of 10 °C/min. An active electrical hood was also used to provide temperature control from above, eliminating the potential for a temperature gradient within the sample (Figure 2).

Results and discussion

The physicochemical and morphological relationships during polymer crystallization are of critical importance for polymer processing. Here we use the new MARSxR RheoRaman system to investigate the crystallization process of polypropylene (PP). Representative Raman spectra for PP at three different temperatures are shown in Figure 3. In general, the spectrum at 53 °C shows sharp peaks across the examined spectral range. These sharp spectral features suggest a high degree of conformational order, indicative of semicrystalline and crystalline structures. As temperature increased to 120 and 173 °C, these peaks began to broaden and merge together. The broadening of spectral peaks is commonly ascribed to melt behavior in polymeric materials.

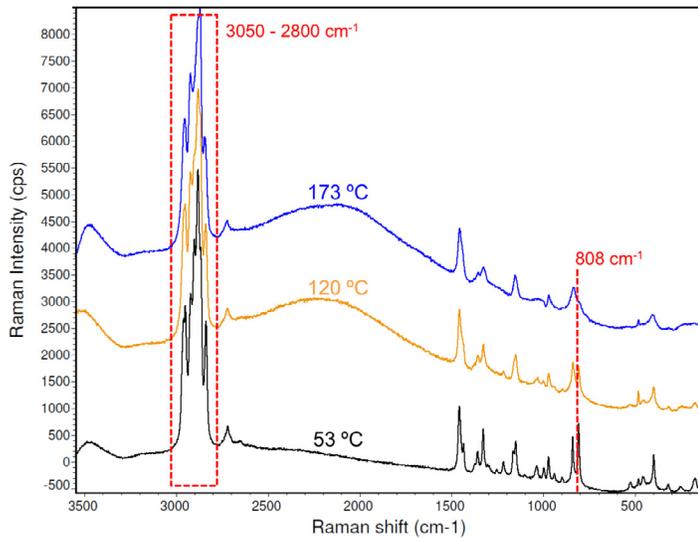


Figure 3: Raman spectra for polypropylene at 53 °C (black), 120 °C (yellow), and 173 °C (blue). The dashed line at 808 cm⁻¹ and dashed box from 3050-2800 cm⁻¹ indicate relevant Raman bands to the recrystallization of polypropylene.

Specific indicators in the Raman spectra for PP are the skeletal deformation of helical chains within the crystal (808 cm⁻¹ peak) and the CH stretching region (3050-2800 cm⁻¹ spectral range). The intensity of the 808 cm⁻¹ peak will be used as a measure of the crystallinity of PP², and the intensity in the CH stretching region is used as a measure of the overall Raman scattering intensity during the crystallization process. For further analysis, the 808 cm⁻¹ peak height was normalized by the peak area between 880 and 780 cm⁻¹. The 880-780 cm⁻¹ spectral region contains skeletal chain vibrations of all conformations during the

melt-to-recrystallization process², while the spectral features in the 3050-2800 cm⁻¹ range were integrated into a total peak area. These indicators (normalized helical chain vibration peak height and overall CH stretching peak area) were then tracked throughout the melt- to crystalline-phase transition and overlaid with the in-situ rheology data (Figure 4).

The melt and recrystallization process of polypropylene was probed rheologically using small amplitude oscillatory shear measurements (Figure 4), where the storage modulus (G') and loss modulus (G'') were measured as a function of temperature. G' and G'' are measures of a material's elastic and viscous behavior, respectively. A liquid-like material will be more viscous than elastic (i.e., viscously dominated), and as a result, G'' will be greater than G'. Conversely, a solid-like material will display more elastic than viscous behavior (i.e., elastically dominated), where G' will be greater than G''.

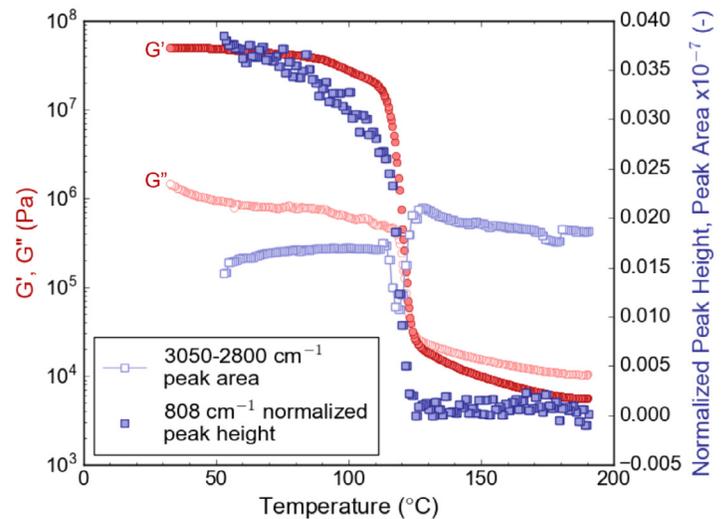


Figure 4: Polypropylene recrystallization: G' and G'' (filled and open circles, respectively; plotted on the left y-axis) and the normalized 808 cm⁻¹ Raman shift peak height and the 3050-2800 cm⁻¹ peak area (filled and open squares, respectively; plotted on the right y-axis) as a function of decreasing temperature from 190 to 30 °C.

