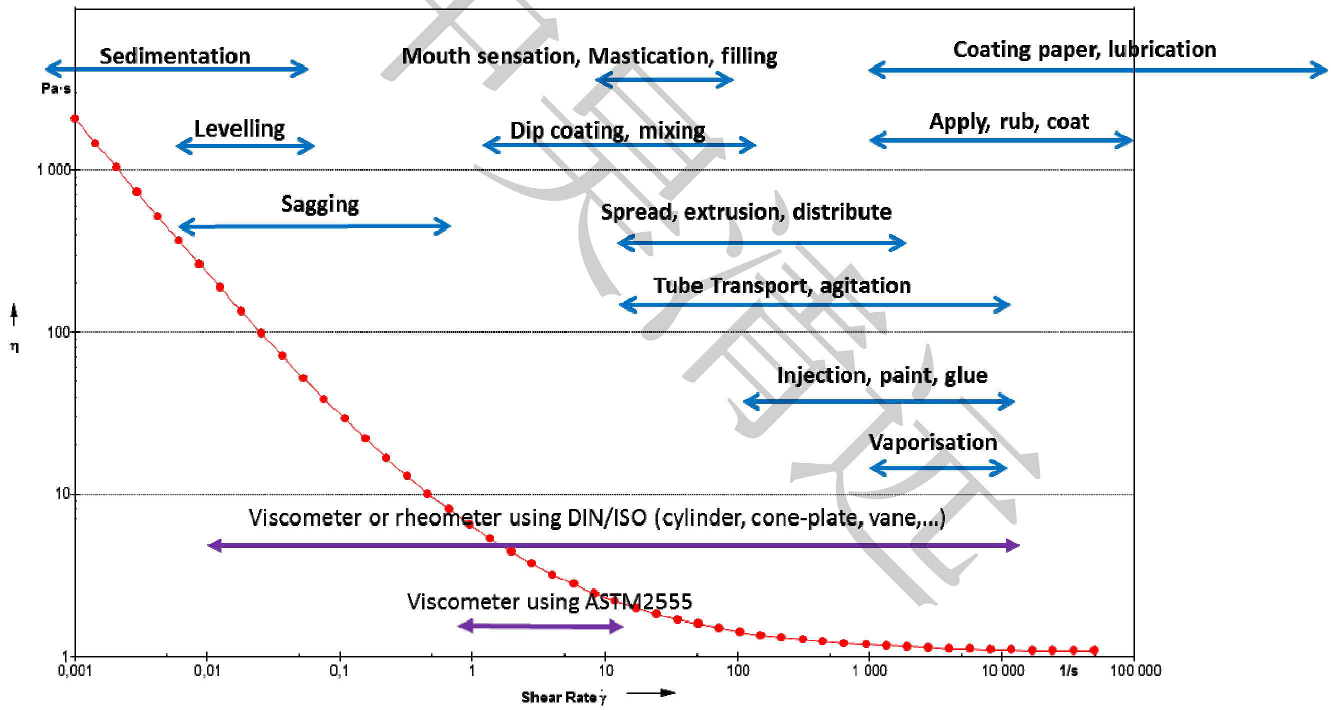
Rheology

1 What is Rheology?

Rheology describes **deformation** and **flow properties** of a material (it is a part of **Physics**, Physics of Solids and Mechanics of Fluids).
For many materials, a large deformation leads to a flow (others, however, are too fragile and break).

2 Viscosity

This physical string is part of the **rheology**. The measurement of the viscosity makes it possible to predict the behaviour of the material during its application, transport, manufacturing, etc. It is sufficient to measure it at shear rate (cf figure below, shear rate and Eta are defined page 3) close to those encountered during the different stages of the life of the material and to compare them.

