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Determination of the Yield Stress of Disperse Systems

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Abstract: The yield stress is defined as the stress below which the substance is an elastic solid, while above it is a liquid with a plastic viscosity. This yield stress is the stress at the yield point. We will report of probably the only system with yield stress according to this definition. The yield stress will be determined from the first visible difference between shear stress and residual shear stress. Shear flow start-up experiments and following stress relaxation will be performed. The relative residual shear stress indicates the strengthening of the structure. It will be reported about systems with pronounced one and two yield stress regions, where the shear stress changes insignificantly with the shear rate. The yield stress regions of these systems can be determined from the flow or viscosity curves and from the residual shear stress curve. System with flow curves without a pronounced yield stress region will be investigated and furthermore the conditions to have a yield stress will be determined. The definition for the yield stress will be modified/extended.

Key words: Yield point, plastic flow behaviour, yield stress, yield stress region.

1. Introduction

Barnes and Walters [1] postulated 1985 "all liquids show Newtonian behaviour at low enough shear rate". A lot of colleagues did not agree with this assertion, they believed on the existence of a yield stress. Hartnett and Hu [2] wrote "The yield stress—an engineering reality"; Astarita [3], "The engineering reality of the yield stress"; Schurz [4], "The yield stress—an empirical reality"; Evans [5], "On the nature of the yield stress"; Spaans and Williams [6], "At last, a true liquid-phase yield stress".

Barnes [7] wrote "However, if viewed on a logarithmic basis, the equally simple Newtonian/power-law/Newtonian description is clearly seen. Although we have shown that, as a physical property describing a critical stress below which no flow takes place, yield stress does not exist, we can, without any hesitation, say that the concept of a yield stress has proved and, used correctly, is still proving very useful in a whole range of applications, once the yield stress has been properly defined".

Barnes [8] stated in "A brief history of the yield stress": "When careful measurements are made below the supposed 'yield stress', flow does take place. The argument for the non-existence of the yield stress as a physical entity now seems insuperable."

We [9] wrote: "The systems with plastic flow behaviour have one or more yield stress regions or yield stresses."

Boger [10] postulated 2004: "To say that a yield stress does not exist is equivalent to claiming there is no such things as a Newtonian fluid, which of course is true in the strictest academic sense."

"The diabolical case of the recurring yield stress" [11] is an interesting discussion about the yield stress.

Møller et al. [12] established that the experimental determination of the yield stress is very difficult.

Barnes [13] defined a "yield stress" region—the shear thinning region between the two Newtonian regions. A lot of authors established the yield stress from the shear thinning region [14-16].

Coussot [17] described an interesting review of experimental data about the yield stress.

2. Experimental

Suspensions with 7.5 wt% Aerosil 380 in the silicone oil M20'000, Araldite CW214-534 and

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suspensions with different concentrations of Cabosil TS 720 in silicone oil M20000 were prepared in a 1.5 L reactor with anchor stirrer with 100 rpm at 40 °C in vacuum.

Aerosil 380 is silica with a specific surface area of 380 ± 30 m^2/g. Cabosil TS 720 is fumed silica with a specific surface area of 100 ± 20 m^2/g. Silica can be added to avoid the sedimentation of the fillers and to obtain a system with desired flow properties. There are strong hydrogen bonds between silica-silica and silica-matrix.

The silicone oil M20000 (Bayer AG) is a polydimethylsiloxane with a weight average molecular weight of 68 kg/mol. This silicone oil shows shear thinning flow behaviour with a zero-shear viscosity of 20 Pa·s at 25 °C.

Araldite CW214-534 (Huntsman AG) consists of Araldite GY260, iron powder and thixotropic additives. The epoxy resin Araldite GY 260 is a Newtonian fluid with a viscosity of 14 Pa·s at 25 °C.

The rheological measurements were carried out with a WRG (Weissenberg Rheo Goniometer), Model R18, Sangamo Ltd., in an air-conditioned room at 25 ± 0.2 °C. A cone-plate arrangement with 4° cone angle and 5 cm diameter was used. All measurements were performed with a strip bar 8 with a diameter of 6 mm.

The distance between cone and plate was reached carefully. The measurement was started after 30 min rest time for the suspension.

The shear stress τ was measured with the time, during stress growth experiments with a constant shear rate $\gamma = \mathrm{const}$, going from low to high shear rates. The stress growth curves were measured up to the steady state value of the shear stress τ_S (Fig. 1). The points of the flow curves represent the steady state shear stress values for different shear rates. The form of the stress growth curves and the phenomenon thixotropy will not be discussed here.

