

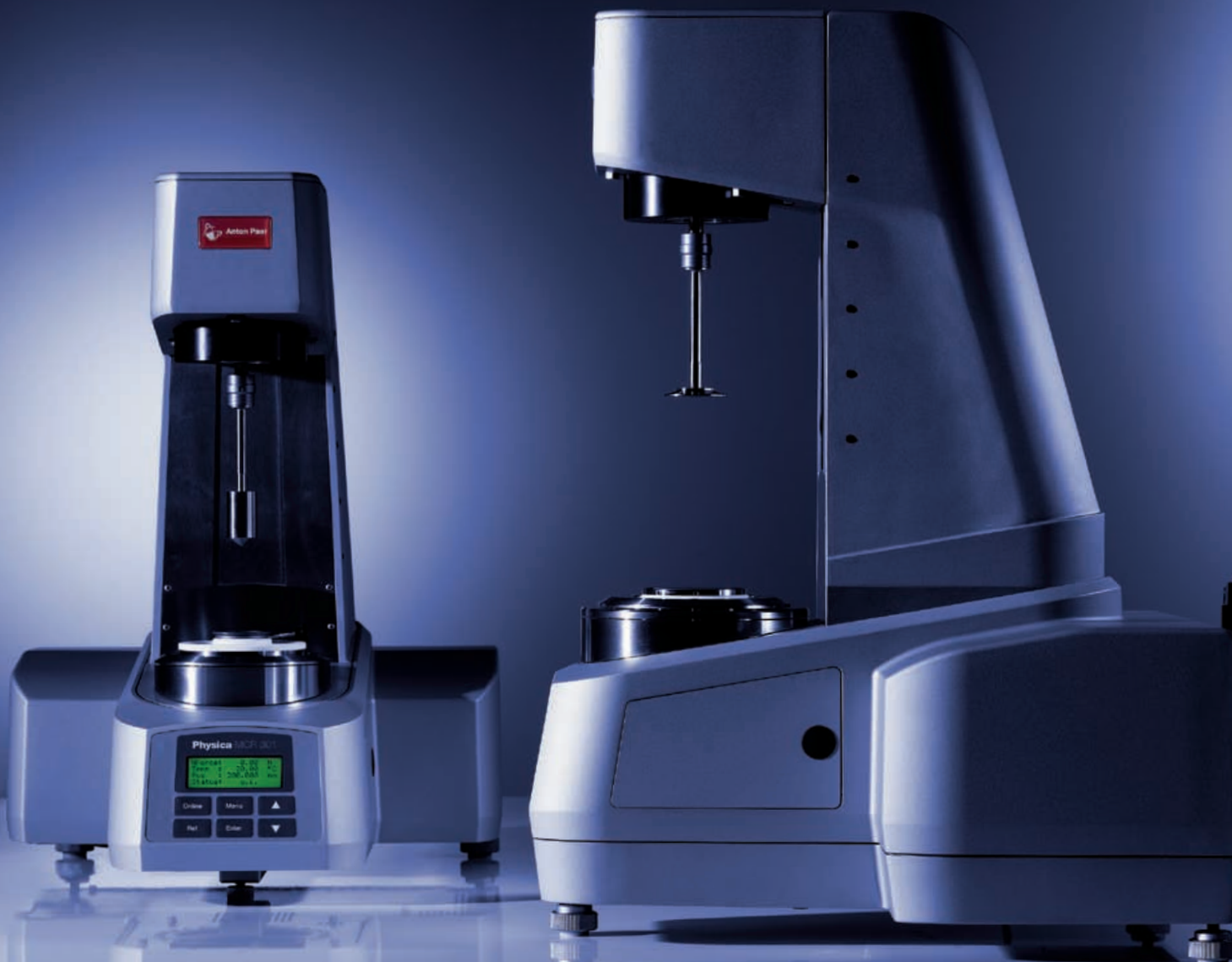


Anton Paar

Physica MCR

The Modular Rheometer Series

::: Intelligence in Rheometry



Physica MCR

Modular Compact Rheometer

At Anton Paar we have a close relationship with our customers, are constantly searching for answers and pushing back physical and technical boundaries. We enjoy the challenge of research and development and take pride in our achievements. The result: customers receive instruments produced to the highest level of technical perfection, tailored to meet their special needs.

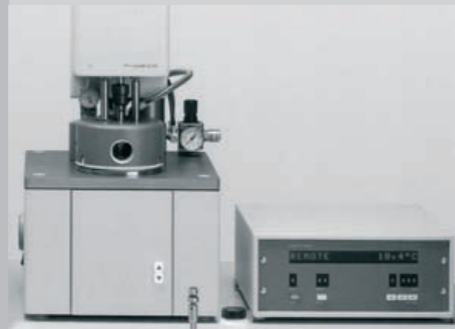
Key factors in our success:

- ▶ Highly motivated employees working on their own initiative
- ▶ More than 20% of the yearly turnover invested in R&D
- ▶ Long-term investment in and cultivation of key technologies
- ▶ An international sales and service network
- ▶ Efficient and respectful use of both natural and human resources
- ▶ A flat decision-making structure consisting of responsible teams
- ▶ A charitable foundation as the owner
- ▶ Thorough and continuous training of employees and apprentices

Over the last ten years, the development of Physica rheometers has been characterized by innovation and the continuous integration of new technologies in the design concept. In keeping with our company philosophy, all improvements were made with the customer in mind, whether that be providing additional technical features or making the instruments easier to use. The new Physica MCR rheometer series is the result of this process.

Setting the standard for rheological measurements since its introduction in 1999, the new MCR series raises the bar even higher.

Discover the difference that years of innovation can make!



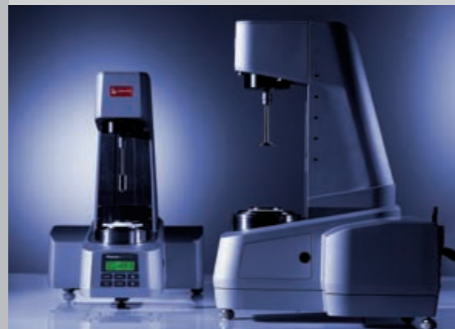
1990
Introduction of Physica Rheolab



1995
Introduction of Physica UDS 200 – First rheometer with EC motor (brushless DC)



1999
Introduction of Physica MCR xx0



2004
Introduction of Physica MCR xx1 with Toolmaster™ and TruGap™ technology



2007
Introduction of High Throughput Rheometer HTR xx1

Physica MCR

The Success Story Continues

The idea

Galileo Galilei's vision is the driving force behind the new Physica MCR rheometer series:

"Measure what is measurable, and make measurable that which is not."

Fulfilling this vision required input from customers, developing the third generation of components, and implementing the use of new technologies. The result: an innovative rheometer series which extends the measuring possibilities to new levels!

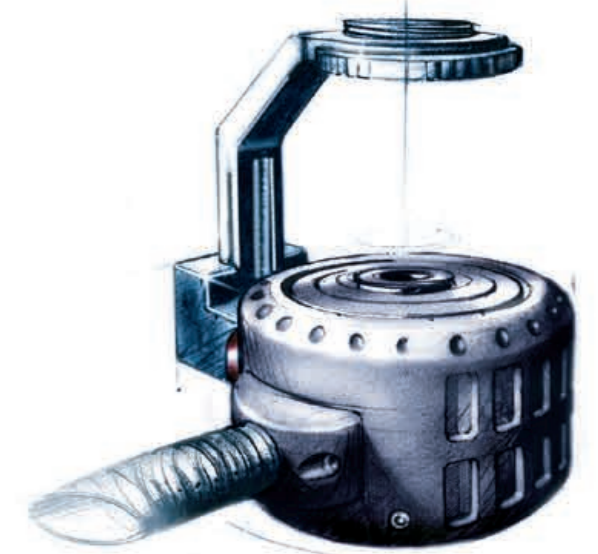
From the basic configuration for quality control to the high-end model for research and development, we have made the new series of MCRs easier to use, more accurate, and have extended the range of applications through the innovative use of new technologies.

The concept

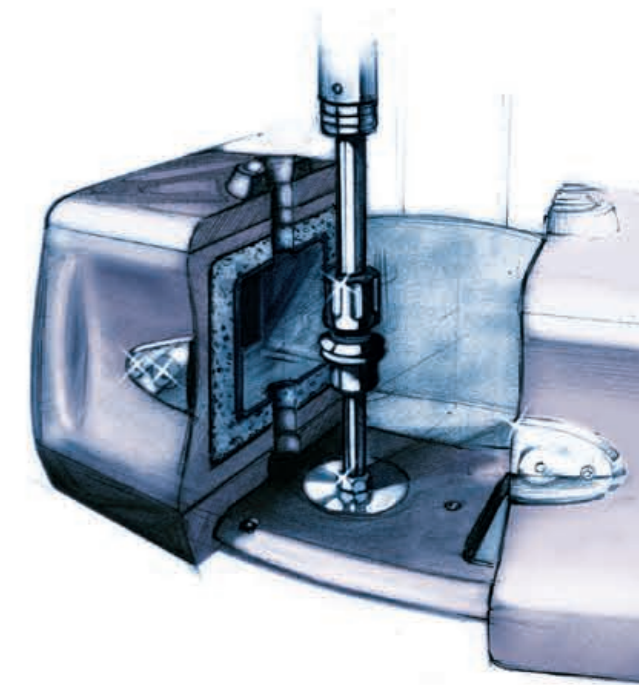
The new Physica MCR series is based on technical concepts at the cutting edge of technology. The revolutionary modular design features innovations such as the Toolmaster™ (US-Patent 7,275,419) – the first automatic measuring and accessory detection system, TruGap™ – a patented measuring gap detection system (US-Patent 6,499,336), an extended torque range, a patented normal force sensor (US-Patent 6,167,752) with improved normal force capabilities, and unprecedented thermal stability of the normal force signal.