Initially, at high temperatures (>150 °C), G'' was consistently greater than G', indicating the PP specimen was in the melt state and displaying liquid-like behavior. As the temperature decreased from 150 °C to 100 °C, an abrupt and drastic increase in both G' and G'' was observed at ~125 °C. By the time the temperature reached 100 °C, G' had increased by four orders of magnitude, while G'' increased by two orders of magnitude. The temperature range from 150 to 100 °C can be viewed as the melt-to-crystalline transition region for this polypropylene material. As the temperature further decreased to below 100 °C, G' was significantly greater than G'' by more than a full order of magnitude, indicating the polypropylene had transitioned into the semicrystalline and/or crystalline state, and was exhibiting solid-like behavior.

The observed plateau regions and increase in G' and G'' are in direct agreement with the Raman spectral data (Figure 4). In the melt region (~ 190 - 130 °C)⁻¹, the normalized 808 cm^{-1} peak height was near zero and remained unchanged by the decreasing temperature. However, as the PP melt began to crystallize, the normalized 808 cm^{-1} peak height significantly increased and was in unison with the abrupt increases in both G' and G'' . Also, as the PP sample started to crystallize, the total peak area of the CH stretching region decreased rapidly before any measurable growth of the 808 cm^{-1} band was observed. The decrease in intensity in the 3050 - 2800 cm^{-1} spectral region is postulated to be caused by the formation of crystallites in the PP matrix. Crystallites with dimensions on the same order of magnitude as the wavelength of the incident laser (532 nm) would scatter light, thereby creating a loss in the Raman signal intensity of the CH stretching bands. The minimum in the CH stretching profile was directly aligned with the observed crossover between G' and G'' and the maximum slope of the normalized 808 cm^{-1} peak profile. The correlation between changes in the Raman spectral features and the rheological response indicate that the crystallization rate was at its maximum when the crystallite concentration was greatest. After the observed decrease in intensity, the integrated area of the CH stretching region returned to a value close to what was detected in the melt phase.

In order to further evaluate the crystallization process of PP, isothermal crystallization studies were performed at 150 and 138 °C. The PP samples were heated at a minimum of 5 min at 190 °C (to fully melt the specimen), rapidly cooled at 10 °C /min to 10 °C above the crystallization temperature, and then cooled at a slower rate of 2 °C /min until the set crystallization temperature was reached. The crystallization temperature was then held constant for a maximum of 1 h (3600 s) to observe the isothermal crystallization of PP as a function of time. Simultaneous rheology and Raman spectroscopy data were acquired in-situ during crystallization at 138 and 150 °C (Figures 5 and 6, respectively). At both isothermal temperatures, the PP material was initially viscously dominated $G' < G''$ displaying liquid-like behavior. As time progressed, a crossover in G' and G'' was observed; where the moduli increased 2 to 3 orders of magnitude. The crossover at 138 °C occurred at 84 s into the isothermal curing process, while it took 2150 s for the crossover to be observed at 150 °C. After the observed crossover, G' and G'' reached a plateau and the crystallization process was considered stabilized and complete.

Similar to the previous experiments, the rheology and Raman data were in agreement during the isothermal crystallization studies (Figures 5 and 6). The observed increase in the elastic and viscous moduli directly correlates with the increase in the normalized 808 cm^{-1} peak height. Although not shown here, a minimum in the CH stretching band intensity was again observed as the specimen transitioned from the liquid to the solid state.

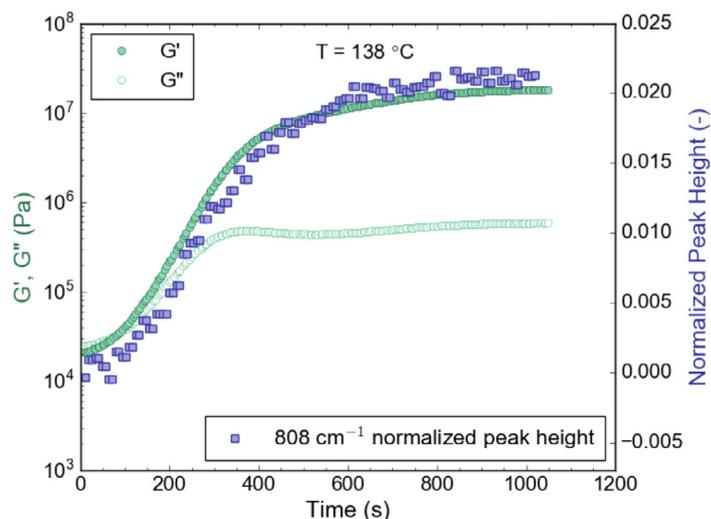


Figure 5: Polypropylene isothermal recrystallization at 138 °C : G' and G'' (filled and open circles, respectively; plotted on the left y-axis) and the normalized 808 cm^{-1} Raman shift peak height (filled squares; plotted on the right y-axis) as a function of time.