The stress deformation is stopped after achievement of the steady state shear stress, and the stress relaxation begins (Fig. 1).

3. Results and Discussion

At the beginning of the stress relaxation, after cessation of the shear deformation, the elastic deformed torsion bar tries to return to the starting-point. If the structure of the system is destroyed in the stress growth experiment (or not existent), the suspension cannot resist the elastic springing of the torsion bar and no residual shear stress τ_R = 0 will be observed (Fig. 1A). If this appears at low shear rates, the system has no structure and cannot exhibit plastic flow behaviour and a yield stress. The systems with shear-thinning flow behaviour (Newtonian region—shear thinning—Newtonian region) do not show a residual

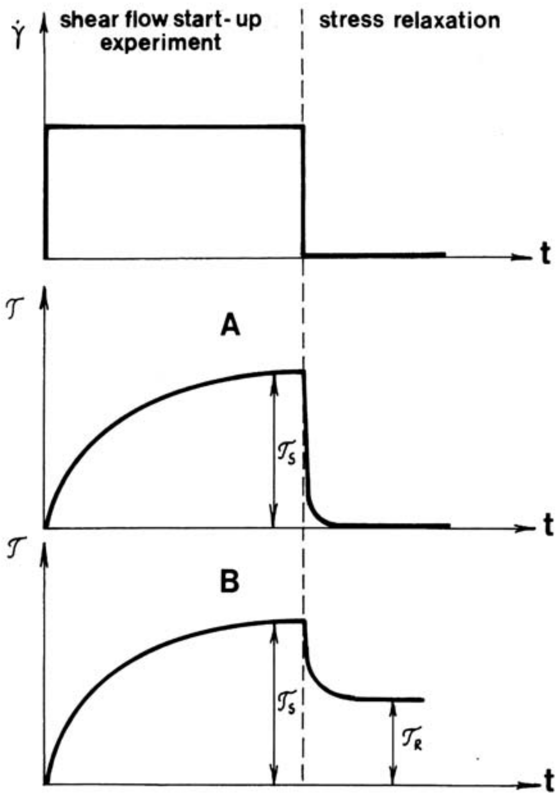

Fig. 1 Stress growth experiment—stress relaxation [18]. A: Stress growth experiment—stress relaxation without residual shear stress τ_R = 0; B: Stress growth experiment—stress relaxation with residual shear stress τ_R > 0.

shear stress [19] and a three-dimensional (3D)-structure. They have consequently only a pseudo yield stress, which may be use for practical purposes [13].

A certain remaining structure after the shear flow start-up experiment can oppose against the elastic springing of the torsion bar to the starting-point and a residual shear stress $\tau_{\mathrm{R}} > 0$ is observed (Fig. 1B). The better remaining structure after the stress growth experiment leads to a higher residual shear stress. The relative residual shear stress is defined as the ratio of residual shear stress to steady state shear stress $\tau_{\mathrm{RR}} = \frac{\tau_R}{\tau_s}$.

If the structure can oppose completely against the elastic springing of the torsion bar, the residual shear stress will be equal to the steady state shear stress $\tau_{\mathrm{R}} = \tau_s$ and the relative residual shear stress will be $\tau_{\mathrm{RR}} = 1$. The structure of such an elastic solid is only elastically deformed. The elastic solid has a kind of a 3D-structure.

An increase of the shear deformation will lead at a certain shear rate to the first partial destruction of the structure or to the transition from an elastic deformation to a viscous flow [20]. We assumed that the first visible sign of the transition from elastic deformation to a liquid will be observed when the relative residual shear stress τ_{RR} changes from 1 to 0.98 [18].

We believe that only systems with pronounced residual shear stress at low shear rates have a strong 3D-structure and respectively plastic flow behaviour, which can lead to a yield stress.

To be sure that such systems have a 3D-structure and plastic flow behaviour, one must perform a stress growth—stress relaxation experiment.

3.1 Systems with 7.5 wt% Aerosil 380 in the Silicone Oil M20000

The viscosity curve of the system with 7.5 wt% Aerosil 380 in the silicone oil M20000 (Fig. 2) shows a yield stress region with approx. 1,000 Pa, where the viscosity does not change significantly with the shear stress.