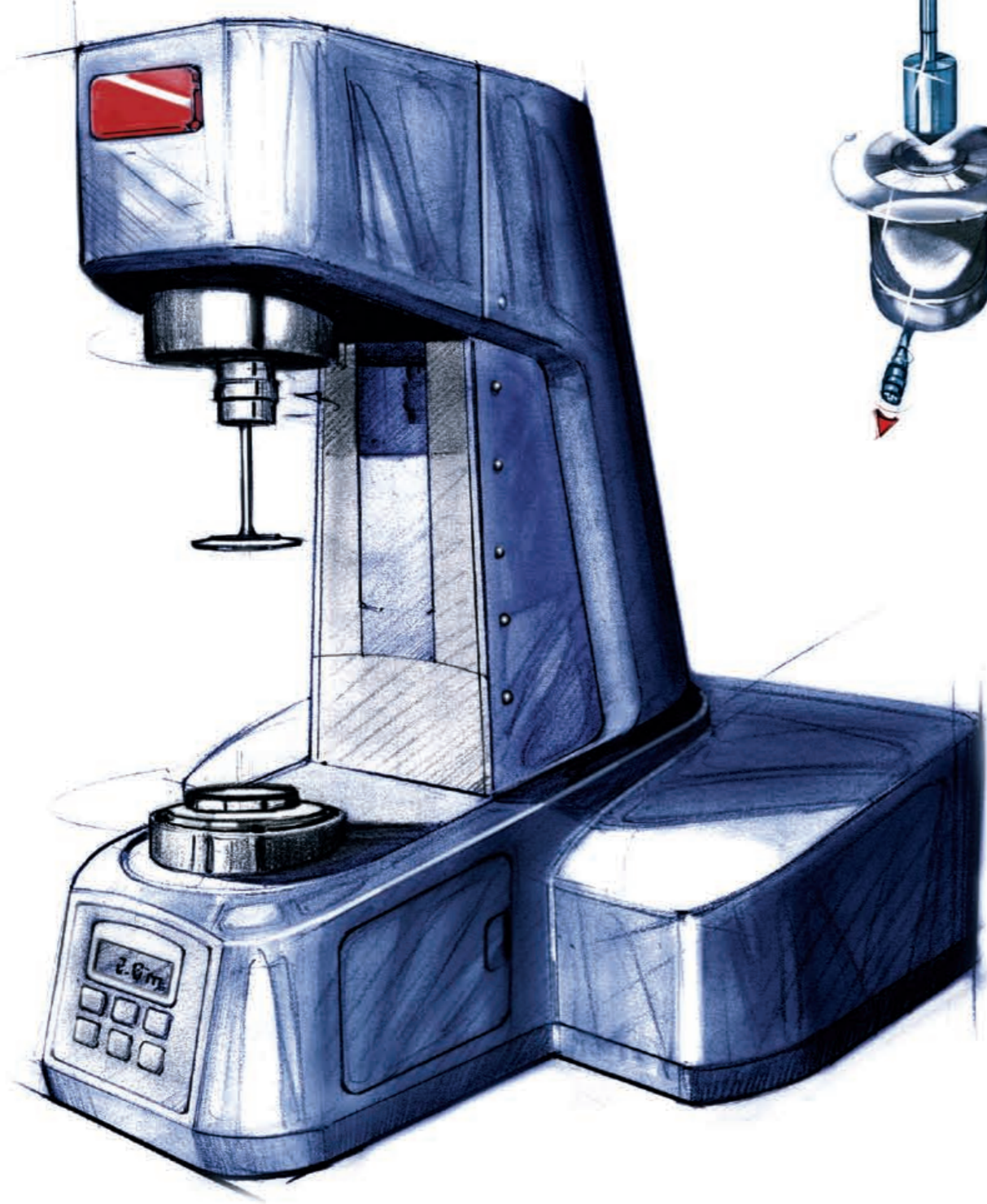
The Physica MCR series incorporates modern design with a compact, low-compliance frame which houses both the mechanical and electronic control components. It provides a wide selection of measurement geometries, interchangeable environmental systems and special accessories.

All the main components, such as the motor, air bearing, electronic control units, and frame have been optimized using state-of-the-art technologies.



LARGE TEMPERATURE RANGES
TEMPERATURE CONTROL SYSTEMS
TO PREVENT TEMPERATURE GRADIENTS WITHIN THE SAMPLE



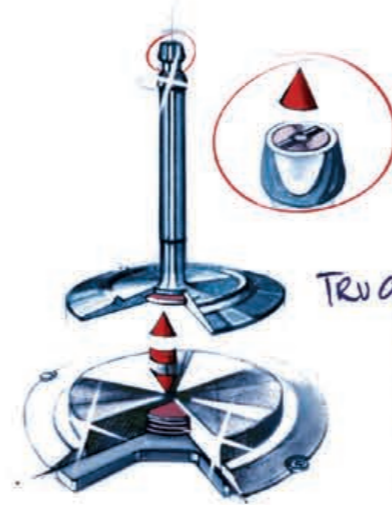


SETS A NEW STANDARD
IN MECHANICAL AND THERMAL STABILITY



TOOLMASTER™

JUST CONNECT THE GEOMETRY
AND ENVIRONMENTAL SYSTEM —
EVERYTHING ELSE IS DONE
AUTOMATICALLY BY THE TOOLMASTER



TRUGAP™

THE SYSTEM
FOR AN EXACT
MEASUREMENT AND
CONTROL OF THE
REAL GAP SIZE



REVOLUTIONARY SYNCHRONOUS MOTOR

WITH IMPROVED EFFICIENCY
LARGER TORQUE RANGE AND
FASTER RESPONSE TIMES



The Technologies

Simple and sophisticated: the housing and frame

Ergonomics and functionality were the major design goals behind the compact, modern housing and frame. All the mechanical and electrical control components are incorporated into one single unit.

- ▶ Fast and simple exchange of environmental systems and accessories
- ▶ Integrated instrument requiring minimum laboratory space; easy installation
- ▶ Extremely rigid and stable frame for optimized mechanical and thermal stability
- ▶ Machined to perfection for durability and longevity
- ▶ Large working area provides optimal access for sample loading and trimming
- ▶ Easy to clean

High resolution: the optical encoder

A high-resolution optical encoder using data oversampling technology enables precise measurements of the angular deflection. This, combined with our proprietary real time position control in oscillation (DSO), provides the ability to control oscillatory strains as low as 100 nanorad – important for studying material with delicate structures. There is no limit to the upper value of the amplitude.

Unrivaled precision: the air bearing

Together with the synchronous motor, the new, very rigid air bearing in the Physica MCR 101/301/501 series sets new standards in drift stability and low torque capabilities. A patented normal force sensor (US-Patent 6,167,752) located inside the air bearing performs a capacitive measurement and detects the natural movement of the bearing due to applied normal forces.

Calling on our many years of experience with air bearing technology, we were once again able to push back the boundaries and develop air bearings which have unmatched accuracy and stability.

- ▶ Position-sensitive torque mapping reduces residual torques to insignificant levels for measurements at the lowest torque values.
- ▶ Excellent normal force measurement with minimal signal drift and high thermal stability is available for all environmental systems and accessories.
- ▶ All bearings are machined and mounted in-house and undergo exhaustive quality control testing. This guarantees the highest quality and reliability of these components.



Maximum ease of use: the quick-fitting coupling

All Physica rheometers have a quick-fitting coupling for maximum ease of use. Geometries can be changed in seconds.

Tireless response: the motor drive

Principle

The air bearing-supported synchronous motor is one of the unique key components of the Physica MCR rheometer series. High-energy permanent magnets mounted on a small rotor disc produce a constant magnetic field, providing fast, delay-free response. The rotor moves at the same speed, i.e. synchronous, with the stator field, which is produced by a series of coils.

It is possible to adjust the torque in such a way that it is linear to the total amount of stator current. A change in the stator current therefore causes a simultaneous change in the torque. In contrast to induction motors, the rotor field in a synchronous motor does not change. This means there are no eddy currents causing heating problems, which significantly alter the motor characteristics and lead to signal drifts. Rapid, linear response coupled with advanced control electronics results in unmatched speed and strain control.

Advantages

- ▶ Highest efficiency
- ▶ Absolute torque calibration due to the linear relationship between the electro-magnetic motor torque and the stator current
- ▶ Suitable for all CSS and CSR tests over large stress, strain and frequency ranges
- ▶ The real time position control in oscillation (DSO) enables strain controlled oscillatory tests at the smallest torques and deflection angles
- ▶ No heat production and no unwanted signal drifts due to the constant rotor field
- ▶ No overshoots in CSS and CSR tests.
- ▶ Over seven decades of torque
- ▶ Speeds as low as 10^{-7} min^{-1} can be set, example: a simple shear flow test for direct measurement of the zero shear viscosity of high molecular weight polymer melt
- ▶ Excellent speed control over more than 9 decades.
- ▶ Precision air bearing allows accurate measurements at extremely low torques
- ▶ Fast response for step tests.

Unique and Error-free

Unique and error-free: the Toolmaster™

The revolutionary Toolmaster™ (US Patent 7,275,419) represents the first completely automatic tool recognition and configuration system.

All Physica measurement geometries and environmental systems are recognized automatically as soon as they are connected to the rheometer.

With QuickConnect, the measuring geometries are easily connected to the instrument using the reliable Physica quick-fitting coupling. A transponder chip integrated in the geometry contains all relevant geometry data, which are automatically transferred to the software. The data from the connected environmental system or accessory is initialized in the software by SmartLink.