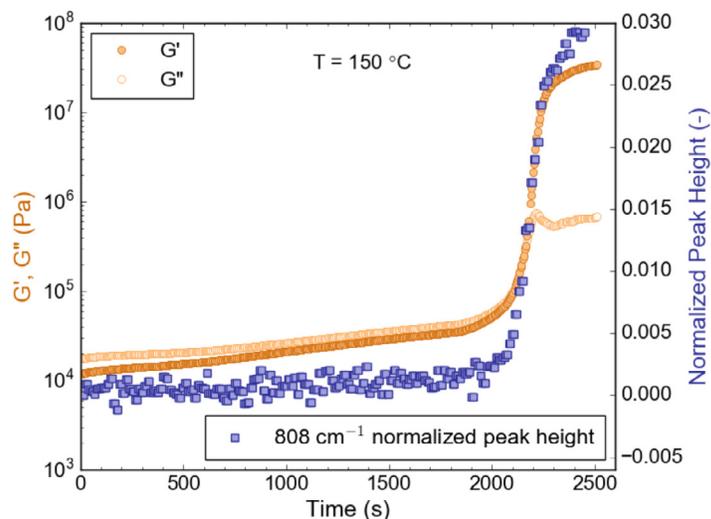


Figure 6: Polypropylene isothermal recrystallization at 150 °C : G' and G'' (filled and open circles, respectively; plotted on the left y-axis) and the normalized 808 cm^{-1} Raman shift peak height (filled squares; plotted on the right y-axis) as a function of time.

Conclusions

A MARS_{XR} system was employed to simultaneously measure the rheology and Raman spectroscopy of polypropylene during the melt-to-crystallization transition process. This multimodal analytical tool allowed the bulk structural properties of polypropylene (G' and G'') to be directly correlated with conformational changes at the molecular level (helical chain vibrations and CH stretching) in real-time. The data revealed that the rate of crystallization reached its maximum (indicated by rapid increases in G' , G'' , and the normalized 808 cm^{-1} peak height) when the crystallite concentration was greatest (signified by a decrease in the overall Raman spectral intensity in the $3050\text{-}2800\text{ cm}^{-1}$ region). The observed correlation between the macroscopic and molecular level measurements exemplifies the unique analytical capability unleashed by hyphenating rheology with Raman spectroscopy. While this work focusses on the melting and crystallization of PP, the underlying principles demonstrated here should be applicable for a wide range of material processes including gelation, polymerization, curing behavior, as well as other shear-induced phenomena.

References

1. A.P. Kotula, M.W. Meyer, F. De Vito, J. Plog, A.R. Hight Walker and K.B. Migler, Review of Scientific Instruments, 87, 105105 (2016); DOI 10.1063/1.4903746.
2. R.A. Khafagy, Journal of Polymer Science: Part B: Polymer Physics, DOI 10.1002/polb

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Rheometer selection guide



Thermo Scientific™ HAAKE™
MARS™ iQ Air Rheometer



Thermo Scientific™ HAAKE™
MARS™ 40/60 Rheometer*



Maximum available temperature range	-40 °C to +400 °C**	-150 °C to +600 °C***
Polymer melt rheology		
Oscillatory amplitude sweeps	Yes	Yes
Oscillatory frequency sweeps	Yes	Yes
Oscillatory time sweeps	Yes	Yes
Oscillatory temperature sweeps	Yes	Yes
Creep and recovery tests	Yes	Yes
Tests with solid specimens		
Dynamic mechanical thermal analysis in torsion with solids clamping tool		Yes
Extensional testing of polymer films with Sentmanant Extensional Rheometer (SER) tool		Yes
Hyphenated techniques		
Rheometry and optical microscopy		Yes
Rheometry and FT-IR spectroscopy		Yes
Rheometry and Raman spectroscopy		Yes

* HAAKE Rheometer Models with different specifications in terms of low torque and max. rotation speed.

** HAAKE MARS iQ Air application setup for testing polymer melts with upper and lower electrical temperature control modules. Lowest available temperature depends on thermostat performance and utilized bath fluids.

*** HAAKE MARS 40/60 with controlled test chamber (CTC) and low temperature option.

HAAKE MARS iQ Air Rheometer for testing polymer melts

Application package order no. 379-0703

Application

Polymers are ubiquitous in our day-to-day life and play an important role in the production of many consumer goods. In their solid state, they are used for example in packaging, clothing and as a component for many composite materials. For these applications, polymers are heated and processed in the molten state. Due to their chemical structure and high molecular mass, polymers exhibit complex flow and deformation behavior. As so-called viscoelastic samples, they possess viscous and elastic properties. Which behavior dominates depends on the molecular structure and the test or process conditions. Understanding the viscoelastic properties of a polymer in its molten state is essential to define and improve processing conditions as well as to develop products for specific applications.

Rheology is a proven method for analyzing the mechanical properties of polymers in their various state forms. The Thermo Scientific™ HAAKE™ MARS™ iQ Air Rheometer is designed to meet the most demanding requirements in advanced quality control. It allows for performing rheological



tests in Controlled Rate (CR), Controlled Stress (CS) and Controlled Deformation (CD) mode. Its sensitive, yet robust normal force sensor enables an accurate and reproducible gap setting as well as the investigation or compensating of thermal expansion of the tested material.

A dedicated application packages for a comprehensive polymer melt analysis is available. It consists of

- the HAAKE MARS iQ Air Rheometer
- a lower electrical temperature module for cone-plate and plate-plate geometries (TM-EL-P)
- an active upper heating system for performing rheological tests up to temperatures of 400 °C (TM-EL-H)
- a 25 mm parallel plate measuring geometry

Typical samples, recommended measuring routines and materials properties

- Amorphous and partly crystalline thermoplastics, thermo sets, elastomers



Figure 1: HAAKE MARS iQ Air Rheometer with upper and lower electric temperature modules for temperature up to 400° C.

