High throughput rheology for polymers

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Shortened product developments cycles, increased quality control requirements and high sample throughput in synthesis, compounding, or formulation lead to a constantly increasing demand for rheological measurements. An automated system for the rheological evaluation of polymer melts is described wherein all facets of sample handling and characterisation are defined. The quantifiable, data drive benefits of this automated system are presented.

Before plastic parts are brought into the final form they are molten into the liquid state for processing. Rheological techniques reveal valuable information on the process behaviour of polymer melts. Moreover, structural information like molar mass distribution, degree of crosslinking or branching as well as crystallisation effects are related to the rheological behaviour of polymeric systems. Mostly oscillatory measurements with rotational rheometers and parallel-plate geometries are used for these investigations. Mounting an additional linear drive in the rheometer and using solid fixtures DMTA (Dynamic Mechanical Thermal Analyses) measurements are possible as well. Such tests allow to characterise the temperature dependence of the polymer samples and offer insight into parameters like secondary relaxation processes, glass transition temperature, extend of the rubbery plateau, cross-linking and melting point.

Shortened product developments cycles, increased quality control requirements and high sample throughput in syntheses, compounding, or formulation lead to a constantly increasing demand for rheological measurements. Increased throughput and reduced operator presence time in front of the instrument is therefore essential for an efficient work process. One way to reduce the time required for the operator to prepare and perform a test is to employ a sophisticated control system for the rheometer and an intuitive user interface for the software. For example, the rheometer software can be configured to run complex measurement routines including steps such as moving to measurement position or data analysis automatically. Preconfigured measuring jobs and the resulting data can be connected and controlled via an interface to a laboratory information and management system (LIMS). Together with the data storage chips, with which all measuring geometry and temperature control units and equipped and which contain all relevant data, including the unique serial number, a high degree of automation and error-free documentation is achieved.

With such an approach, the test itself can be preconfigured and then run fully automatically, including the analyses of the data. However, sample must be loaded before and the fixtures must be cleaned after the test, which often takes the longest time during which the rheometer is idle. In addition, loading and cleaning requires frequent user interaction when multiple samples are to be run.

Although high-throughput technologies are used in a wide range of testing applications and recently reviewed for design and development of formulations [1], such attempts are scarce in the case of rheological measurements.

For example, microrheological techniques have been employed to measure aqueous block copolypeptide solutions [2]. A combinatorial squeeze-flow setup has been described for the rheological characterisation of asphalt [3]. A prototype consisting of an array of Couette cells with embedded permanent magnets moved by an oscillating magnetic field was reported that can apply a uniform force to many samples [4]. A system utilising the transient flow of a complex fluid through pipettes, based on the analysis of the mass flow behaviour and the modelling of the pressure profile along the tips of multiple pipettes, was proposed for viscosity estimations and shown to be accurate for Newtonian liquids [5]. Recently, high-throughput measurements of bulk mechanical properties using the concept of centrifugation were proposed [6]. Although these techniques are valuable for certain applications, they are often limited to measuring the viscosity of a narrow range of samples and do not provide the flexibility and range of testing capabilities offered by rotational rheometers. The limitations of existing solutions for automated and combinatorial rheology resulted in the development of a first fully robotically operated rotational rheometer [7].

Several high throughput solutions based on standard rotational rheometers and the standard environmental control units have now been developed to enable all rheological test capabilities, commonly used in rheology laboratories. They range from a standardised benchtop unit for concentric cylinder geometries, to a more generally adaptable floor-based system for cone-and-plate and parallel-plate geometries including an automatic trimming tool, to scalable robotic systems. This can include a fully automated fluid handling, sample preparation, and geometry cleaning and can be combined with a variety of additional measurements techniques.

For polymer melt applications all relevant steps such as loading clean geometries in the rheometer, placing sample discs on the bottom plate, or removing the used geometries are executed by six-axis robotic arm. An essential step for preparing a sample in a cone-and-plate or parallel-plate geometry is the trimming of excess material after lowering the geometry. An automated trimming tool, in which a blade is rotated around the geometry, provides accurate and repeatable trimming results, leading to better reproducibility of rheological measurements compared to manual trimming by experienced users.