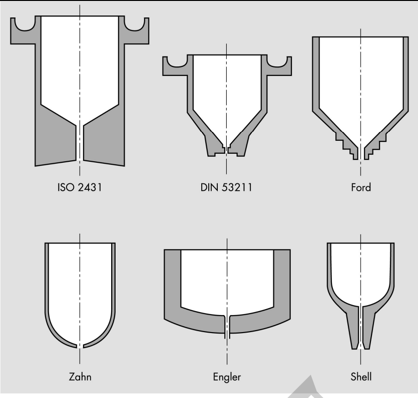


For example, if a material has a lower viscosity than another at 1000 s -1, it will be more easily pumped.
All companies using product as liquid, gel, cream, paste, soft-solid, need to know at least viscosity value or for some of them rheological behaviour. Target for them is to make quality control, formulation, research, competition knowledge,…. For example, everybody uses product as shampoo or paint, and like to get all the time same aspect and easy to use product. Manufacturer know that and try to get good behaviour by formulation. Before production, customer needs to check if new composition will be producible or if process will not destroy it (structure, thixotropy,…). And after we have storage (check sedimentation), transport by truck (temperature variation).

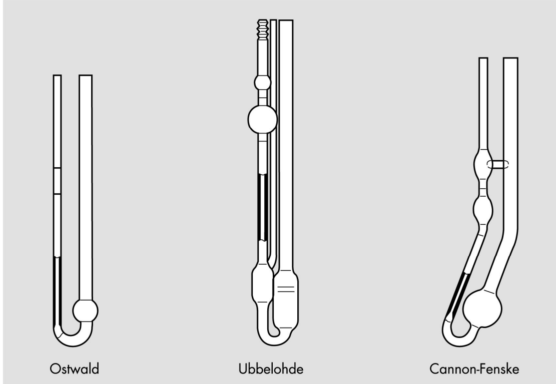
A lot of different methods exist to measure viscosity or rheological behaviour. Some of them are just used by specific companies (FORD with Flow Cup), specific norms (Asphalt with ASHTO) and specific brand (Brookfield and norm ASTM2555).

2.1 Methods for viscosity measurement.

- **Flow cup**: ISO cup, Ford cup according to ASTM, DIN cup,…
- **Capillary Viscometers (**Ostwald, Ubbelohde, Cannon-Fenske)



Flow Cup



Capillary Viscometer

- **Falling Ball** Viscometer or **Rolling Ball** Viscometers
- **Stormer Viscometer** (using Krebs spindle)
- **Rotational Viscometer** (Brookfield type, norm ASTM/ISO 2555) **B-ONE PLUS, FIRST PLUS, RM100 PLUS**

According to ASTM/ISO 2555 (Brookfield type)

Shear gradient not known. Viscosity measurement
Dependent to spindle, rotational speed, container and temperature

MK-R1 à R7

6 disks + 1 axis

Sensibilities
RV/HA/HB

Medium and high viscosity

MK-L1 à L4

1 Cylinder + 2 disks
+ 1 axis

Sensibility LV

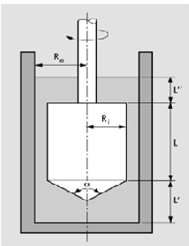
Low Viscosity

- **Rotational Rheometers and Viscometers** (according to DIN 53019 and ISO3219)
  with **measuring systems : Cylinders (CC), Cone-plate (CP), Plate-plate (PP)**; **FIRST PLUS, RM100 PLUS** and **RM200 PLUS**

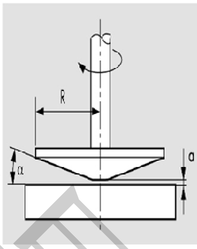
Rotating mobile for viscometer and rheometer

According to DIN 53019 et ISO 3219

Shear rate known. Apparent and absolute viscosity measurement.
Rheological study (thixotropy, yield stress, flow behaviour,…)



Cylinders:
Very good for low viscosity
Not good for paste
(air bubbles)



Cone-plate:
For all sample,
Dispersions with
particles below 5 µm

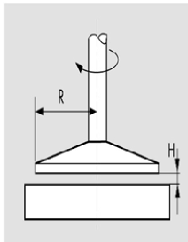


Plate-plate:
Usable for high viscosity
As gel or paste, melt, and
Dispersion with big particles