- Oscillatory measurements including amplitude, frequency, time and temperature sweeps
- Creep and recovery tests
- Storage and loss modulus, complex viscosity, melting temperature, crystallinity, damping

Features

- Modular rheometer platform for individual demands
- Easy-to-operate, multilingual Thermo Scientific™ HAAKE™ RheoWin™ Software for beginners and experts, with optional software module for applying Time-Temperature-Superposition (TTS), calculating relaxation time spectra and molecular weight distribution (MWD)

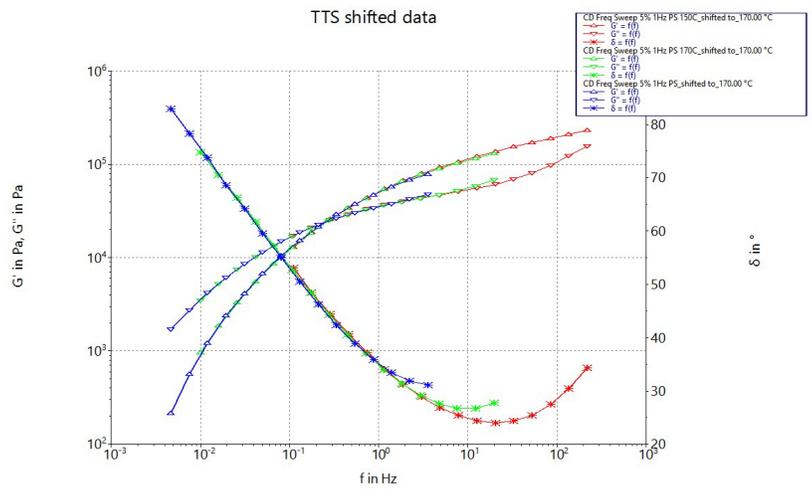
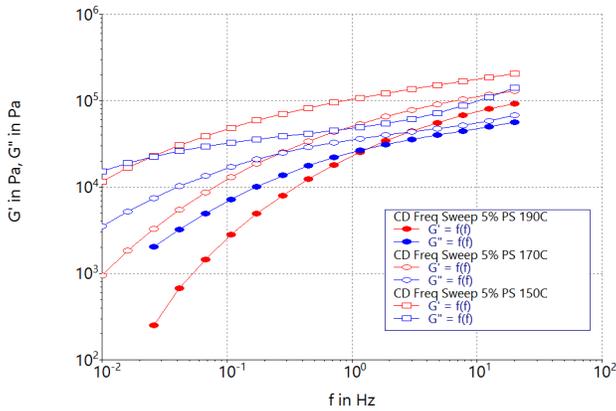


Figure 2: Frequency sweeps of polystyrene melt at three temperatures (left) and TTS shifted data (master curve, right).

Table: Ordering information of the application package

Product	Order no.
Package HAAKE MARS iQ Air Rheometer "Polymers" consisting of:	379-0703
HAAKE MARS iQ Air Rheometer	379-0700
HAAKE RheoWin Software for HAAKE MARS iQ Air Rheometer (single user licence)	098-5077
Holder for guide bar HAAKE MARS iQ series	222-2384
Lower electrical temperature module TM-EL-P	222-1860
Upper temperature module TM-EL-H	222-2353
Lower plate TMP 25 for temperature modules	222-1928
Plate rotor P25 Ti with "Connect Assist" and ceramic shaft	222-2105
Necessary accessories	
Compressed air with standard filter unit	222-1211
Compact compressor model Silent incl. filter unit (230 V)	222-2288
Compact compressor model Silent incl. filter unit (115 V)	222-2289

- State-of-the-art user interface with multifunctional 7" touchscreen for instrument operation and the execution of Standard Operating Procedure (SOP) with a fingertip
- "Connect Assis" functionality with quick coupling and automatic recognition of measuring geometries and temperature control modules
- Sensitive normal force sensor for applying and measuring positive and negative normal forces

Product	Order no.
Optional accessories	
Pressure reducer set for cooling with compressed (for performing tests above room temperature)	222-1784
Thermostat for faster cooling and measurements at and below room temperature. Different models available.	
Optional HAAKE RheoWin Software modules for polymer analysis:	
Time Temperature Superposition	098-5045
Relaxation Time Spectra	098-5066
Molecular Weight Distribution	098-5067

Reference

1. Compendium C004 HAAKE MARS Rheometers for polymer analysis

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Application packages for polymer analysis - HAAKE MARS Rheometer

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.



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

Typical samples, recommended measuring routines and materials properties

- Amorphous and partly crystalline thermoplastics, thermosets, elastomers
- Oscillatory measurements including amplitude, frequency, time and temperature sweeps
- Storage and loss modulus, complex viscosity, glass transition temperature, melting temperature, crystallinity, molecular weight (distribution), extensional properties



Figure 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.

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
- For standardized measurements e.g. according to ISO 6721-10:2015

Table: Ordering information of the application packages

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

Product	Order no.
HAAKE MARS 60 Rheometer for polymer solids and melts from -150 °C up to 600 °C	379-0630
includes:	
HAAKE MARS 60 Rheometer with mounting rods and HAAKE RheoWin Software	379-0600
Standard filter unit	222-1211
Controlled Test Chamber	222-1913
Low Temperature Option	222-1720
Lower holder for exchangeable plates (incl. temperature sensor)	222-2251
P20 lower plate	222-2143
Rotor P20-CTC/Ti with "Connect Assist" and ceramic shaft	222-2223

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. Oldörp Klaus, Nijman Jint, Küchenmeister Cornelia, "Measurements on selected (semi)-solids in a wide temperature range using new solid clamps", Thermo Fisher Scientific Application Note V220.
2. Plog Jan Philip, Meyer Fabian, Schulz Ulrich, "Characterizing long-chain branching in polyethylene with extensional rheology", Thermo Fisher Scientific Application Note V261.
3. Küchenmeister Cornelia, Soergel Fritz, "Thermo Scientific HAAKE RheoScope module: image acquisition at (very) high shear rates using a stroboscope light source", Thermo Fisher Scientific Product information P040.