Advantages

- ▶ No more errors resulting from a user inserting the wrong geometry or making the wrong selection in the software
- ▶ Intelligent auto-configuration system for user-specific rheometer packages
- ▶ Calculation of exact geometry factors using real geometry data, e.g. truncation, diameter and cone angle
- ▶ Unique identification of individual measuring geometries by the transfer of geometry serial numbers
- ▶ No more errors when documenting a configuration – perfect for traceable documentation (e.g. 21CFR Part11)



Meas. System: CP 50-2 SN0301
Meas. Cell: P-PTD200+H-PTD200
Measuring Gap: 0,050 mm

True Innovation



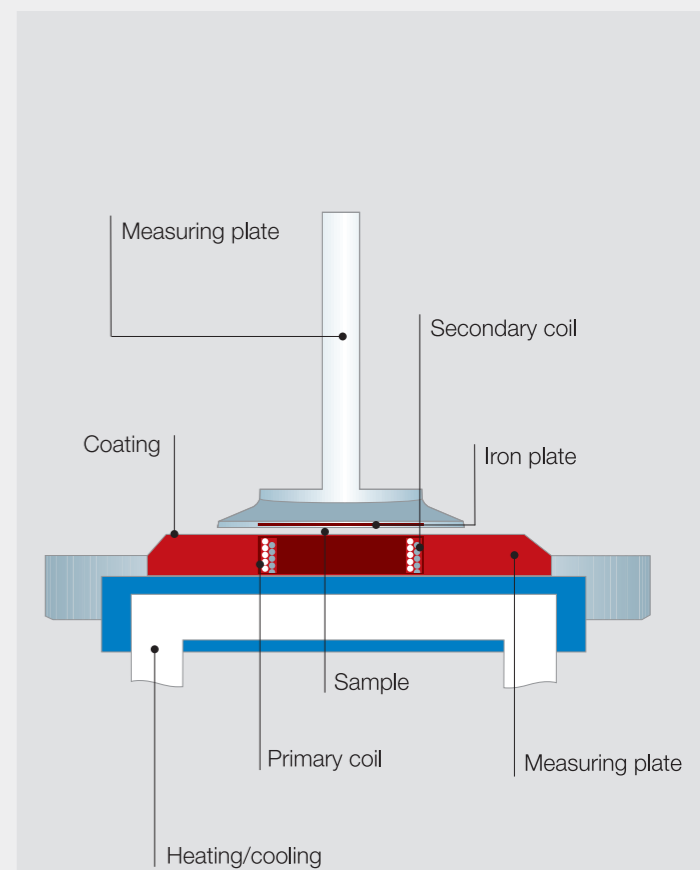
True innovation: the TruGap™ function

For the first time it is possible to monitor and control the real gap in cone-and-plate or parallel-plate measurements. The new, patented (US Patent 6,499,336) technology is based on an induction method which determines the exact gap size, therefore eliminating errors from thermal expansion and normal force.

The TruGap™ function is available for Peltier elements, electrically heated, and convection-based environmental systems. It uses special measuring geometries and lower plates for each environmental system.

Advantages

- ▶ Allows truly accurate temperature sweeps with cone-and-plate geometries
- ▶ Works over wide temperature ranges and heating rates
- ▶ Determination of the measuring gap at all times, independent of the rheological test



Environmental Systems, Accessories and Geometries

Temperature control technologies

Temperature greatly influences the rheological behavior of almost all substances. Anton Paar engineers have invested a lot of time and effort in the development of new temperature control systems. The result is a complete range of environmental control systems. All the temperature control systems are highly accurate and virtually gradient-free in horizontal and vertical directions. In addition, traceable automatic temperature calibration sensors are available to ensure the system is always operating within specification and measures the real sample temperature. The product line covers a temperature range from $-150\text{ }^{\circ}\text{C}$ to $+1000\text{ }^{\circ}\text{C}$.

Environmental systems for the MCR rheometer series

Cone-and-plate/parallel-plate thermal chambers

- ▶ Liquid temperature control (-30 to $+180\text{ }^{\circ}\text{C}$).
- ▶ Peltier temperature control (-40 to $+200\text{ }^{\circ}\text{C}$) with actively heated Peltier hood (US Patent 6,571,610).
- ▶ Electrical resistance heating with low temperature option (-130 to $+400\text{ }^{\circ}\text{C}$).
- ▶ Convection oven (-150 to $+1000\text{ }^{\circ}\text{C}$).

Concentric cylinder thermal chambers

- ▶ Liquid temperature control (-30 to $+180\text{ }^{\circ}\text{C}$).
- ▶ Peltier temperature control (-20 to $+200\text{ }^{\circ}\text{C}$) (US Patent 6,240,770).
- ▶ Electrical resistance heating (RT to $+300\text{ }^{\circ}\text{C}$).

Additional accessories for the MCR rheometer series

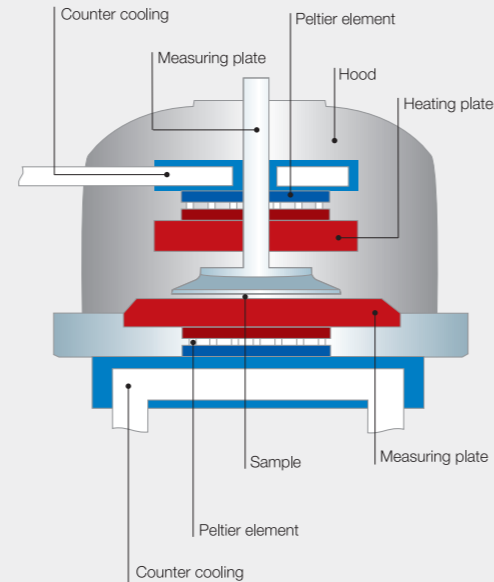
- ▶ Pressure cells
- ▶ UV chambers for UV-curing inks, adhesives, and coatings
- ▶ Magneto-rheology and electro-rheology systems
- ▶ Measuring chamber for starch gelatinization testing
- ▶ Interfacial rheology measuring cell
- ▶ Immobilization cell for controlled drying of paper coatings
- ▶ Rotating ball system for samples containing large particles
- ▶ Dielectric measuring system
- ▶ Standardized solid bar and film fixtures for DTMA testing
- ▶ Additional options for simultaneous structural investigations, e.g. Small Angle Light Scattering (SALS), Small Angle Neutron Scattering (SANS), Small and Wide Angle X-Ray Scattering (SAXS/WAXS) as well as chambers for flow visualization, microscopy and particle imaging velocimetry (PIV)
- ▶ Tool for extensional rheology (SER)

Geometries

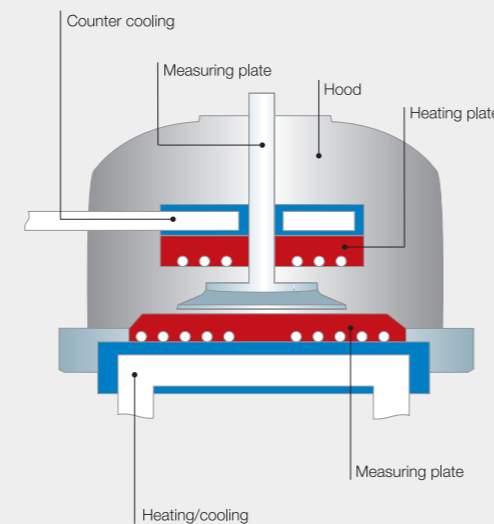
Anton Paar offers a wide selection of geometries for concentric cylinder, cone-and-plate and parallel-plate systems. Almost any diameter, cone angle, truncation, surface treatment, coating and material can be supplied to cover all application needs. Special geometries include stirrers, disposable systems, and customer-specific designs for unique samples and applications.



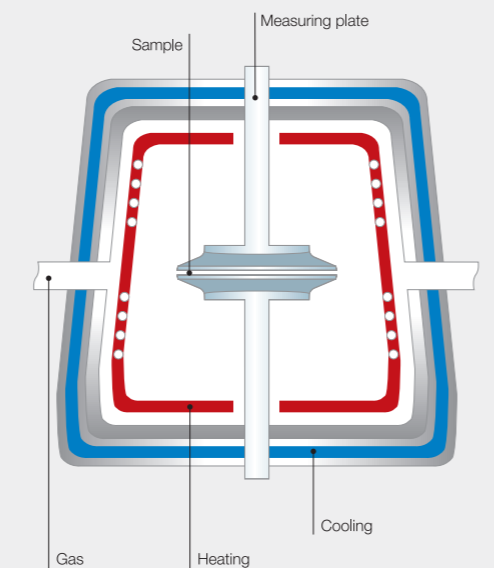
Peltier temperature control



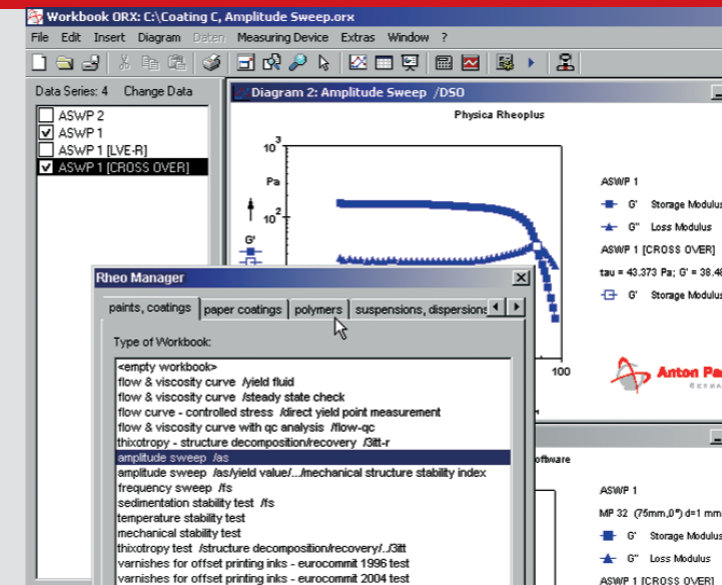
Electrical resistance heating



Convection oven



Physica RheoPlus



Like our rheometers, the Physica RheoPlus user software is a modular system which can be configured to meet individual requirements, from quality assurance to R&D. RheoPlus is multilingual, speaking to users in the language of their choice.

RheoManager

The RheoManager helps users who are new to the software or rheology in general. It condenses our application know-how and suggests suitable measuring methods for a large number of applications. Standardized methods for numerous industrial branches are easy to find. Over 70 methods and 200 templates are provided.

Of course, users can also create and manage their own test profiles. The file structure helps keep files under control even when managing a large amount of data.

Convenient analysis routines are an integral part of the predefined RheoManager templates. All analysis routines run in RheoManager can be adapted to suit individual needs and organized in an analysis script. Reports can be configured automatically, and "pass/fail" tests are easily developed using the automation feature.

Auto-configuration

The Toolmaster™ is an intelligent configuration system, which automatically transfers geometry data and control parameters for the measuring and temperature control systems to the RheoPlus. This eliminates user errors, which can occur when manually entering data for accessories.

Compatibility

Users of Microsoft® Office will recognize many of the features in the RheoPlus software and use them intuitively. Drag & drop is just one of the many features which make working with RheoPlus easy and efficient. Data from earlier Physica software versions can be imported and data and graphs from RheoPlus are easily exported into MS Excel®, MS Word® or as ASCII data.