The destruction of the structure occurs consequently in only one step/region from 1,255,714 Pa·s up to 14,394 Pa·s (Fig. 2) or for the relative residual shear stress from 0.95 to 0.59 (Fig. 3).

The high value of the first point of the relative residual shear stress at a shear rate of $\gamma_{\mathrm{y}} = 0.0007$ 1/s makes the appearance of Newtonian behaviour at lower shear rates impossible and unexpected.

The relative residual shear stress of the first point has a value of 0.95 (Fig. 3). This value is close to the point, where the transition from elastic deformation to

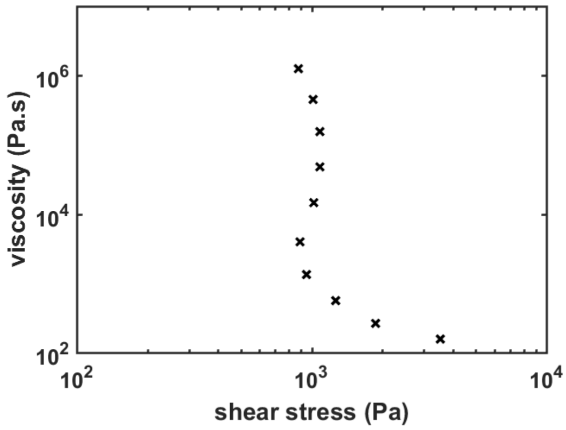

Fig. 2 Viscosity curve of the suspension with 7.5 wt% Aerosil 380 in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C).

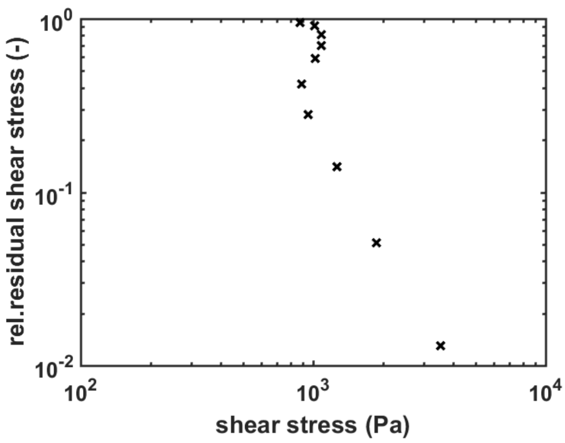

Fig. 3 Relative residual shear stress curve of the suspension with 7.5 wt% Aerosil 380 in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C) [18].

liquid occurs and we can assume that this is the yield point. This yield point is determined with the yield shear rate γ_y = 0.0007 1/s and the yield stress with τ_y = 879 Pa. The yield stress at the yield point corresponds to the definition—"The stress below which the substance is an elastic solid and above it a liquid with a plastic viscosity". It is now sure that the yield stress really exists, according to the definition. Since no other such systems are described in the literature, some authors doubt on the existence of the yield stress.

We have found the yield point in only one suspension, but it is sure that few more such systems, for example systems with more than 7.5 wt% Aerosil 380 in silicone oil M20000, will have the elastic solid state.

The existing definition of the yield stress considered only systems with a solid state, but the most rheological systems do not reach solid state. It is obviously necessary to modify the definition of the yield stress. Since the systems in the elastic solid state have a strong 3D-structure, only rheological systems with a 3D-structure can have a yield stress. Consequently, we can extend the definition of the yield stress to include all rheological systems—the rheological systems must have a three-dimensional network at low shear rates, but it is not necessary to be an elastic solid. The yield stress can be determined from the region of the flow curve, where the shear stress does not change significantly with the increase of the shear rate [19, 21-27] by extrapolation of the shear stress to the *y*-axis.

3.2 Araldite CW 214-534

The viscosity curve of Araldite CW 214-534 shows two regions, where the viscosity changes insignificantly with the shear stress (Fig. 4). There is a strong decrease in the viscosity—from 60,714 Pa·s to 28,571 Pa·s in the first yield stress region and from 6,445 Pa·s to 1,821 Pa·s in the second yield stress region (Fig. 4). The yield stresses can be established by extrapolation of the yield stress regions to the *x*-axis with 80 Pa and 270 Pa.

The plateau between the two yield stress sections has a viscosity of 10,600 Pa·s (Fig. 4) and a relative residual shear stress of approx. 0.61 (Fig. 5). The high value of the relative residual shear stress shows that this is only a pseudo-Newtonian region. A rearrangement of the structure takes place in this transition section, without a destruction of the structure.