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Controlled Test Chamber (CTC) for HAAKE MARS Rheometers

Authors: Cornelia Küchenmeister-Lehrheuer and Fabian Meyer

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 (Figure 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 (Figure 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 (Figure 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



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

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 (Figure 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.

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 (Figure 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
- Coaxial cylinder measuring geometry for testing low viscous fluids at very high temperatures

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

* with low temperature option

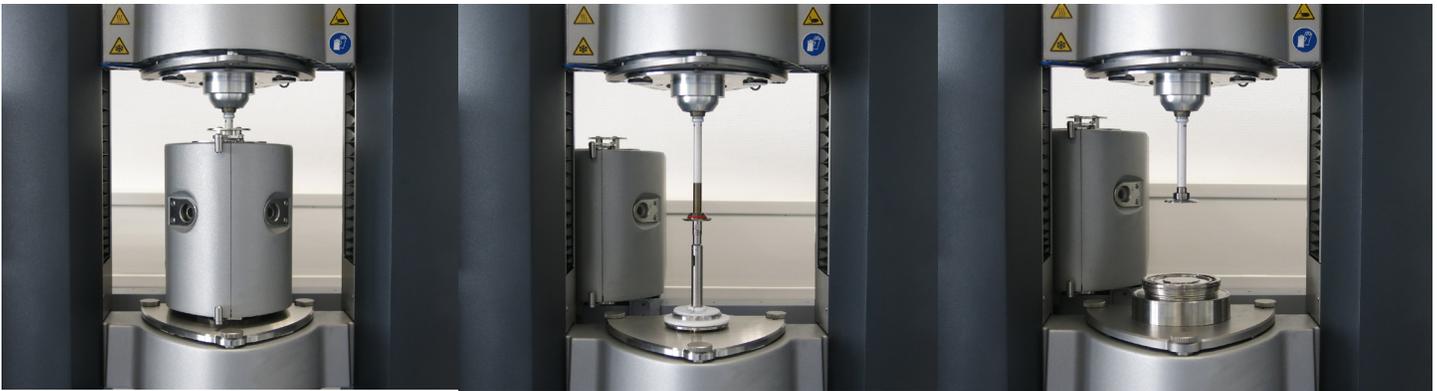


Figure 2: HAAKE MARS Rheometer with Controlled Test Chamber (CTC) in measurement position (left); in parking position (middle); in parking position and Peltier temperature control modules for parallel plates and cone & plate mounted (right).



Figure 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).

Table 1. Ordering information

Product	Order no.
Controlled Test Chamber for temperature range 30 °C up to 600 °C, if input voltage is not 230 V transformer is needed (222-1768)	379-0600
Mounting rods (needs to be ordered for HAAKE MARS 40 Rheometer, in HAAKE MARS 60 Rheometer included)	222-1914
Option "low temperature" with low energy consumption for temperatures down to -150 °C	222-1730
Dewar vessel (50 l)	222-1733

Table 2. Standard measuring geometries- lower plates

Product	Order no.
Lower holder for exchangeable measuring geometries incl. temperature sensor 222-1769	222-2251
Rotor insert P35-CTC/St	222-2141
Rotor insert P25-CTC/St	222-2142
Rotor insert P20-CTC/St	222-2143
Rotor insert P8-CTC/S	222-2144

Table 3. Upper rotors with "Connect Assist" and ceramic shaft

Product	Order no.
Plate P35-CTC/Ti (CS)	222-2221
Cone C35 4°-CTC/Ti (CS)	222-2225
Cone C35 1°-CTC/Ti (CS)	222-2226
Plate P25-CTC/Ti (CS)	222-2222
Plate P20-CTC/Ti (CS)	222-2223
Cone C20 1°-CTC/Ti (CS)	222-2227
Plate P8-CTC/Ti (CS)	222-2224

Table 4. Disposable measuring geometries

Product	Order no.
Lower holder for exchangeable measuring geometries incl. temperature sensor 222-1769	222-2251
Adapter P2 (CS) Adapter for disposable plates D PXX /Al (upper adapter for CTC) with "Connect Assist" and ceramic shaft	222-2151
D P8 /Al Plates D P8 /Al (40 pcs., as lower or upper plate)	222-2152
D P10 /Al Plates D P10 /Al (40 pcs., as lower or upper plate)	222-2153
D P20 /Al Plates D P20 /Al (40 pcs., as lower or upper plate)	222-2154
D P25 /Al Plates D P25 /Al (40 pcs., as lower or upper plate)	222-2155
D P35 /Al Plates D P35 /Al (40 pcs., as lower or upper plate)	222-2156

Table 5. Recommended accessory - Collection device for disposable plates

Product	Order no.
For P20 mm Al Ex	222-1778
For 25 mm Al Ex	222-1779
For 35 mm Al Ex	222-1787

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Solids clamping tool for Dynamic Mechanical Thermal Analysis (DMTA)

In combination with HAAKE MARS Rheometers

Authors: Cornelia Küchenmeister-Lehrheuer, Klaus Oldörp and Fabian Meyer

Keywords

Dynamic Mechanical Thermal Analysis (DMTA), Solids clamping tool, HAAKE MARS Rheometer, 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 losing 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.