Reliability

Physica RheoPlus was developed according to ISO 9001 guidelines and runs as C/C++ software for the latest Windows™ operating systems. The electronic signature, audit trail, archiving and retrieval of data comply with the regulations in 21 CFR Part 11 from the US Food and Drug Administration (FDA).

PC connection

The LIMS-SAP module means results can be automatically saved in an external data base. Measuring profiles can also be activated by other programs via the interface, allowing users to work through the script.

RheoPlus is the first rheometer software to provide both a serial interface (RS 232) and an Ethernet interface for communicating with the instrument.

Flexibility

There are no limits for programming and linking test sequences. Test types can be combined in real time in whichever order required. Additional instruments or signals such as power supplies, relays and magnetic valves are supported by RheoPlus in real time and can be synchronized with the rheological measuring profile. This makes RheoPlus the perfect platform for setting up measuring procedures which simulate processes and applications.

Applications

Fig. 1: FLOW AND VISCOSITY CURVE...or: how to get information about the flowability of a polymer

Flow and viscosity curves reveal information about the flowability of polymers under different shear and simulated process conditions. The zero shear viscosity η_0 at low shear rates is an important material property and is directly proportional to the average molar mass M_w . To determine a viscosity curve over a broad range of shear rates, a master curve can be calculated using the time-temperature superposition (TTS) in combination with the conversion method according to the Cox-Merz rule.

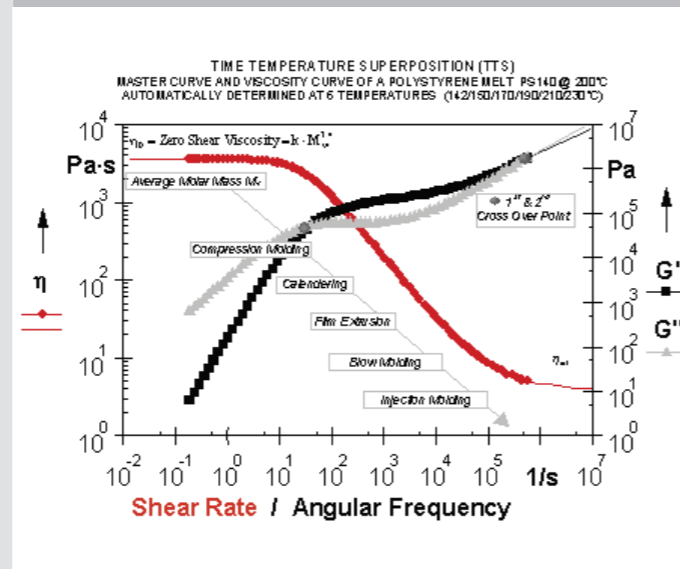


Fig. 1

Fig. 2: AMPLITUDE SWEEP...or: how to determine the deformation stability and yield stress of a suspension or emulsion

Rotational tests, often used in the past, can deliver very different results when calculating the yield stress. Using G' and G'' of an amplitude sweep with preset strain (Direct Strain Oscillation, DSO) plotted over the shear stress permits more reliable and practically relevant results for the yield stress value. Significant parameters for evaluating the mechanical stability of a material can be calculated using automated analysis routines in the software.

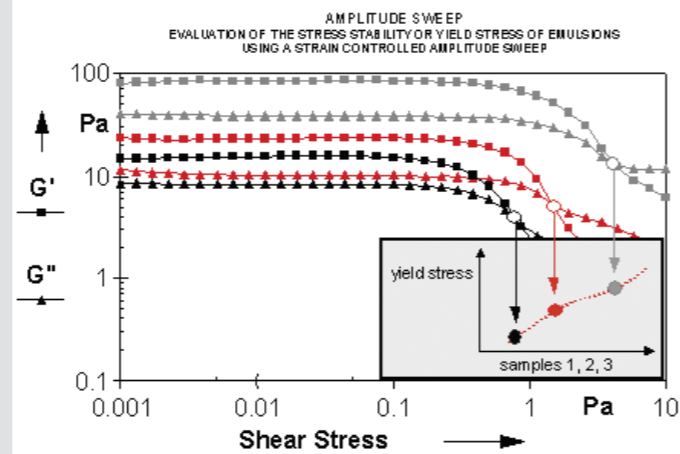


Fig. 2

Fig. 3: INTERVAL THIXOTROPY TEST...or: how to measure the structural regeneration of a material after a short period of high shear

Almost every coating process consists of 3 phases (1 – at rest, 2 – structural decomposition, 3 – structural regeneration). In Fig. 3, the material's behavior is described by G' and G'' over time. Time-dependent effects such as leveling and sagging, dot sharpness, layer thickness and separation stability of emulsions and dispersions can be correlated directly to the curve progression.

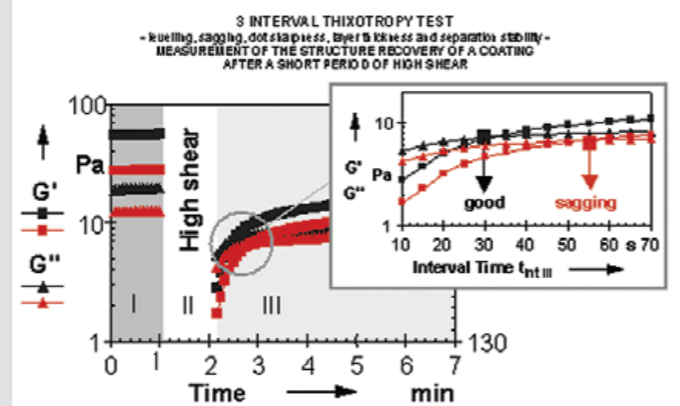


Fig. 3

Fig. 4: NANO TORQUE MEASUREMENTS... or: how sensitive is the rheometer

In order to measure sensitive structures in the linear and non-linear range it is necessary to have a reliable rheometer system with an excellent and proven control mechanism. The Physica MCR rheometers are capable of measuring nano torques and nano strains due to their unique EC motor (brushless DC), the high-precision air bearing and the Online Position Control in oscillation (DSO).

The torque limit of a rheometer system strongly depends on the measuring conditions and data sampling. Figure 4 proves that in a limited frequency range it is possible to perform measurements down to torque values as low as 1 nanoNm. The torque and strain limits given in our brochure are valid over a wide range of frequencies. The new Physica MCR series provides excellent nano strain resolution. Nano materials are not necessarily low-viscous. For example nano composite polymers can be filled with nano particles (tubes) in order to obtain higher stiffness which requires high permanent torque without signal drift. The MCR 501/300 offers a maximum torque of 300 mNm. On the other hand it is sensitive enough to measure secondary relaxations of nano composites and thus gives insight into a material's impact behaviour.

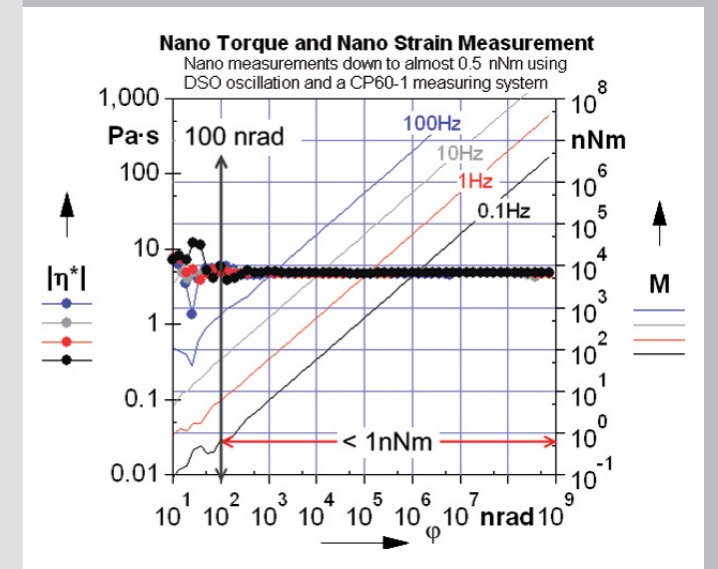


Fig. 4

Fig. 5: TRANSIENT TEST TYPES (creep, stress relaxation tests)...or: what can we learn from the first normal stress difference?

Step stress (creep & recovery), step strain (stress relaxation) and step rate (stress growth/start-up flow) experiments are typically performed to measure the transient response of a material to a given constant shear stress, strain or rate. Besides the shear viscosity, the measurement of the first normal stress difference N_1 and coefficient ψ_1 also gives valuable information about the sample. Physica MCR rheometers include a patented normal force sensor (US-Patent 6,167,752) which allows the evaluation of the first normal stress difference N_1 and the coefficient ψ_1 over a large range with virtually no thermal drift.

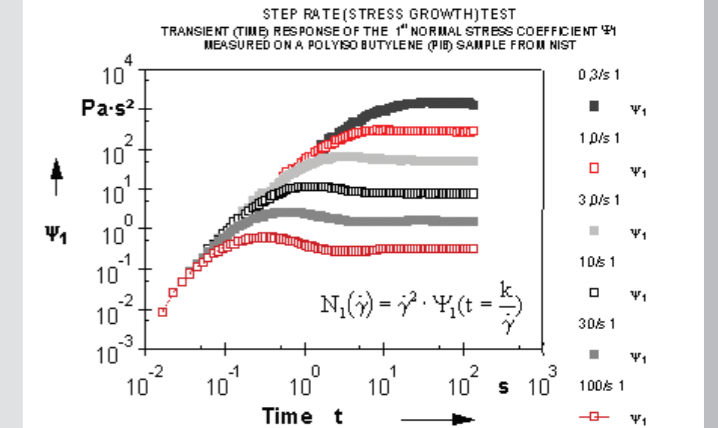


Fig. 5

FIG. 6: COMBINATION OF SMALL ANGLE LIGHT SCATTERING AND RHEOLOGY...or: how to get information about both the micro- and macrostructure

The combination of a Physica MCR rheometer and the small angle light scattering (SALS) system enables the simultaneous determination of microstructural properties (using the optical method) and macroscopic, or bulk, material properties (using rheology).

The flow behavior of a polymer blend (1% Polyisobutylene (PIB) in Polydimethylsiloxane (PDMS)) can be explained by looking at the scattering images. At rest and in the zero viscosity range the scattering patterns have a symmetrical shape. This is due to the circular PIB droplets in the PDMS matrix. At higher shear rates, the viscosity decreases and the sample starts to flow. The scattering patterns become elliptical, indicating the orientation and deformation of the PIB domains in the direction of flow.