The first point of the flow curve is obtained by the stress growth experiment with γ = 0.0014 1/s and has a steady state value of τ_s = 85 Pa. The stress relaxation after this start-up experiment shows a residual shear stress τ_R = 67 Pa or a relative residual

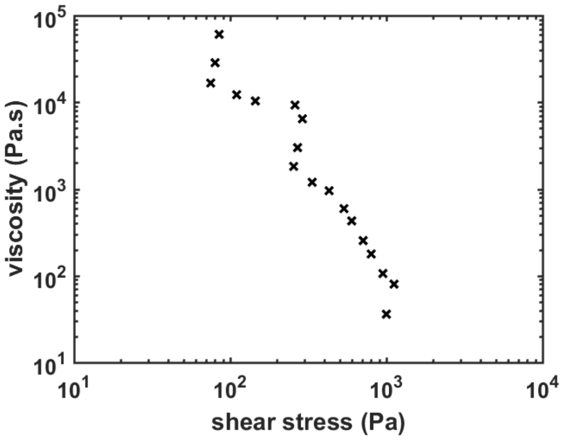

Fig. 4 Viscosity curve of Araldite CW214-534, 6 months after production (WRG, cone-plate, 4°, 25 ± 0.2 °C).

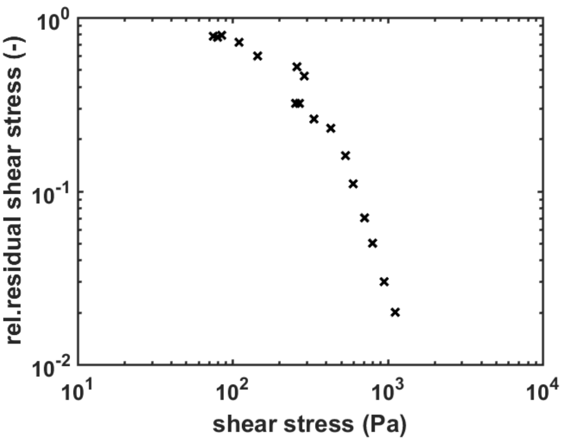

Fig. 5 Relative residual shear stress curve of Araldite CW 214-534, 6 months after production (WRG, cone-plate, 4°, 25 ± 0.2 °C).

shear stress of τ_{RR} = 0.79 (Fig. 5). About 0.21 of the structure is destroyed during the shear stress growth experiment and 0.79 can be accepted to be the size of the remaining structure. The system has therefore a strong three-dimensional network and consequently plastic flow behaviour.

The first three points of the relative residual shear stress curve have nearly the same value of 0.78 (Fig. 5). Therefore, the value of the first yield stress cannot be determined. It is not possible for a Newtonian region to appear at lower shear rates. The second yield stress is found out as 260 Pa by extrapolation of the corresponding points of the relative residual shear stress curve (Fig. 5) to the x-axis. This value is close to the second yield stress region from the viscosity curves. The destruction of the 3D-network of this system occurs obviously stepwise through the first yield stress region, the transition section and the second yield stress region. The relative residual shear stress begins to decrease after the second yield stress region with a slope of $n = -2$.

The existence of one or two yield stress regions depends on the type of the structure.

The observed two suspensions have a pronounced yield stress region and it is not difficult to determine the yield stress. But not all systems have such pronounced yield stress regions and it is not easy to measure the "whole" flow curve and determine the yield stress or yield stress region.

3.3 Systems with Different Concentration of Cabosil N 70 TS in the Silicone Oil M20000

3.3.1 System with 3 wt% Cabosil N 70 TS in the Silicone Oil M20000

This suspension exhibits shear thinning flow behaviour with a zero-shear viscosity of 90 Pa·s (Fig. 6).

The values of the residual shear stress are insignificant, or the structure of the suspension is very week or non-existent. The low concentration of 3 wt% Cabosil N 70 TS is obviously not in condition to build a 3D-structure in the silicone oil M20000.

3.3.2 System with 5 wt% Cabosil N 70 TS in the Silicone Oil M20000

The viscosity curve of the system with 5 wt% Cabosil does not show any more a first Newtonian region with a zero-shear viscosity and consequently shear thinning flow behaviour. But does this suspension exhibit plastic flow behaviour? (Fig. 7).