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



Figure 1: HAAKE MARS Rheometer with controlled test chamber and solids clamping tool.

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.

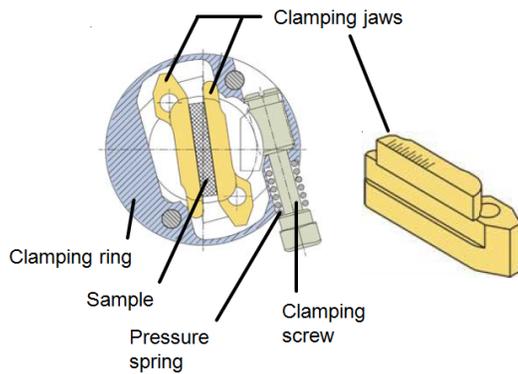


Figure 2: Technical drawing of solids clamping tool.

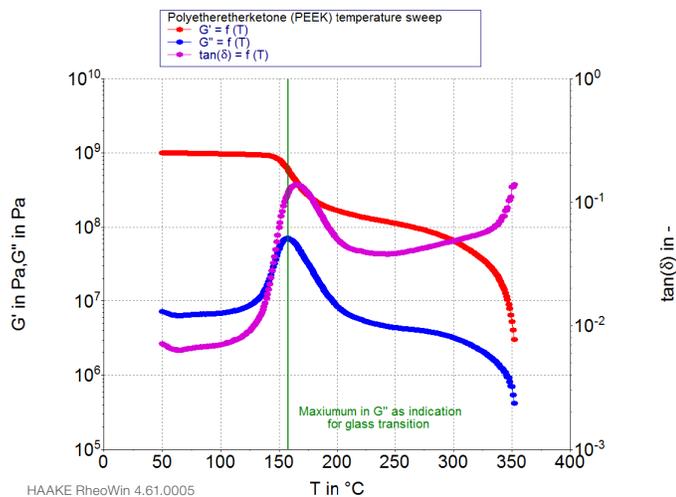


Figure 3: Dynamic mechanical analysis with Polyether ether ketone (PEEK).



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

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).

Table 1. Ordering information - Solids clamp

Product	Order no.
For HAAKE MARS Rheometer models I, II, III	222-1734
For HAAKE MARS models 40 & 60 with "Connect Assist"	222-2231

Table 2. Ordering information - Optional accessories

Product	Order no.
Jaws for soft samples (4 pcs.)	222-1781
Jaws for medium samples (4 pcs.)	222-1782
Jaws for hard samples (4 pcs.)	222-1783
Triangular adapter plate for CTC measuring geometries	222-1856

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Sentmanat extensional rheometer (SER) for the HAAKE MARS Rheometer

Authors: Cornelia Küchenmeister-Lehrheuer and Fabian Meyer

Keywords

HAAKE MARS Rheometer, Controlled test chamber (CTC), 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 addition to the measurement of the 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.

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 1: SER3 tool with HAAKE MARS Rheometer and CTC.

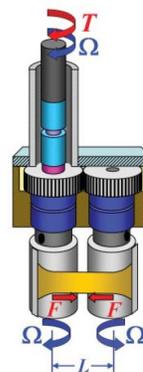


Figure 2: Schematic setup of the SER tool (image taken from: http://www.xinst.com/products_specs.htm).

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).

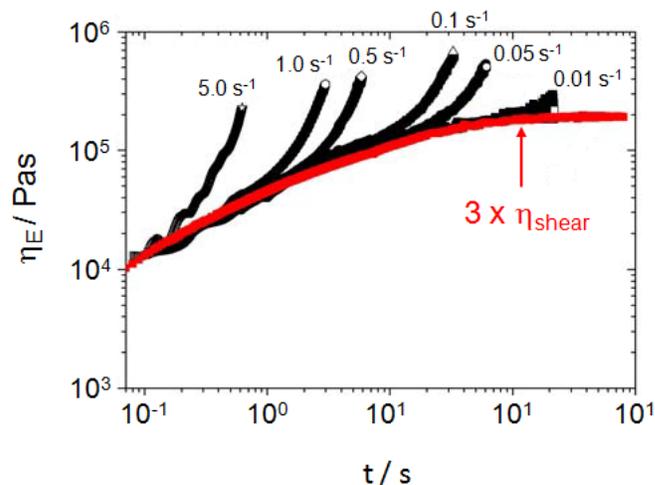


Figure 3: Extensional viscosity as a function of time for branched LDPE at different extensional rates.

Table 1. Specification SER - Extensional Rheology System

Property	Value
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

Table 2. Specification sample

Property	Value
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

Table 3. Ordering 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:

Product	Order no.
SER tool G2 incl. adapter for HAAKE MARS II Rheometer	222-1935
SER tool G2 incl. adapter for HAAKE MARS I/III Rheometers	222-1803
SER tool G3 incl. adapter for HAAKE MARS 40/60 Rheometers with “Connect Assist“	222-2176
Triangular base plate with lower holder and Pt100 sensor as accessory for SER tool (for all HAAKE MARS rheometer models)	603-1205

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Spectroscopical insight into rheology with the Rheonaut module

In combination with HAAKE MARS Rheometers

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Keywords

Rheonaut, HAAKE MARS Rheometer, 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™ 20 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, Figure 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.