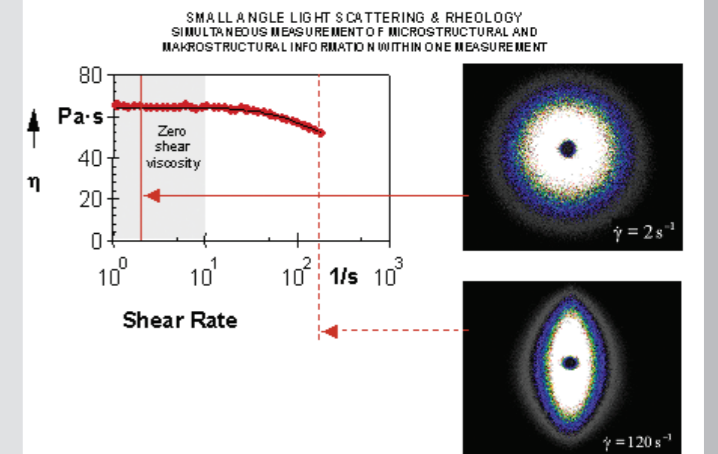


Fig. 6

Specifications

	Unit	Physica MCR 51	Physica MCR 101	Physica MCR 301	Physica MCR 501
Bearing	-	ball	air	air	air
EC motor (brushless DC) with high resolution optical encoder	-	yes	yes	yes	yes
Permanent maximum torque, no signal drift	-	yes	yes	yes	yes
Minimum torque rotation	µNm	250	0.1	0.05	0.05
Minimum torque oscillation	µNm	-	0.1	0.01	0.01
Maximum torque rotation/oscillation	mNm	125	150	200	230, 300*
Torque resolution	nNm	100	0.2	0.1	0.1
Angular deflection, set value	µrad	1 to ∞	1 to ∞	0.1 to ∞	0.1 to ∞
Angular deflection, resolution	µrad	0.01	0.01	0.01	0.01
Minimum speed, CSS	1/min	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁷
Minimum speed, CSR	1/min	10 ⁻³	10 ⁻⁵	10 ⁻⁷	10 ⁻⁷
Maximum speed, CSS/CSR	1/min	3000	3000	3000	3000
Minimum angular frequency	rad/s	10 ⁻³	10 ⁻⁵	10 ⁻⁵	10 ⁻⁵
Maximum angular frequency	rad/s	628	628	628	628
Normal force range	N	-	0.1 to 30	0.01 to 50	0.01 to 50
Normal force resolution	N	-	0.02	0.002	0.002
Dimensions	mm	440x600x620	440x600x620	440x600x620	440x600x720
Weight	kg	43	43	43	50
Toolmaster™, measuring system	-	yes	yes	yes	yes
Toolmaster™, measuring cell	-	yes	yes	yes	yes
QuickConnect for measuring systems, screwless	-	yes	yes	yes	yes
Electronic trim lock	-	yes	yes	yes	yes
More than 25 modular measuring cells, see catalogue	-	yes	yes	yes	yes
Digital Eye, Rheoplus video option and camera	-	optional	optional	optional	optional
Virtually gradient-free (horizontal, vertical) temperature control systems	-	yes	yes	yes	yes
Maximum temperature range	°C	-150 to +1000	-150 to +1000	-150 to +1000	-150 to +1000
Automatic gap control/setting, AGC/AGS	-	yes	yes	yes	yes
TruGap™	-	no	no	optional	yes
Real time position control oscillation, DSO	-	no	no	optional	yes
Sample (direct) strain control, virtually compliance free	-	-	yes	yes	yes
Sample torque control, virtually inertia-free	-	-	yes	yes	yes
Gap control, normal force and velocity, Tack/Squeeze	-	no	optional	yes	yes
1st normal stress measurement N1	-	no	optional	yes	yes
Waveform and Lissajous**	-	no	optional	optional	yes
Multiwave and higher harmonics**	-	no	yes	yes	yes
Steady state**	-	no	yes	yes	yes

* MCR 501/300 available on request with 300 mNm EC motor
 ** Monitoring and Recording

We Accompany Our Customers



Total expertise assures flexibility

Anton Paar has a long tradition of experienced and highly skilled employees researching and developing key technologies. All components of the MCR rheometers are manufactured at our high-precision facilities, certified to ISO 9001. The rigorous quality control throughout the whole development and production process is essential for attaining the high quality we expect from our instruments.

Application know-how

We are proud to provide our customers with unmatched application know-how in the field of rheology. New applications are constantly tested and analyzed in our laboratories. In addition to our own rheology book, we offer a comprehensive collection of publications, application reports, and technical information covering all aspects of rheological testing.

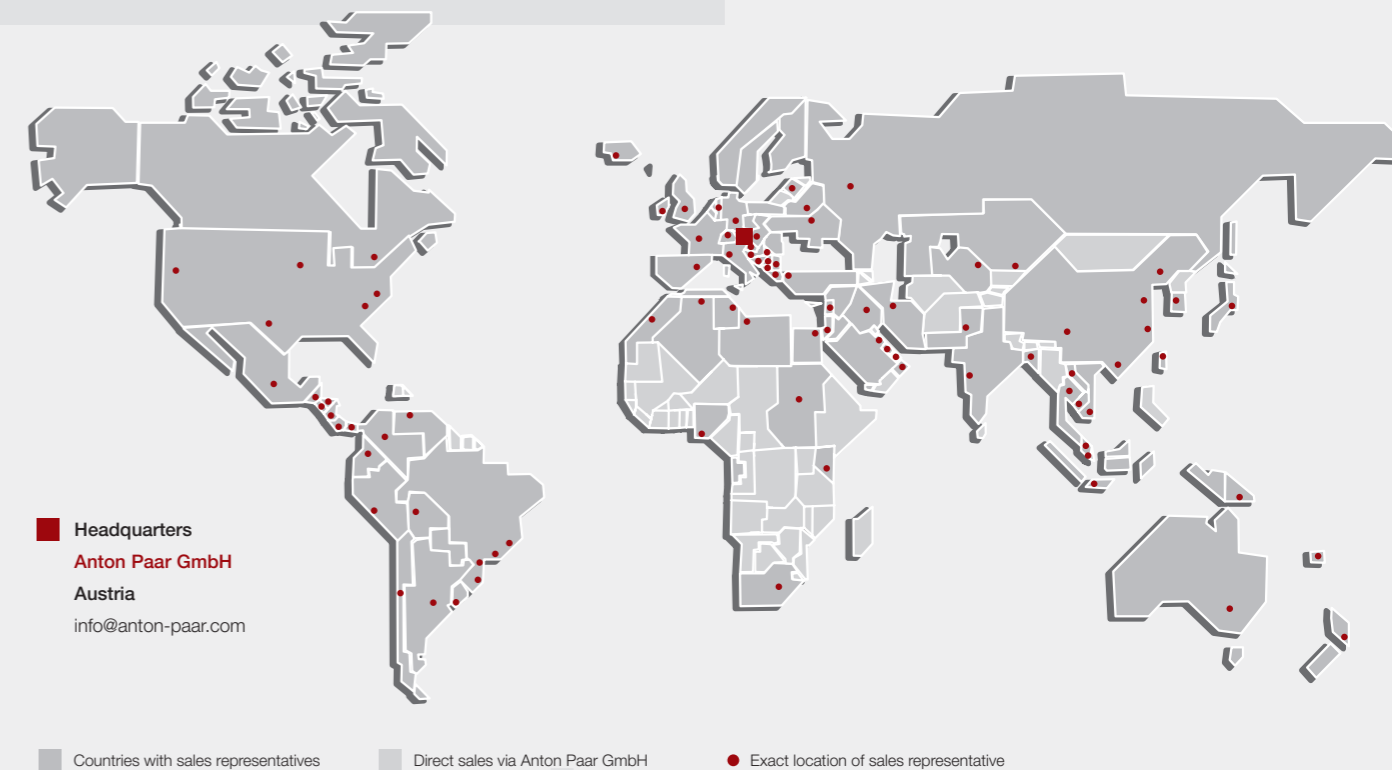
Learn from the experts

When performing and interpreting rheological measurements, it is especially important to have a good understanding of the rheological background and the correlation between the rheological data and the practical application. To help customers expand their knowledge of rheology and better utilize some of the advanced features of our instruments, we offer classes and seminars throughout the year. Course schedules and locations can be found on our website.

Professional after-sales service

Rheometers are high-precision measuring instruments. We therefore recommend regular adjustment checks and maintenance, and offer maintenance contracts. Our worldwide after-sales service is carried out by qualified engineers who undergo regular and systematic training at our headquarters.

Our international sales network





Photos: Croce & Wir



Anton Paar

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subject to change
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01/09 C22IP01-D

Modern Rheology Measurements in Today's Coatings Industry

Thomas Mezger, Anton Paar Germany GmbH, Germany
Detlef van Peij, Elementis GmbH, Germany

Introduction

For people working in the coatings industry it is important to have as much information as possible on the following aspects of a coating system:

- (1) structural strength and behavior at rest
- (2) flow behavior
- (3) structural recovery after the coating (application) process

Many different tests and analytical methods are used in today's lab practice to describe the above mentioned behavior. With this paper we aim to show ideas for the modern evaluation of coatings in daily practice. A critical look will be taken on conventional test methods, which are still in use but in many cases no longer state-of-the-art. We further want to give an outlook of some modern methods illustrated with measuring results from daily practice.

Structural Strength and Behavior at Rest

Information about the coatings behavior at rest is very important for the evaluation of dispersion stability, e.g. long-term storage. Many users in the coatings industry use rheological additives which create a three-dimensional network, to achieve a sufficient high structural strength at rest, keeping the pigments and extenders in suspension. To detect the strength of this three-dimensional network of forces, many industrial laboratories use the yield point measurement (also called the yield stress as it is the minimal value of the shear stress applied before the internal gel structure breaks). One thing has to be stated clearly: A yield point is no material constant as its value depends on the testing as well as on the method of analysis.