Fig. 8 shows the dependence of the relative residual shear stress on the shear stress.

The first point has a value of 0.15. Stress growth experiments with lower shear rates will present higher relative residual shear stress values. The appearance of a Newtonian region seems improbable.

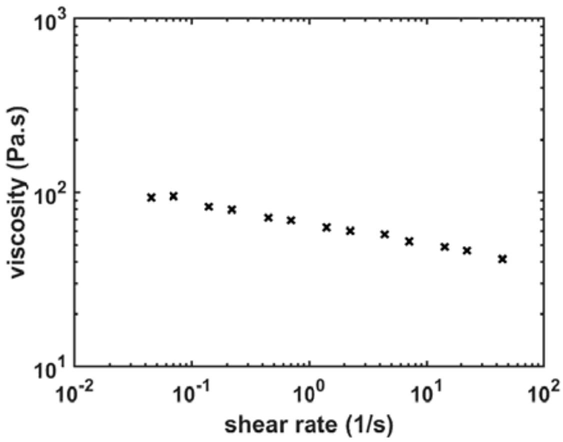

Fig. 6 Viscosity curve of the suspension with 3 wt% Cabosil N 70 TS in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C).

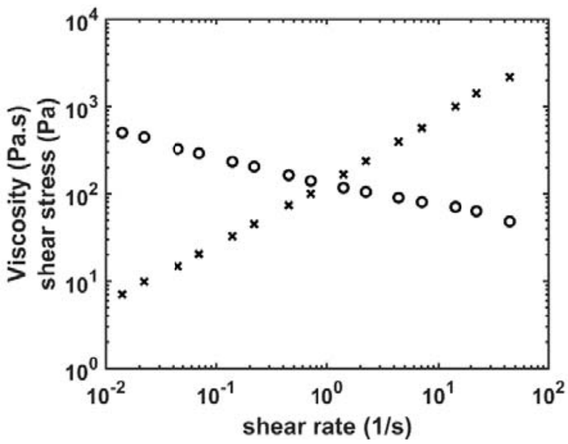

Fig. 7 Flow (*x*) and viscosity (*o*) curves of the suspension with 5 wt% Cabosil N 70 TS in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C).

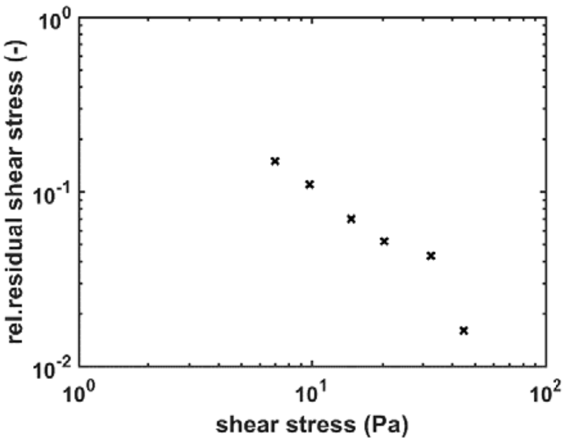

Fig. 8 Relative residual shear stress curve of the suspension with 5 wt% Cabosil N 70 TS in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C).

This suspension has obviously a week 3D-structure. The concentration of 5 wt% Cabosil is not able to build a good 3D structure, but the system does not have shear thinning flow behaviour. We would like to extend the definition for the yield stress—if a system has a week structure, and the first point of the relative residual shear stress has a value more than 0.1, one can assume for practical purposes a 3D-structure and plastic flow behaviour with yield stress. This system does not have a pronounced yield stress region and therefore the practical determination of the yield stress can occur by extrapolation of the flow curve (Fig. 7) to the *y*-axis.

3.3.3 System with 7 wt% Cabosil N 70 TS in the Silicone Oil M20000

The increase of the Cabosil concentration to 7 wt% causes a rice of the shear stress (Fig. 9), compared with the suspension with 5 wt% (Fig. 7).

It is not evident from the flow curve if this suspension has a 3D-structure, plastic flow behaviour and a yield stress.

The relative residual shear stress curve (Fig. 10) exhibits high values.