High-throughput rheometer for concentric cylinder geometries

Figure 1 shows a benchtop automation system, which includes a rheometer with a temperature chamber for concentric cylinders, a three-axis handling system with a cup gripper, a cleaning unit for the upper measurement geometry with hot- and/or cold-water brushes and drying with pressured air, and sample racks for up to 54 samples. Optionally, a code-reader and handheld scanner, a tempered sample rack, a pre-tempering unit, and pH-measuring station with cleaning unit can be added. Instead of water cleaning of the measuring geometry, an advanced cleaning unit is available that uses cleaning detergents. Measuring bobs with various diameters, spindles or stirrers can be employed. A complete process and data integration into the customer's data network are possible, and a pharma data security package ensures full traceability and transparency of each step of operation.

Figure 1: High-throughput rheometer for concentric cylinder geometries with a 3 axis handling system.

In a typical workflow for an automatic operation, the cup gripper picks a cup from the rack and held over a scanner with an integrated code reader. Now, the automated benchtop rheometer has all the sample information ready and can either place the cup into the takeover unit, which finally positions the cup in the rheometer or place it in a pre-tempering chamber. As soon as the previous measurement is finished and the rheometer is ready for the next sample, the cup is retrieved from the pre-tempering station and inserted in the temperature control unit of the rheometer where it is firmly fixed. As soon as the cup is in position, the measuring head of the rheometer moves down and brings the measuring bob into the measuring position and a predefined rheological measuring profile is started. The test routine can include any measurement the rheometer can perform, such as pre-shear, hold time, rotational measurement, oscillatory measurement, or a complex combination of different measurements. If desired, a different test routine can be assigned to each cup. When the test routine is finished, the lifting motor of the rheometer moves the measuring head with the measuring bob upwards. The cup gripper then removes the old sample and returns it to the rack or to a pH station for further analysis.

A cleaning station is brought in, the bob is rotated and cleaned with brushes and cold, hot or a combination of cold and hot water in a predefined manner. After cleaning the bob is dried with compressed air and the cleaning station is removed from the rheometer. For samples that are difficult to clean, a cleaning agent pump can be added to the cleaning unit to ensure effective cleaning of the upper measurement geometry. Now everything is ready for the next measurement, and this entire cycle can be repeated up to 54 times without human intervention.

Many of these fully automated benchtop rheometer solutions have been successfully utilised for measurements of e.g. paints and coatings, personal care products, agricultural chemicals, and dairy products.

High-throughput rheometer for cone-plate and parallel-plates geometries

For paste like samples or polymer melts, or in cases where only small sample volumes are available cone-and-plate or parallel-plate geometries are a better choice compared to concentric cylinders or vanes. In addition, with the fully automated benchtop rheometer the samples must be prepared and placed in the measuring cups before automation.

Since a robotic arm offers greater motion flexibility compared to a three-axis motion system, a six-axis robotic arm with gripper is used in a floor based high-throughput solution for fully automated rheological measurements. This allows the implementation of automation solutions for cone-and-plate and parallel-plate solutions, and provides the possibility for additional automatic sample preparation and loading.

Some of the steps are sketched in *Figure 2* for an implementation for liquid-like samples with cone-and-plate geometries. The sample vials are placed on a rack by the operator and a vial is gripped by the robotic arm for a measurement, the code on the vial is read by a reader and placed in a mixing station for automatic homogenisation. During sample mixing, a clean measuring cone is mounted in the coupling of the rheometer and a clean plate is fixed to the bottom in a Peltier temperature device. The Peltier hood is then closed, the corresponding rheometer routine determines the zero-gap position, and then the Peltier hood and the rheometer head with the upper measuring geometry are moved into the loading position. After mixing the sample, the vial is placed in a decapper, the cap is removed and the required amount of sample is taken off in a disposable pipette or syringe. The sample is then dispensed precisely onto the bottom plate and with the exact volume required for the respective measurement geometry. The measuring cone is subsequently brought into the measuring position and the automated sample trimming tool performs the trimming process in order to achieve highest reproducibility on the measurement results. The Peltier hood is then closed and the rheological measurement begins after temperature equilibrium has been reached.

During the measurement, an automated pH-measurement can optionally be performed on the same sample vial. As soon as the rheological measurement is completed, the Peltier hood and the measuring head are moved back to the loading position and the measuring cone and the base plate are placed in a cleaning station tailored to the respective sample type and are cleaned according to a predefined routine and dried afterwards. To reduce rheometer downtime, two sets of measurement geometries can be used, so that while one set is being cleaned the other can be used for the measurement.