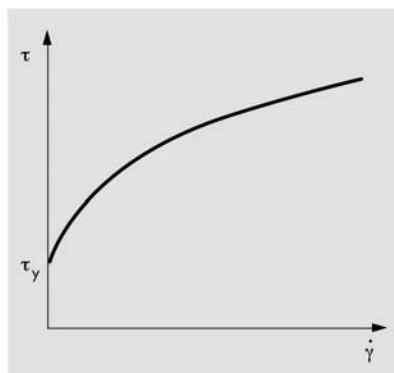


Fig. 1: Flow curve, linear scaled

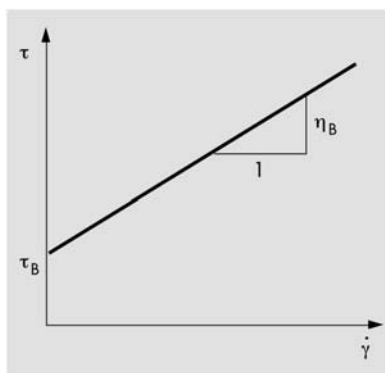


Fig. 2: Bingham fitting model for a linear scaled flow curve

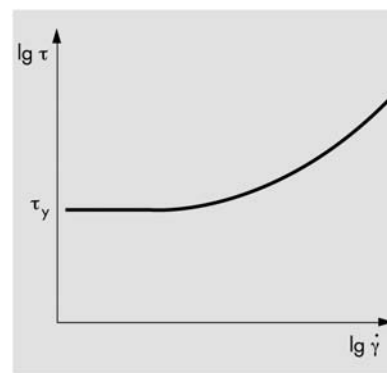


Fig. 3: Flow curve, log. scaled

The conventional methods for yield point evaluation

A frequently used test method for yield point evaluation is the flow curve measurement by a rotational test (shear stress τ versus the shear rate $\dot{\gamma}$), presetting a shear stress or a shear rate ramp. There are various simple analysis methods currently in use:

(YPM 1) Showing the flow curve in a linear scaled diagram, the yield point is taken as the intersection point of the flow curve on the shear stress axis (**Fig. 1**; here as τ_y).

(YPM 2) Using a mathematical curve fitting model for the flow curve, the yield point is calculated via extrapolation of the shear stress value at a shear rate of zero. The most common fitting models are: Bingham, Casson, or Herschel / Bulkley. (**Fig. 2**; here τ_B as the "Bingham yield point")

(YPM 3) Showing the flow curve in a logarithmic scaled diagram, the yield point is taken as the shear stress value of the flow curve at the lowest shear rate (**Fig. 3**; here as τ_y).

(YPM 4) Sometimes users evaluate the yield point as the shear stress value at a very low shear rate of $\dot{\gamma} = 0.01$ 1/s (**Fig. 4**; here as τ_i).

After many years of experience, it can be stated, that a practice-relevant structure is present, when the strength at this low shear rate applies $\tau \geq 10$ Pa. "No structure" is present if $\tau \leq 1$ Pa. For values in between further tests should be carried out.

Note: With the inaccurate methods (YPM 1) and (YPM 2) yield point values are often reported, although the investigated material has none in reality (Example: "Casson yield points" for very slowly flowing offset printing inks at rest).

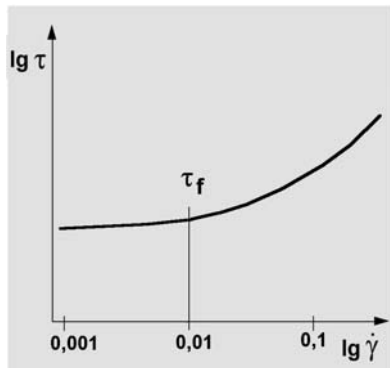


Fig. 4: Log. scaled flow curve, yield point at the low shear rate 0.01 1/s

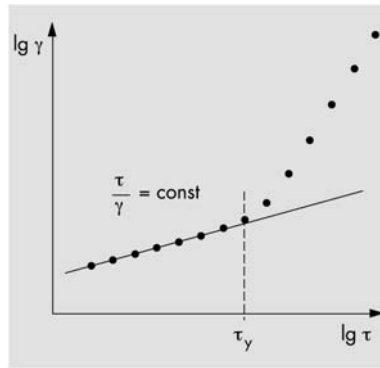


Fig. 5: Tangent method

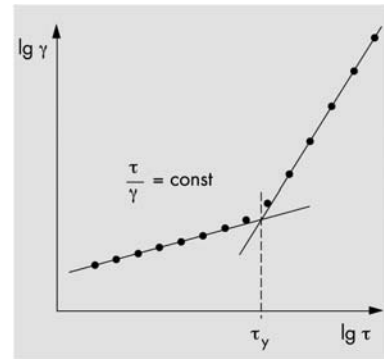


Fig. 6: Tangent crossover method

The more useful and accurate methods for yield point evaluation

A material with a yield point is showing viscoelastic behavior. Under low shear forces it therefore shows a reversible elastic behavior (like solids or gels), according to the elasticity law of Hooke (proportionality of shear stress τ and shear deformation γ). Under higher shear load, exceeding the yield stress value, the internal structure will break irreversibly. The material starts to flow, while showing an idealviscous (like a liquid following Newton's law) or shear-thinning (or shear thickening) behaviour depending on the structure of the coating. The yield point is read off at the limiting value of the shear stress where the behavior changes from elastic to viscous. The great advantage of the following yield point analytical methods is considering the viscoelastic behaviour of a coating system. Another advantage is the detection of measuring points already in the state of rest (i.e. in the linear-elastic range) before the material's internal structure breaks and it finally starts to flow.

(YPM 5) Presenting the result of a flow curve test (measured in a rotational mode, best presetting a controlled shear stress ramp) in a double-logarithmic shear deformation γ versus shear stress τ diagram, a transition point can be clearly seen if a yield point is present. Two methods of analysis using tangents can be selected here. For the first method a tangent is fitted to the low shear values. The yield point is the last measuring point observed on this tangent (or in a limited range of tolerated deviation, respectively), before the measuring curve deviates to clearly higher values compared to the tangent values (**Fig. 5**; here as τ_y).

(YPM 6) Using the second tangent method, additionally to the first tangent at low shear, a second tangent is fitted to the high shear range of the measuring curve. The crossover point of the two tangents is taken as the yield point (**Fig.6**; here as τ_y).

(YPM 7) Viscoelastic effects can be evaluated most desirably with oscillatory tests as both components of the viscoelastic behavior are represented by the parameters storage modulus G' (elastic portion) and loss modulus G'' (viscous portion). Presenting the amplitude sweep as a function of the shear stress, the yield point can be evaluated as the shear stress value at the limit of the linear viscoelastic (LVE) range. This can be seen at the point where the G' or G'' function is leaving the plateau value (**Fig 7**; here as τ_f). The advantage of this method is that the behavior can be analysed in a range of lowest stress without any irreversible structure change in terms of viscoelasticity. It provides further values of the viscous as well as of the elastic portion or for the ratio of both, respectively.

(YPM 8) In order to evaluate long-term dispersion stability the oscillatory tests offer another possibility using a frequency sweep. Long-term effects are simulated by low frequencies. If $G' > G''$, the investigated material shows a gel character, and thus, dispersion stability at rest can be expected (**Fig. 8**; with the angular frequency ω). If $G'' > G'$, it has a liquid character, and thus, there is no stability, and sedimentation must be taken into account (**Fig. 9**). Sometimes users evaluate - similar to the "yield point" - the G' value at the very low angular frequency $\omega = 0.01$ 1/s.

(Note: This is not a shear stress value, even when the unit is also Pa. Often under the condition $G' > G''$, users in the coatings industry say that there is a practice-relevant structure strength if at this point $G' \geq 10$ Pa, and there is “no structure” if $G' \leq 1$ Pa. For values in between further tests should be performed.)

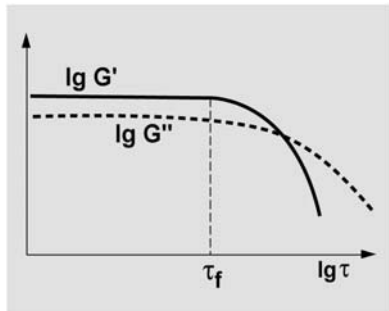


Fig. 7: Oscillatory test, amplitude sweep

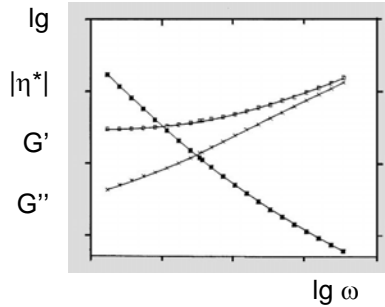


Fig. 8: Oscillatory test, frequency sweep, here: $G' > G''$ at low frequencies (gel)

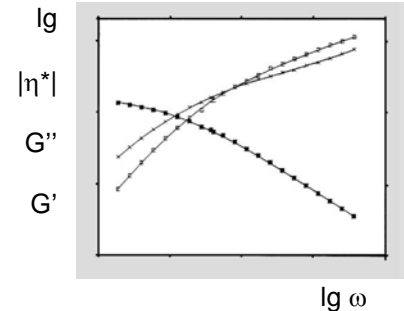
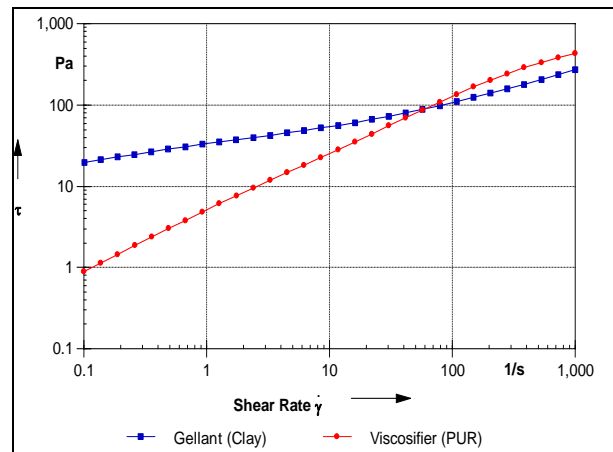
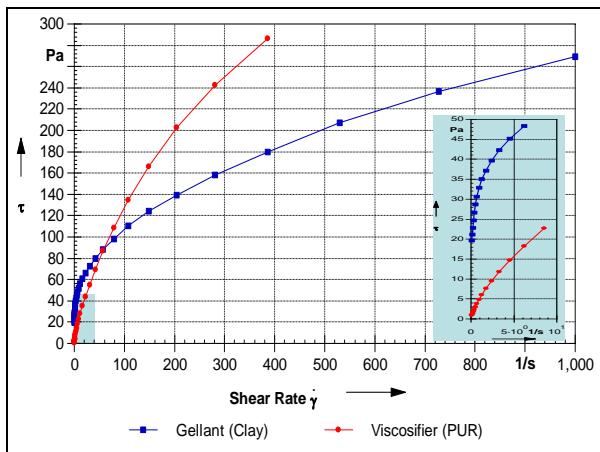


Fig. 9: Oscillatory test, frequency sweep, here: $G'' > G'$ at low frequencies (liquid)

Measuring examples

Fig. 10 shows the flow curves of an emulsion paint with a gellant (clay) and a viscosifier (PUR) as rheological additives. At rest or in the low-shear range, respectively, the gellant produces a higher structural strength (yield stress), whereas in the medium and high-shear range the viscosifier produces comparably higher viscosity values. With particular regard to the low-shear range, this effect can be seen more prominently if the curves are presented in a double-logarithmic diagram (**Fig. 11**).



