Chapter 1 – Introduction Rheology

Flow Behaviour and Rotational Rheometers

1 Introduction

The term “viscosity” has a special connotation in the coatings industry. Many application properties such as ease of processing, sagging and levelling are influenced by “viscosity”, in other words the coating’s flow behaviour. This means that consistently high product quality can only be guaranteed by an exact knowledge of the coating’s rheological behaviour, i. e. its flow characteristics. The unequivocal rheological characterization of the materials used requires flow curves to be produced with rotational rheometers.

2 Rotational rheometers

The various rotational rheometers on the market are based on two different measuring principles (rate-controlled or stress-controlled).

In the case of rate-controlled rotational rheometers (CR) the material is subjected to shear in a gap and the resulting shear stress is measured. This is done e. g. by using coaxial measuring systems by rotation of the outer cylinder of a Couette system (or inner cylinder of a Searle system). The shear rate for any rotational speed can be calculated from a knowledge of the test equipment geometry. Fig. 1 shows a coaxial cylinder measuring system consisting of outer (left) and inner cylinder (right). In a so-called cone-plate measuring system (fig. 2), the shearing occurs in the gap that is formed between a plate and the cone.

Fig. 1: Coaxial cylinder measuring system, left outer cylinder, right inner cylinder

Fig. 2: Cone-plate measuring system, cone angle 1°

3 Flow behaviour

These measuring geometries for rotational rheometers are described in various DIN standards (e. g. DIN 53019, DIN Paperback 398 Rheology). The recording of a flow curve (shear stress vs. shear rate) finally allows to describe the investigated material with regard to its flow behaviour. Shear stress τ and shear rate $\dot{\gamma}$ are linked via the relationship

$$\tau = \eta \, \dot{\gamma}$$

η is the (dynamic) viscosity in this respect, and, for non-Newtonian fluids, also 'apparent' viscosity.

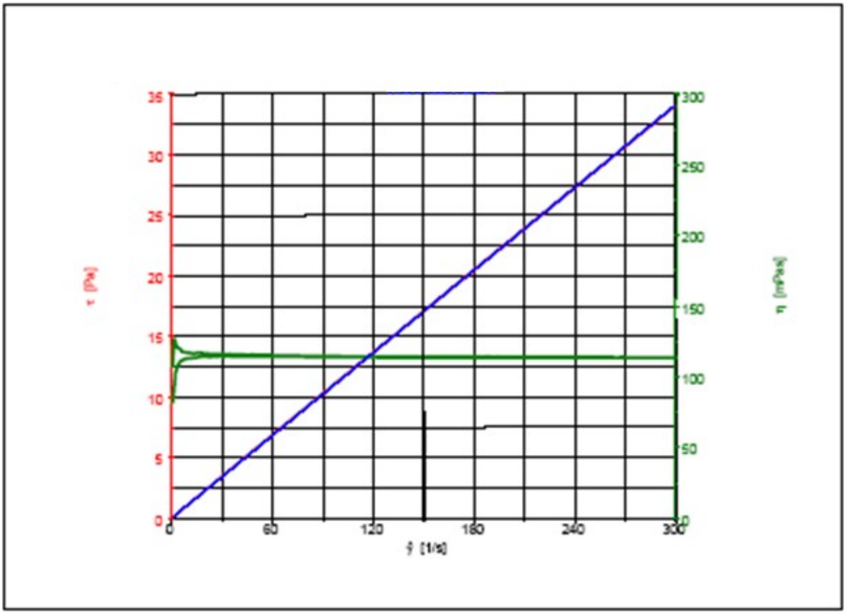


Fig. 3: Newtonian flow behaviour

Rotational rheometers must always be used for the rheological characterization of a substance, if it is not certain whether a purely Newtonian flow behaviour is present. A Newtonian flow behaviour is characterized by a constant viscosity independent of the shear (shear rate). Fig. 3 (acc. [3]) shows a typical flow and viscosity curve of a Newtonian mineral oil up to a shear rate of 300 s^{-1} (blue flow curve, green viscosity curve).

If Newtonian flow behaviour is present, the viscosity can also be determined with the aid of flow cups (e. g. according to DIN EN ISO 2431). In contrast, purely Newtonian behaviour cannot be observed practically in modern, in particular waterborne coating systems. Rather, flow anomalies such as shear thinning (pseudo-plasticity), thixotropy or even viscoelastic behaviour occur.