Figure 2: Attaching the cone, dispensing the sample, and loading in the cleaning unit for a high throughput rheometer with a six-axis robotic arm and a rheometer equipped with a Peltier temperature device and cone-plate geometries.

High-throughput rheometer for polymer melts

While for liquid-like materials the specimens can be dispensed onto the bottom plate and the measurement geometries can be cleaned relatively easily after the measurements, for materials with high viscosity, paste like samples, or polymer melts, which are typically solid at room temperature, different strategies for perfect loading of the specimen in the rheometer and providing clean geometries are required.

Figure 3 shows a high throughput system that includes a sample storage rack and a rack for storing measuring geometries.

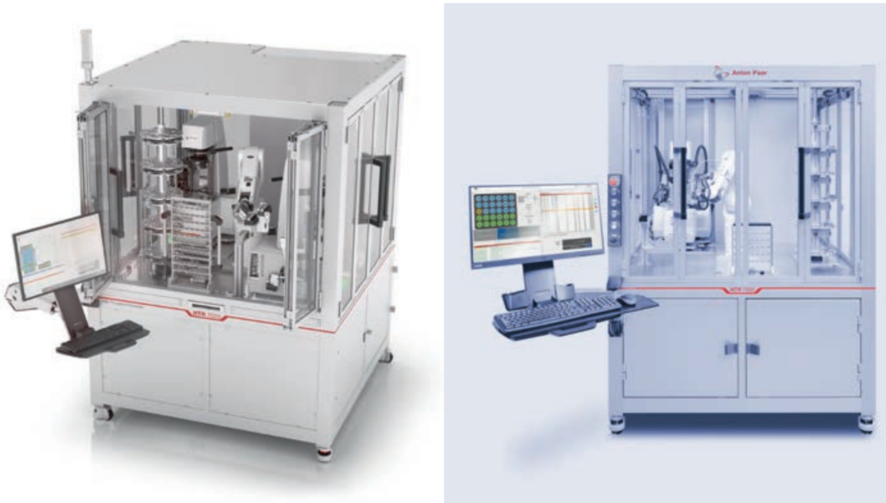

Figure 3: High-throughput rheometer for polymer melts with a rheometer and an automatic trimming tool, a robotic arm, and storage racks for sample discs and sets of measurement geometries.

As clean geometries are required for each new measurement, in an implementation for polymer melt samples, 30 pairs of parallel-plate measurement geometries, consisting of a bottom plate and an upper measurement geometry, are stored in a rotary vertical storage rack. After loading the geometries into the rheometer, the temperature control unit is closed and after reaching temperature equilibrium at the desired temperature, the zero-gap position is established by the corresponding rheometer routine. The prepared solid-like polymer discs, which are stored in a sample layer rack, are gripped with a vacuum gripper and positioned centrally on the bottom plate. Now the sample is heated up to the measurement temperature and trimmed, and then the rheological measurement starts according to the predefined order. After the measurement is completed, the measurement geometries are transferred back to the storage rack.

An essential step in preparing a sample in a cone-and-plate or parallel-plate geometry is removing the excess material by trimming the sample after lowering the geometry. Only trimming ensures the correct loading conditions with an ideal sample shape at the edge. To enable trimming in an automated situation, a special device is used where a blade is brought in contact to the edge of the geometry at an angle and rotated around the entire diameter of the sample by a drive motor and gear wheels [8]. This automated trimming tool as shown in *Figure 4*, can be incorporated in Peltier and electrically heated base plates, which in combination with the corresponding tempering control hoods ensure good temperature control. To achieve the best trimming results, the blade is mounted within the tempered sample environment and is therefore at the same temperature as the sample before trimming. For trimming, the hood is opened and trimming is started. After trimming the blade is separated from the geometry, a photo is taken by a camera to document the trimming result and the hood is then closed again. The whole process is fairly quick, keeping the sample close to the set temperature and reducing the time to reach temperature equilibrium after trimming. After the measurement the used blade is transferred to a waste box where all disposable blades are collected after use. A new blade is picked up from a trimming blade rack that stores the disposable trim blades.

Results of the trimming process lead to a very good reproducibility of the rheological measurements. In an extensive internal study on various polymer materials, it was found that automatic trimming using the trimming tool increased measurement accuracy significantly compared to manual trimming by the same experienced operator. Since different operators may trim slightly differently with manual trimming, the actual increase in measurement quality is even greater. In addition, the camera snapshots after trimming allow documentation of the trimming results and ensures complete traceability of the process trimming process.