Figs. 10 and 11:

Flow curves in linear (Fig. 10) and in logarithmic scales (Fig. 11) of an emulsion paint modified with two different rheological additives

Fig. 12 is showing the deformation-stress diagrams of a paint with two different gellants. The yield stress values can be read off at the end of the linear-elastic range where the measuring points deviate from the tangent; here at 30.5 Pa with gellant 1, and 18 Pa with gellant 2.

The amplitude sweeps (oscillatory tests) of an emulsion paint with in one case a gellant (clay) and in the other a viscosifier (PUR) as rheological additives are illustrated in **Fig 13** as a function of the shear stress. The character of the modified paints at low-shear conditions can be seen in the linear viscoelastic (LVE) range: the gellant producing $G' > G''$ (and therefore with a yield point, here read off at the limit of the LVE range as about 7 Pa), and the viscosifier with $G'' > G'$ (thus, as a viscoelastic liquid showing no significant yield point).

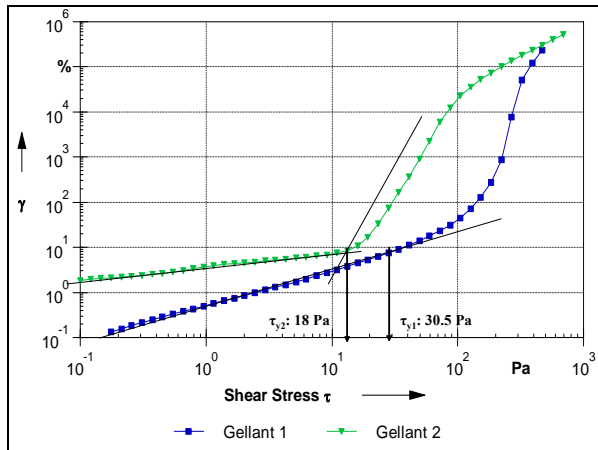


Fig. 12: Tangent method and tangent crossover method, respectively, to analyse the yield point values of a paint modified with two different gellants

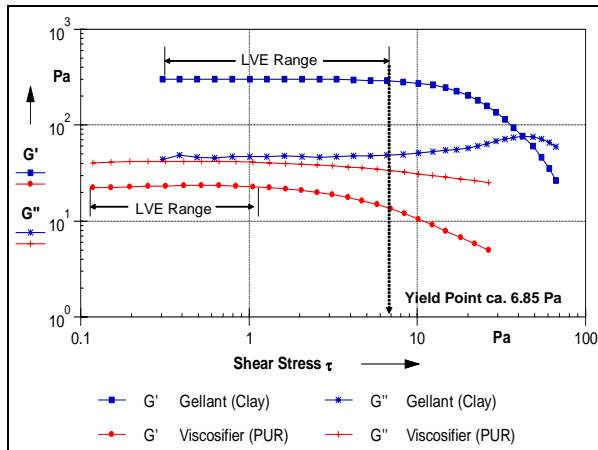


Fig. 13: Amplitude sweeps of an emulsion paint modified with two different rheological additives

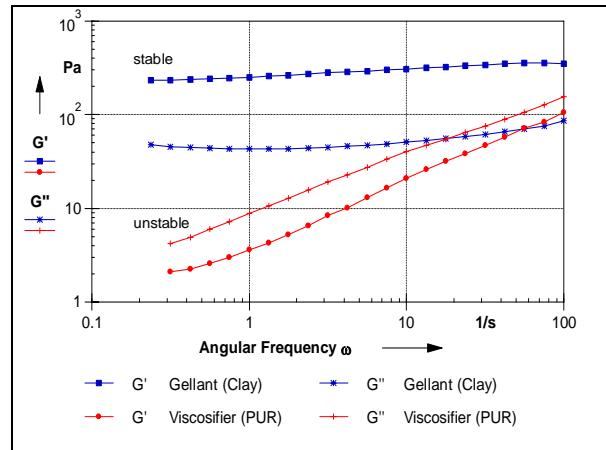


Fig. 14: Frequency sweeps of an emulsion paint with two different rheological additives

In **Fig. 14** frequency sweeps (oscillatory tests) of these modified paints are shown. For the evaluation of the long-term stability the values are compared in the low-frequency range. Here (and also in the whole measuring range) the gellant produces a gel structure with $G' > G''$ and thus, stability. The viscosifier produces no gel structure as the modified paint shows liquid character ($G'' > G'$), and therefore, no stability.

Flow Behavior

Information about the flow behavior is very important for the evaluation of the coating's behavior during the application (workability, spraying, rolling). Many users in the coatings industry use rheological additives to improve the viscosity values at low, medium and high shear rates. If the viscosity values are too high at high shear for example, the application process can lead to problems. If the values are too low, uncontrolled spattering or limited film build must be taken into account. A typical test is the flow curve test (shear stress τ versus the shear rate $\dot{\gamma}$), preset is a shear stress or a shear rate ramp. In diagrams the viscosity curves are presented (with the shear viscosity η) using the following methods.

The conventional presentation of viscosity diagrams

(VM 1) Showing the viscosity curve in a linear scaled diagram (**Fig. 15**). The disadvantage of this presentation becomes clear: Linear diagrams show above all high values, but differences between different samples can hardly be seen at low values. For most of the curves this is not useful as the greatest changes in a sample's structure (or in the curve slope, respectively), take place in the low-shear range.

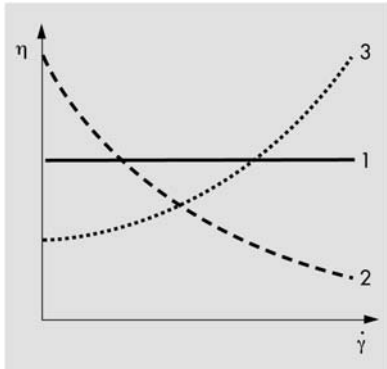


Fig. 15: Linear scaled viscosity curves; (1) for ideal viscous, (2) for shear-thinning, (3) for shear-thickening behavior

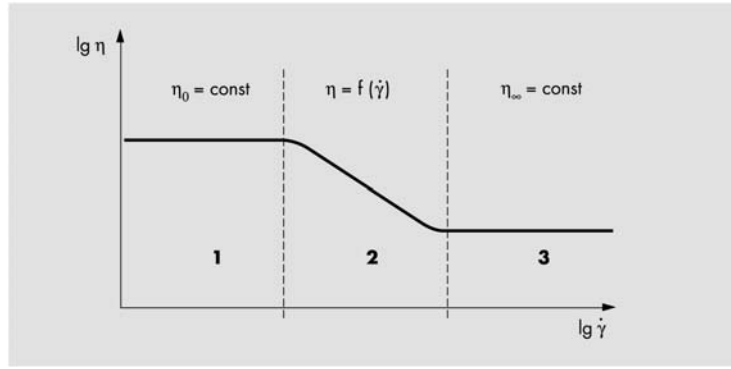


Fig. 16: Log. scaled viscosity curve; showing here the typical function for polymers, with the zero-shear viscosity plateau at low shear rates, shear-thinning behavior in the medium shear range, and the infinite-shear viscosity plateau at high shear rates

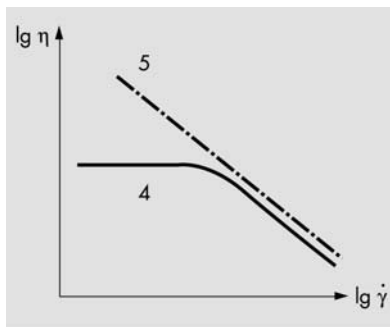


Fig. 17: Log scaled viscosity curves; (4) with, and (5) without zero-shear viscosity plateau

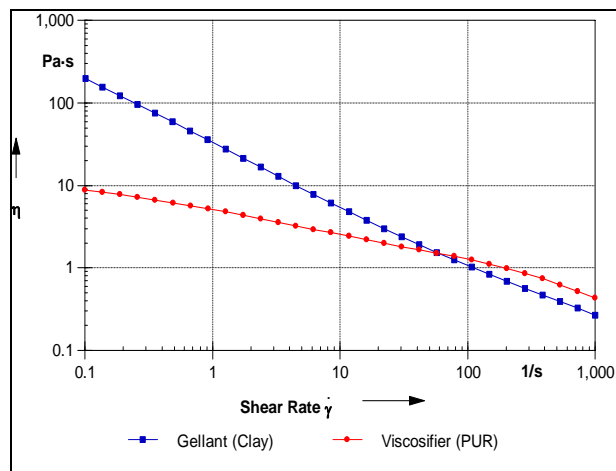


Fig. 18: Viscosity curves of an emulsion paint modified with two different rheological additives

The more useful and accurate presentation of viscosity diagrams

(VM 2) Showing the viscosity curve in a logarithmic scaled diagram (**Fig. 16**; here for a polymer, and **Fig. 17**), all the different shear load ranges can be clearly illustrated. For users is important to evaluate the flow behavior in the low-shear range in order to see if a rheological additive is forming a gel structure: showing the zero-shear plateau a material is not stable at rest and it flows with time even when this takes longer (for example: a polymer solution acting as a thickening agent, but not as a gel-forming agent). On the other hand, if there is no zero-shear plateau value in the low-shear range the material is stable at rest, for example, a gel or a paste with a yield point, i.e. containing a gel-forming agent. For further information about the behavior at rest and the viscoelastic character of the sample: see the above chapter.