Figure 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 (Figure 4) to set the polarization direction for the infrared radiation both parallel and perpendicular to a fixed reference direction.

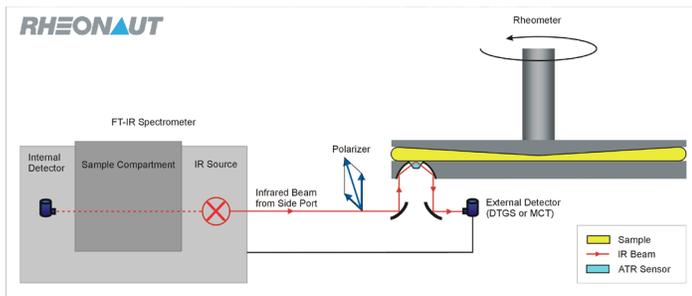


Figure 2: Scheme of the Rheonaut module.

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.

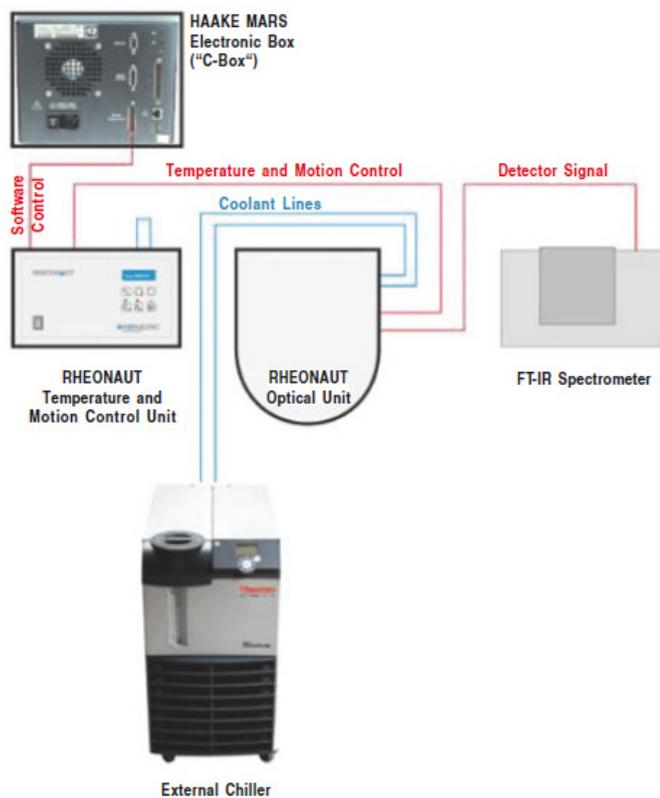


Figure 3: Peltier temperature module for Rheonaut with extended temperature range down to -20 °C.

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.



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

The Rheonaut module consists of an optical unit (ready to enable purging) with integrated detector with preamplifier, temperature control unit and a HAAKE MARS Rheometer 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 Scientific Nicolet iS20 or iS50)
- HAAKE MARS 40 or 60 rotational rheometer
- Cone or plate rotor for HAAKE MARS Rheometer

*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

Table 1. Ordering information

Product	Order no.
Rheonaut module incl. frame extension for e.g. Nicolet iS10 (603-0751) or iS50 (603-0754)	603-0600
Lower ATR plate (exchangeable), electrical controlled heating	603-0601
Lower ATR plate (exchangeable), Peltier controlled heating and cooling	603-0604
Electrical temperature module TM-EL-H for upper geometries for HAAKE MARS 40 & 60 Rheometers for temperatures up to 400 °C, holder 222-1902 and safety ring 222-2271 required	222-2172
DTGS detector	603-0607
MCT detector, for fast spectra acquisition trigger box 603-0886 required	603-0606
FT-IR spectroscopy tool for HAAKE RheoWin Software	098-5061

Table 2. Ordering information - Manual Polarizers

Product	Order no.
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.	603-2133

Table 3. Ordering information - Rotors with “Connect Assist” and ceramic shaft, e.g.

Product	Order no.
Rotor P60/Ti	222-2063
Rotor P35/Ti	222-2089

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Thermo Scientific HAAKE MARS_{xR} RheoRaman System