Other application-specific measuring systems

Vane for heterogeneous products
Shear rate not well known

Krebbs spindles
Unit KU

Anchors mobile for heterogeneous products
Shear rate calculable

If you want to compare data, you have to use the same spindles

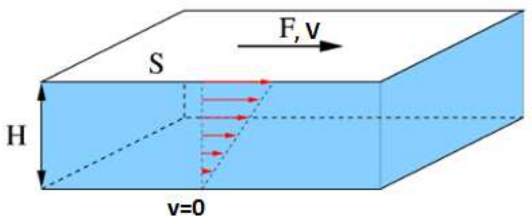
The distinction between a viscometer and a rheometer is sometimes blurred. Let us say that a viscometer measures the viscosity and that a rheometer allows a more complete rheological study (Flow behaviour, yield stress, Thixotropy, temperature...)
We sell viscometers and rotational rheometers. The B-ONE only uses ASTM-type geometries, while all other models allow the use of all measuring systems (see table below).
Most of the time, ASTM spindle are uses only for one point measurement (control). FIRST PLUS is able to work with DIN measuring system, but shear rate range (speed range) are smaller than RM100 or RM200 PLUS.

Table for measuring system choice

Géométries Type of products	Mobile ASTM	Cylinder (CC)	Cone-Plate (CP)	Plate-plate (PP)	Vanes, anchors (FL or MS-R)
Low viscosity (solid particles < 10µm) ex : Paint, inks, shampoo, oil, lotion, drinks…	X	X (or DG)	X	X	
Low viscosity (solid particles >10µm) ex : Paint, inks, suspension, chocolate…	X	X		X	X
Medium viscosity (solid particles < 10µm) ex : Cosmetic cream, paint, daily cream, inks, ketchup, emulsion,…	X	X	X	X	X
Medium viscosity (solid particles > 10µm) ex : Cosmetic cream, road paint, emulsion, grease…	X	X		X	X
High viscosity ex : Polymer, gum, cheese, gel, asphalt…				X	
Fragile Products ex : cheese, yogurt, gel…			X	X	X
Solid product ex : Polymer,				X	
Heterogeneous products ex : Sauce, soup, cement, mortar…		X			X

2.2 Shear rate and Shear stress definition

In norm ISO/DIN, we are able to define shear rate (Gamma point) and shear stress (Tau) by using called "TWO PLATE MODEL" (Figure below). Reason is that this string are needed to be able to calculate viscosity (Eta). In norm ASTM2555 (Brookfield spindle), shear rate is not known.

	**shear stress**: τ ("tau") = F / S (= shearing force / shearing area) **unit: 1 Pa ("Pascal")** = 1 N/m² (compare: air pressure in a weather forecast 1000 hPa = 1000 mbar) **shear rate**: $\dot{\gamma}$ ("gamma-dot") = v / H (= velocity / gap dimension) **unit: 1/s** (= 1 s^{-1} , "reciprocal second")

This theory is applicable with "Laminar flow" conditions. We consider that liquid is composed of many layer, who move at different speed each other. But this "Laminar Flow" exists only for small distance (H on figure above), directly in contact with mobile. This is why DIN measuring system should be uses always with adapted cup (cylinder) or small gap (cone and plate).

With viscometer, we have rotational speed (n) and torque (M). Each DIN measuring system get two constant, K_{Tau} and K_D. This two constant are calculated according to DIN/ISO norm. And we use it to calculate $\dot{\gamma}$ (shear rate, called Gamma point) and τ (shear stress, called Tau)

$$\dot{\gamma}\ (s^{-1}) = n \times K_D \quad \text{and} \quad \tau(Pa) = M \times K_{Tau}$$

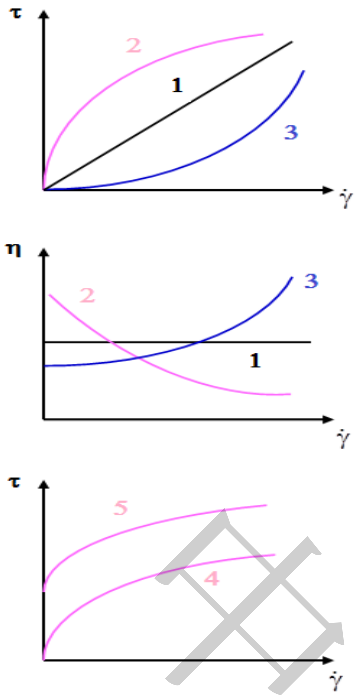
2.3 Viscosity definition

(Shear-) **Viscosity**: η ("eta") = τ / $\dot{\gamma}$ (viscosity law according to Newton)
unit: 1 Pas ("pascalsecond");
[previously used unit: 1 cP ("centipoase") = 1mPas ("millipascalsecond")]

Kinematic viscosity: ν ("ny") = η / ρ (with the density ρ)
unit: 1 mm²/s;
[previously used unit: 1 cSt ("centistokes") = 1mm²/s]
Kinematic viscosity is measured ever then, if the shearing force is caused by gravity; thus, if the weight of the sample is causing the flow (e.g. using flow cups, and pressureless capillary viscometers).