Measuring example

Fig. 18 shows the viscosity curves of the modified emulsion paint in the shear rate range of $\dot{\gamma} = 0.1$ to 1000 s^{-1} . The thickening effect of the gellant in the low-shear range can be compared to the thickening effect of the viscosifier in the high-shear range. For the paint with viscosifier, the slope value of the viscosity curve decreases slightly towards low shear rates. Within this measuring range there is a tendency for a zero-shear viscosity but no plateau reached at these shear rates. The paint with gellant showed no corresponding tendency at all, with a slope in the low-shear range remaining constant.

Structural Recovery after the Coating Process

Information about the behavior after the coating (application) process is very important for the evaluation of levelling and sagging behavior. Many users in the coatings industry use rheological additives to balance this process which is often called “thixotropic behavior” (but in many discussions

with users in different laboratories, it becomes clear that there is no logic to what is meant by this term).

The conventional method for the evaluation of “thixotropy”

(TM 1) A frequently used test method for the “thixotropy” evaluation is the flow curve test with three intervals, mostly performed using the controlled shear rate mode: ramp upwards, holding time, ramp downwards. As a typical result the upwards and downwards flow curves are presented in linear scales (**Fig. 19**). The area in between the two flow curves is evaluated as the “thixotropic area” or the “hysteresis area”. The disadvantage of this method is that only the process of structural break-down is measured, and no data is obtained from the structure recovery phase at rest afterwards (but exactly that process is most important for the users in the coatings industry ...).

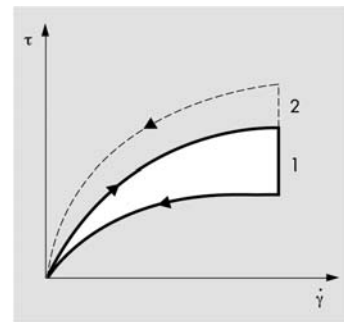


Fig. 19: Flow curve diagram with so-called “thixotropy” or “hysteresis area”

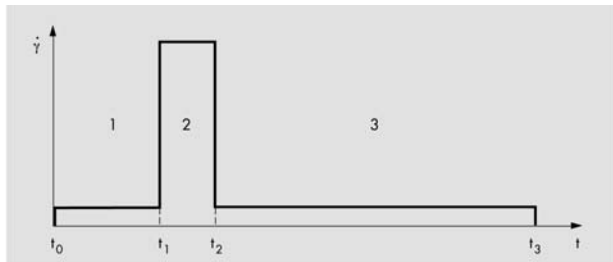


Fig. 20: Rotational step test preset with three intervals: low, high, low shear rate

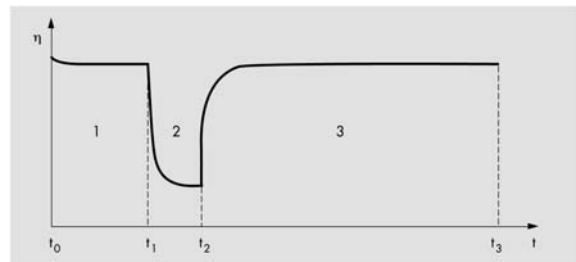


Fig. 21: Time-dependent viscosity curve resulting from the rotational step test

The more useful and accurate methods for the evaluation of the structure recovery (levelling, sagging)

In order to simulate the coatings process and the behavior of the coating afterwards, it is recommended to make a test with the following three intervals: (1) rest (before the application process, reference value), (2) high-shearing (to simulate the coatings process), (3) rest (to measure the time-dependent structure recovery).

(TM 2) Performing a rotational test, with the following preset (**Fig. 20**):

- (1) low shear rate (i.e. $\dot{\gamma} = 1 \text{ s}^{-1}$ or, with an air-bearing rheometer 0.1 s^{-1} or even lower)
- (2) high shear rate (i.e. $\dot{\gamma} = 1000 \text{ s}^{-1}$)
- (3) low shear rate (similar to interval 1)

It is analysed in Interval 3, in which time which percentage of structure regeneration that takes place within a certain time period (**Fig. 21**; here in terms of viscosity, compared to interval 1). A slow regeneration improves levelling but often results in sagging problems (perhaps in a too small wet layer thickness), a fast regeneration prevents sagging but often leads to bad levelling (e.g. as brush marks).

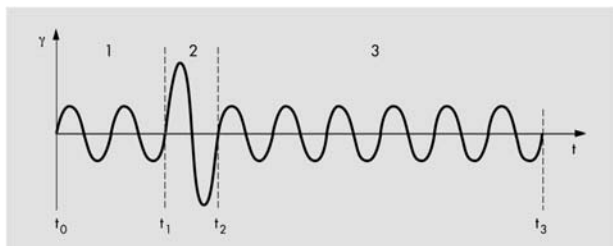


Fig. 22: Oscillatory step test preset with three intervals: low, high, low shear deformation

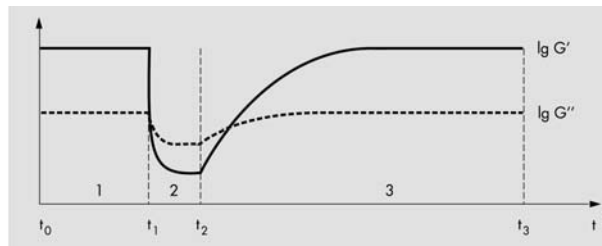


Fig. 23: Time-dependent G' and G'' curves resulting from the oscillatory step test

(TM 3) Performing an oscillatory test, the preset is the shear deformation γ (after running an amplitude sweep to detect the limit of the LVE range); and the angular frequency which is typically selected for all three intervals as $\omega = 10 \text{ s}^{-1}$ (**Fig. 22**):

- (1) low shear deformation (within the LVE range)
- (2) high shear deformation (outside the LVE range, e.g. $\gamma = 100 \%$)
- (3) low shear deformation (similar to interval 1)

In interval 3, the percentage of structure regeneration that takes place within a set time is analysed (**Fig. 23**; here in terms of the “elastic” storage modulus G' and the “viscous” loss modulus G'' , compared to interval 1). A slow regeneration (showing $G'' > G'$ over a certain time period) improves levelling but may result in sagging problems. A fast regeneration (showing $G' > G''$ after a short time) prevents sagging but may lead to bad levelling. The great advantage of this test is the possibility to get the crossover point of the G' and G'' curves in the third interval: Before this point $G'' > G'$ (liquid character) levelling and sagging takes place. After this point $G' > G''$ (gel character) levelling as well as sagging is stopped. Sagging can therefore be controlled easily by shifting the crossover point.

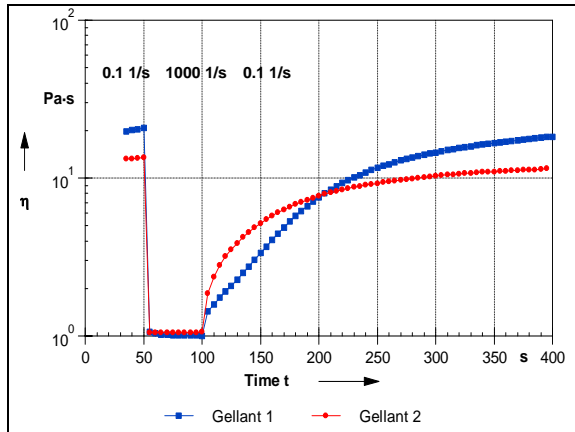


Fig. 24: Rotational step tests of a paint modified with two different gellants

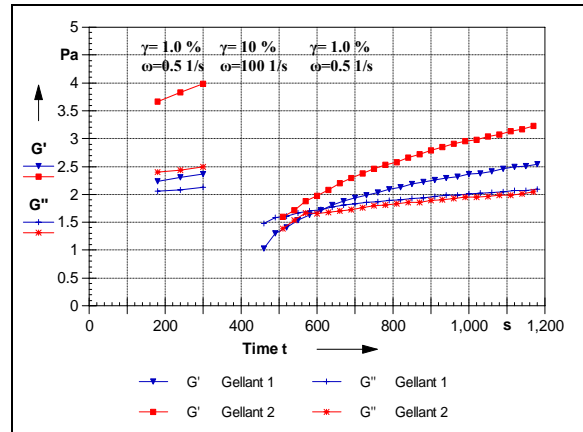


Fig. 25: Oscillatory step tests of a paint modified with two different gellants

Measuring examples

In **Fig. 24** step tests in the rotational mode are presented. Under high shear, both gellants were similar. Structure recovery after shearing is quite different. Gellant 2 shows a quicker recovery compared to gellant 1 and reaches a plateau earlier after shearing. This also confirms the application properties as the paint with gellant 1 shows better levelling and slightly lower sag resistance compared to gellant 2.

Fig. 25 shows a step test in oscillatory mode. The change of the structure characteristics depending on the shear load can be clearly seen: under low load for both samples applies $G' > G''$ (gel structure). As expected for gellant 2, after shearing (the high-shear interval is not presented in the diagram) the gel structure recovery takes place in a shorter time (showing immediately $G' > G''$) period compared to gellant 1 (showing the crossover point of G' and G'' not before a certain time has passed).

Note: Figures 1 to 3, 5 and 6, 15 to 17, 19 to 23 are taken from [1], Figs. 4 and 7 from [2], and Figs. 8 and 9 from [3].

Summary

This paper describes new ideas for state-of-the-art evaluation of the rheological behavior of coatings for daily practice concerning structural strength at rest (dispersion stability, sedimentation), flow behavior (workability), and structural recovery after a coating process (levelling, sagging, wet layer thickness). When viscoelastic behavior is measured and analysed performing oscillatory tests in the low-shear range, this can be especially useful for achieving useful application relevant information.

Literature

- [1] Mezger, T. G.: The rheology handbook. Vincentz: Hannover, 2002
- [2] DIN technical report of the NPF / NAB-AK 21.1 „Rheology“: Modern rheological test methods, part 1: Determination of the yield point, fundamentals and comparative testing methods. Berlin, 2004.
- [3] Meichsner, G., et al.: Lackeigenschaften messen und steuern. Vincentz: Hannover, 2003