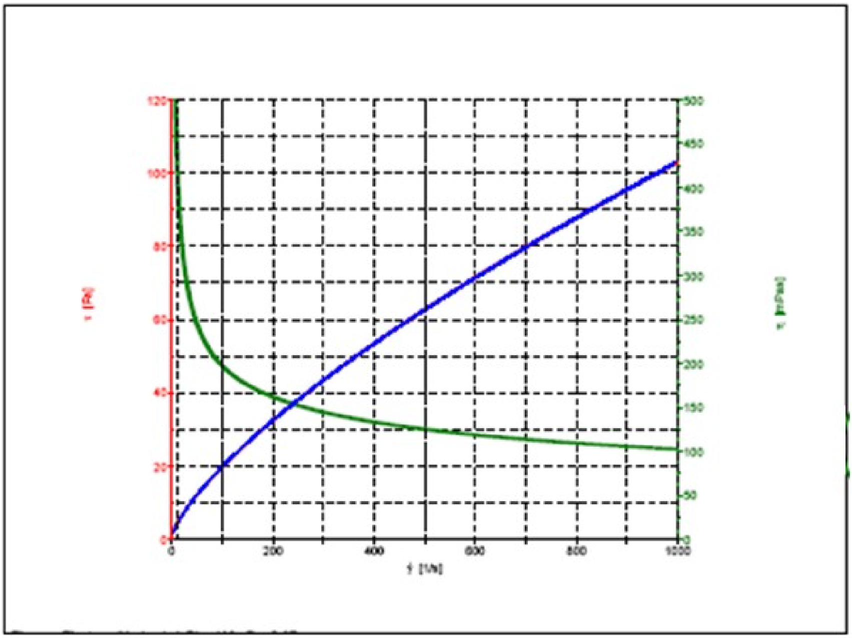


Fig. 4: Pseudo-plastic flow behaviour

If a material has a pseudo-plastic flow behaviour, the viscosity decreases with increasing shear (shear rate), in English usage it is referred to as ‘shear thinning’. Fig. 4 (acc. [3]) shows flow and viscosity curves of a pseudo-plastic coating up to a shear rate of 1000 s^{-1}.

In the phenomenon of thixotropy, a temporal dependence of the viscosity is also observed (see next chapter). In contrast, the case of increasing viscosity with increasing shear (dilatant flow behaviour or rheopexy) is extremely rare for coating systems. Thixotropy and the meaning of yield points will be discussed in the next chapter.

In the case of stress-controlled rotational rheometers (CS) it is not the shear rate that is specified as in CR instruments, but the shear stress.

Here one determines deformation (rotation) and thus the shear rate. Extremely small shear rates can be realized with stress-controlled instruments, so that these instruments are especially useful for accurately determining small yield points (< 1 Pa). For a dynamic experiment (oscillation, see next chapter) typical deformations vary between < 1 % and a few 10 %; the oscillation frequency range normally varies between about 0.001 Hz and a few 10 Hz. Often used is the oscillation test with a fix frequency of 1 Hz.

An extensive general representation of rheology and rheometry can be found, for example, in [5]. It exists a detailed collection of DIN standards [2] on the usual methods of viscosity measurement. The DIN EN ISO 3219 series of standards now describes modern methods and procedures [6].

References

01. DIN 53019

02. DIN-Taschenbuch 398, Rheologie, Beuth (2019)

03. M. Osterhold, Vortragstagung der GDCh-Fachgruppe Lackchemie, Paderborn (2016)

04. DIN EN ISO 2431

05. T. Mezger, The Rheology Handbook, Vincentz, Hannover, Germany, 4. Edition (2014)

06. Standard series DIN EN ISO 3219

Chapter 2 – Rheological Measurements

Rheological Characterization of Coatings Yield Point, Thixotropy and Oscillation

1 Introduction

Many applicational and technological properties are influenced by the flow behaviour of the coating. High product quality can only be guaranteed through an exact knowledge of the rheological behaviour of the coating and the used raw materials, respectively. In view of the increasing use of waterborne systems flow anomalies as thixotropy, yield points or also viscoelastic behaviour can be observed more often. Such behaviour is not normally observed in conventional, solvent-borne coatings. If, however, so-called SCA agents (Sagging Control Agents) are added to directly control rheological properties, phenomena like thixotropy, yield points or viscoelasticity can appear as well [1-3].