2.4 Flow Behaviour (Rotational Tests)

These flow properties are very interesting for all industrials. Indeed, it is advantageous to obtain a stable low shear material, such as a high viscosity (stability in the pot, sedimentation, etc.) and low to high shear, in order to facilitate transport or application (eg painting, shampoo , Toothpaste, etc.). The interest of obtaining these curves is to control against a standard, to formulate to improve…
We can find three main behaviour as shown below



Diagrams:

Flow curve:
shear stress τ and shear rate $\dot{\gamma}$

Viscosity curve:
viscosity η and shear rate $\dot{\gamma}$
(or: viscosity η and shear stress τ)

Flow behavior:
1 ideal-viscous (Newtonian)
Examples: mineral oils, silicone oils, water

2 shear-thinning (pseudoplastic)
Examples: polymer solutions and melts
(e.g. aqueous methyl cellulose: wallpaper glue)

3 shear-thickening (dilatant)
Examples: highly concentrated dispersions
(e.g. ceramic suspensions, plastisol pastes with too low amount of softener)

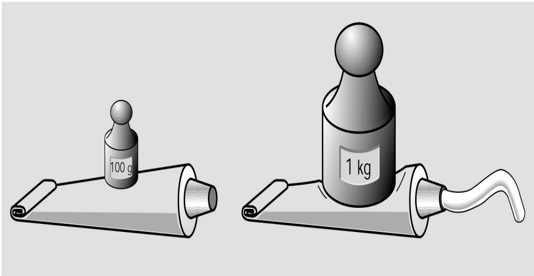
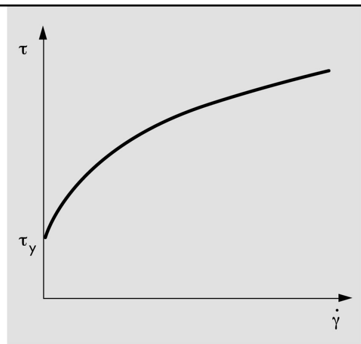
4 Without yield point

5 With yield point

We can say that simple product as water, oil, syrup, some resins, honey get Newtonian behaviour. It doesn't matter if you measure viscosity at different shear rate or speed because it will be constant (depending only of temperature, please see below). This why ASTM spindle (Brookfield type) are well adapted for this kind of product as we are not able to know exactly shear rate.
Then product is more formulated, they get shear-thinning behaviour (may be 80% of products as paint, food, cosmetic, pharma…) or shear-thickening behaviour (rare). The best is to check viscosity in good shear rate conditions (please see diagram in first page). A lot of companies use ASTM spindle to measure viscosity of this kind of product. This is not perfect but can be use only for production control. But you have to know that if they change speed or spindle, shearing conditions are not the same and viscosity value will be different. For non-Newtonian product, best is to use DIN measuring systems (DIN MS) and sometime specific system as Vane or anchors (used then you have particles or heterogeneous sample).

2.5 Yield Point

Yield stress is defined as the minimum force required for product to flow. Any structure has a internal cohesive force. If the external forces are stronger, the structure breaks and the product flows. As earth gravity applies to everything and if internal forces are stronger, structure resists and does not flow. The yield stress value is often used as information about the strength of the material structure.
The benefits for the user are: stability evaluation of dispersions, gels or presence of sedimentation. The product is therefore very stable at rest and, under the action of a stress greater than yield stress, flows to allow its application or transport. In some cases, the measurement of this yield stress can serve as a control of finished product or sizing of packaging.
Examples: concentrated dispersions, pastes, gels (eg toothpaste, ketchup, cosmetic cream, dispersion, paint ...)