Deepen materials understanding through multi-modal analysis

Product description

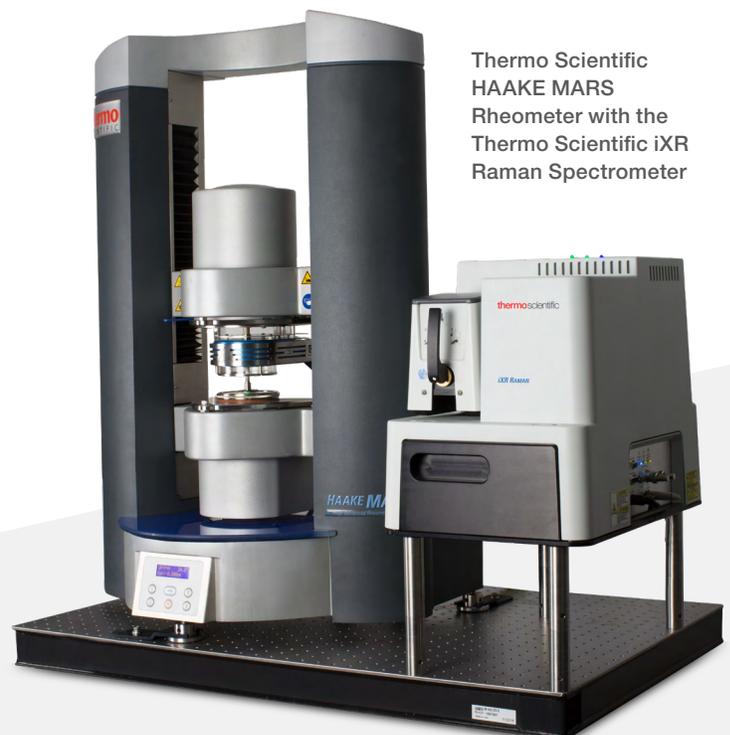
- The integration of a Thermo Scientific™ HAAKE™ MARS™ Rheometer and the Thermo Scientific™ iXR™ Raman Spectrometer
- Collect simultaneous rheological and Raman data
- Rheometry tells us what, while Raman spectroscopy tells us why
- The rheometer discloses how a sample behaves under given stress or strain
- Raman spectroscopy provides positive chemical identification and a spectral fingerprint unique to a material, and also reveals morphology and structural changes during phase transitions
- Unambiguous correlation of results because they are collected on the same sample, at the same time, under the same conditions
- Saves time compared to sequential measurements on two different instruments

Applications

- Advanced polymeric materials
- Pharmaceutical hotmelts
- Food and cosmetic emulsions
- Coatings
- Adhesives

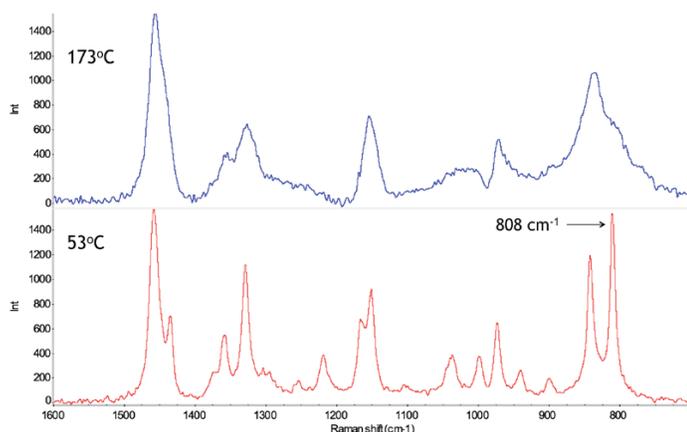
Key benefits

- Obtain real-time insight into molecular changes that drive a shift in rheological behavior
- Obtain deeper insight into phase transitions, crystallization, and product stability
- Correlate rheological properties and molecular changes on the same sample under identical conditions
- Increase information content while saving time

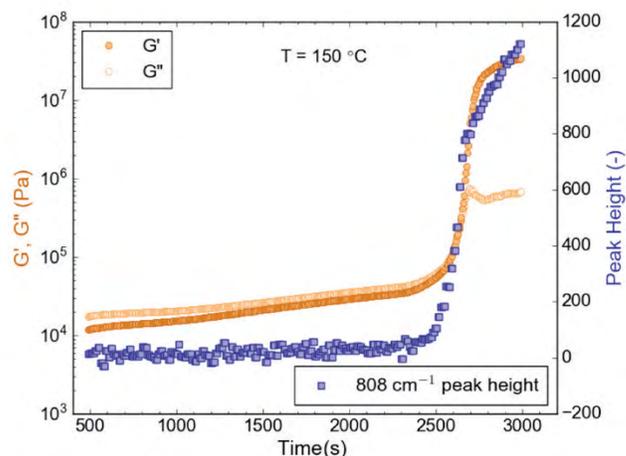


Thermo Scientific
HAAKE MARS
Rheometer with the
Thermo Scientific iXR
Raman Spectrometer

Tracking high density polyethylene crystallization using the HAAKE MARS_{XR} RheoRaman System



Raman spectrum of the molten (top) and crystalline (bottom) states of polypropylene, measured on the MARS_{XR} Rheo-Raman System during a rheological measurement. The band at 808 cm⁻¹ is due to the skeletal deformation of helical chains within the crystal, and its intensity can be used as a measure of crystallinity of polypropylene.



Shear storage modulus (G'), shear loss modulus (G'') and the 808 cm⁻¹ Raman shift peak height as a function of time during the isothermal recrystallization of polypropylene measured on the MARS_{XR} Rheo-Raman System. G' and G'' were obtained from the MARS Rheometer. The 808 cm⁻¹ peak height was determined from the iXR Raman spectra.



Order information

912A0908	iXR Spectrometer Mainframe	
840-294300	HAAKE MARS _{XR} RheoRaman Interface Kit	
Select at least one of:		
840-285900	785 nm High Brightness	Laser Kit
840-286000	785 nm High Power	Laser Kit
840-285600	532 nm High Brightness	Laser Kit
840-285500	455 nm High Brightness	Laser Kit

Order information

379-0600	HAAKE MARS Rheometer
222-2313	RheoRaman Module
222-1817	20x Long Working Distance Objective
222-1812	Lower glass measuring plate
222-2089	Plate 35 mm with ceramic shaft (or alternate rotor if required)
222-1897	Temperature module power supply (2 required for high temperature version)
For high temperatures:	
222-2172	Electrical temperature module TM-EL-H
222-1902	Holder for TM-EL-H

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