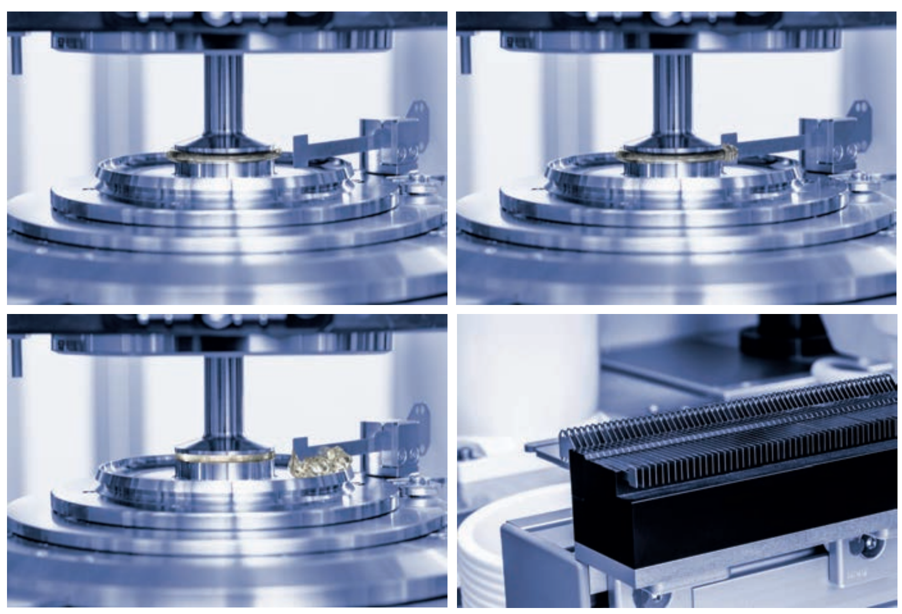

Figure 4: Blade of the trimming tool before, during and after the trimming process; and blade rack with disposable blades.

Discussion

An automated robotic system for polymer melts as described was used, for example, for the rheological characterisation of polypropylene/polycarbonate blends [9]. The experiments were carried out at 230°C with the electrical heated temperature device using parallel-plate geometries with 25 mm diameter and a gap of 1 mm. The high productivity and the automatic operation of the robotic system made it possible to screen the different prepared blends in amplitude sweeps at a fixed frequency to identify the linear viscoelastic regime (LVE) for all different blends before carrying out the actual frequency sweep measurements on a fresh specimen of the same polymer blend and to measure all different samples characterised in at least triplicate to avoid issues with sample inhomogeneity. Various polyethene and polypropylene melts are among the polymers that were successfully analysed using the robotic high throughput rheometer. To reduce robotic arm downtime and further boost productivity, two rheometers can be integrated into the system, so that while one rheometer is running the test, the other rheometer can be prepared with the next specimen.

Instead of using new geometries sets for each specimen, an automated cleaning method using a brass brush would avoid cleaning of all geometries after a full run with measurements of all samples is completed and will be implemented in a next version of the device for polyethylene melts.

For samples that cannot be prepared as solid discs at room temperature, such as past-like materials or bitumen, the samples can be prepared and placed on the bottom plates and stored in a rack. The sample is then transferred to the rheometer together with the bottom plate. In such a situation, an individual determination of the zero-gap position for each set of measurement geometries is not possible, which might lead to an extra error, but which is rather small for parallel-plates. All sequential steps including trimming are the same or similar to the case of polymer melts.

The robotic high throughput rheometer has been configured for polymer melts, adhesives and all kind of samples from personal care industry.

With a high-throughput rheometer based on a robotic arm, all steps throughout the entire automation process can be individually configured in order to match the desired measuring task in the most productive and time efficient manner possible and to provide rheological measurement results with highest reproducibility, while ensuring full traceability of all details of the entire process.

Conclusions

With a high-throughput rheometer based on a six-axis robotic arm, all steps throughout the entire automation process can be individually configured in order to match the desired measuring task in the most productive and time efficient manner possible and to provide rheological measurement results for polymer melts with highest level of reproducibility. Complete documentation and traceability of all details of the entire process, as well as data, is guaranteed, while productivity is significantly increased compared to manual operations.

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