The first point of the residual shear stress curve at γ = 0.0014 1/s has a value of 0.48. This high value points to a strong 3D-structure. The suspension with the concentration of 7 wt% Cabosil has obviously plastic

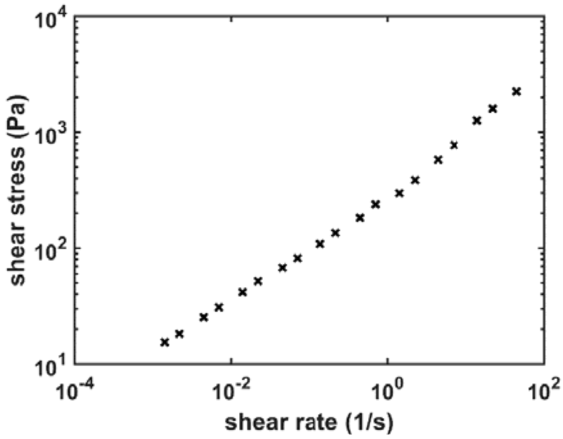

Fig. 9 Flow curve of the suspension with 7 wt% Cabosil N 70 TS in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C).

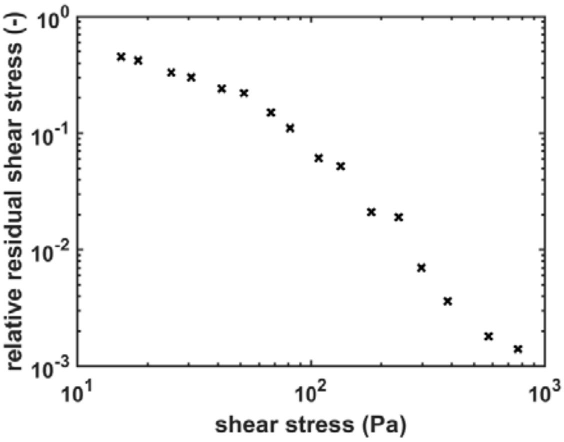

Fig. 10 Relative residual shear stress curve of the suspension with 7 wt% Cabosil N 70 TS in the silicone oil M20000 (WRG, cone-plate, 4°, 25 ± 0.2 °C).

flow behaviour and a yield stress. The flow curve does not have a pronounced yield stress region and the "whole" curve is not registered. Therefore, the yield stress can be ascertained for practical purposes by extrapolation of the flow curve to the *y*-axes (Fig. 9) or described by the Herschel-Bulkley model.

4. Conclusions

The stress relaxation, after a stress growth experiment, is a good tool for establishing the strengthening of a structure. The better built structure, the bigger residual shear stress and relative residual shear stress respectively.

The first point of the relative residual shear stress curve of the disperse system with 7.5 wt% Aerosil 380 in the silicone oil M20000 has a value of 0.95. This value is close to the transition from elastic solid to a liquid and can be assumed to be the yield point. This system is the proof of the existence of the yield stress, according to the existing definition.

The suspensions with Cabosil N 70 TS in silicone oil M20000 show, depending on the Cabosil concentration, either a shear thinning flow behaviour (3 wt%) or a plastic flow behaviour with a week 3D-structure (5 wt%) or a plastic flow behaviour with a strong 3D-structure (7 wt%).

The existing definition of the yield stress considers only systems in the elastic solid state. But most of the rheological systems do not reach the yield point. Therefore, we would like to extend the definition of the yield stress to include all rheological systems and assume that there are three kinds of systems with a yield stress:

- Systems in the elastic solid state, with a yield stress at the yield point, according to the existing definition,
- Systems, that do not reach the yield point, but have a strong three-dimensional network at low shear rates. We accept that systems with a relative residual shear stress more than 0.30 at low shear rates have a strong 3D-structure, plastic flow behaviour and a yield stress.
- Systems with a week 3D-structure. We assume for practical purposes that a system has a 3D-structure if the relative residual shear stress at low shear rates has a value of more than 0.1.

The yield stress can be determined from the flow curve with a pronounced yield stress region as the region where the shear stress does not change significantly with the shear rate. It is also possible to find the yield stress from the viscosity curve and from the relative residual shear stress curve.

When a system has a 3D-structue, but there is no pronounced yield stress region and the "whole" flow curve is not registered, the yield stress can be determined for practical purposes by extrapolating the flow curve to the *y*-axis or it can be described using the Herschel-Bulkley model.

One can conclude that:

- The systems with shear thinning flow behaviour do not exhibit a relative residual shear stress and consequently have no 3D-structure and yield stress.
- The systems with relative residual shear stress more than 0.1 at low shear rates have a 3D-structure and plastic flow behaviour and yield stress.

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