	Yield point as **limiting shear stress** τ_y (synonyms: yield stress, yield point)	

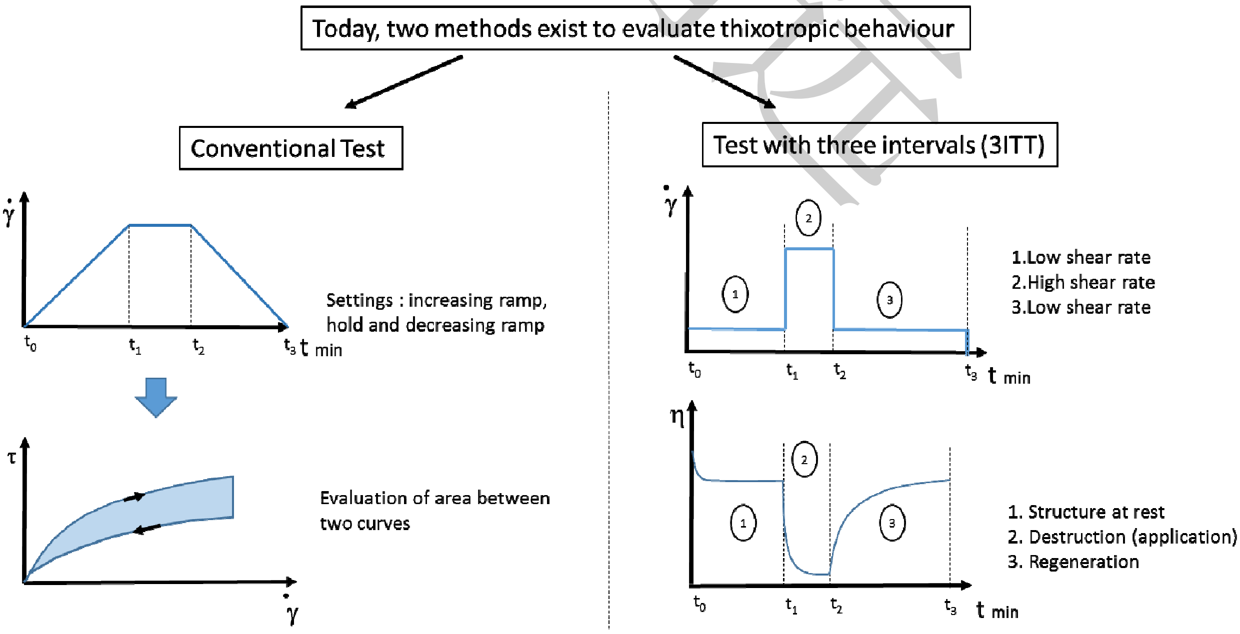
Several methods exist for measuring the yield stress of a product. The most used are the rheological regressions such as CASSON, BINGHAM, WHINDAB.

As we need to get flow curve to use regression, the best is to use DIN MS and make a shear rate ramp (for example for chocolate 1 s^{-1} to 50 s^{-1} with IOCCC norm)

2.6 Time-dependent behaviour (Rotational Test)

"**Thixotropic behaviour" (thixotropy):** Complete regeneration of the structure after shearing during the process, application, transport.... This property is highly interesting. Indeed, it is very damaging for the industrial to see that his product completely destroy after its use (example of mayonnaise, bad appearance, paint that remains "liquid" after its application). The industrial will therefore seek to reformulate its material to provide it with the required properties. We find this interest in practically all sectors, from cosmetics to food processing, painting, inks...

To evaluate time dependant behaviour, we can find two kind of test



Interest of 3ITT test is to get information about time to recover viscosity after application. But for this two methods, best is to use DIN MS.

2.7 Temperature-dependent Behaviour (Rotational Test)

Temperature has effect on all products. Generally we can say that then you heat sample, its viscosity decrease. This effect could be reversible (for example water) and irreversible (for example resins, starch). Test could be done by setting constant shear and temperature (time effect) or constant shear and temperature variable.
Then you want to work with resin, our GT300 PLUS could be a very good solution. But if you just want to check temperature effect, you have to use one of our temperature control unit.
Temperature is very important during measurement. If you don’t know exactly it, viscosity value should not be the same. We can say that an error of 1 °C could change the viscosity of 15%.
Sometime, customer need to measure viscosity of product at different temperature to anticipate problem or to adjust process. Some of them heat sample to decrease viscosity and make easy transfer by tube, or to know effect of transport during winter, best temperature to cure sample, best temperature to melt sample…