Yield point and thixotropy influence important materials properties as storage stability, pumping behaviour or levelling and flowing. Against this background the Working Group “Rheology” of the Standards Committee coatings and coating materials (NAB) within the DIN (German Institute of Standardization e. V.) has followed up intensively on the measuring characterization of yield points and thixotropy in the last years. Two technical reports on these items have been prepared [3, 8].

The measuring possibilities of characterizing the rheological properties with rotational rheometers concerning yield point and thixotropy will be presented in this chapter.

2 Definition and importance of yield point and thixotropy

The yield point is defined as the lowest shear stress above which the behaviour of a material, in rheological respect, is like that of a liquid; below the yield point its behaviour is like that of an elastic or viscoelastic body.

Thixotropy describes a flow behaviour, where the rheological parameters (viscosity) decrease due to a mechanical constant load to a timely constant limiting value and after reducing the load, the initial state is completely reached depending on time. In practice, only a limited time frame is considered in which the initial state is not always reached.

With yield point and thixotropy important material properties can be characterized, e. g.

- Effectiveness of rheological additives
- Storage stability (e.g. against sedimentation, separation, flocculation)
- Behaviour when starting to pump
- Wet film thickness
- Levelling and flowing behaviour
  (e. g. without brushmarks and sag formation)
- Orientation of effect pigments

3 Methods for determining the yield point

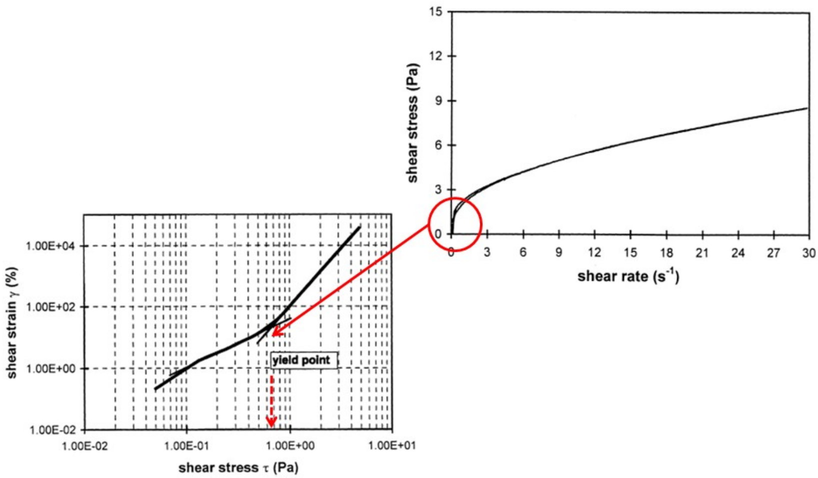
The individual methods for determining the yield point are summerized and critically discussed in the DIN technical report 143 [4]. The presented results for evaluating yield points in this report base on interlaboratory tests, which were carried out by the participants of the Working Group "Rheology" of the Standards Committees "Pigments and Extenders" and "Coatings and Coatings Materials" at DIN.

In first preliminary tests different waterborne basecoats with low and dispersions with distinctly higher yield points have been examined as well. It was found that some methods showed unexpectedly good qualitative relationships. On the other hand, some participants reported problems with the preparation of the samples. In addition, in the course of the preliminary tests certain methods of measurement have been found to be unsuitable for the samples examined and were therefore no longer considered. In this connection, the method of maximum viscosity and the method using a vane measuring system have to be mentioned. Also the method for determining the yield point using a linear stress ramp was not helpful as there are not enough measuring points in the lower measuring range. Also evaluation procedures based on traditional regression methods (e. g. according to Bingham or Herschel-Bulkley) were not considered in further tests. The results depend too strongly on the theoretical model used and the measuring specifications (ramps) (according to [3, 4]).

3.1 Tangent method in a representation of a lg γ / lg τ diagram

Based on the experiences made in preliminary tests, the participants agreed on the method "stress ramp" to be used in a continued interlaboratory test. The results are presented in the technical report 143. Therefore, below and above the assumed yield point one decade for the evaluation should be available. The (logarithmic) shear stress ramp should begin at least one decade below the assumed yield point and should reach at least one decade beyond the yield point value.

Exact test conditions have been agreed by the Working Group and definitely been specified for all participants of the comparative testing programme (see [4]). Five different samples have been examined in total: two waterborne basecoats with low yield points of a magnitude of 1 Pa or smaller, two dispersions and one sample with well known yield point provided by the Physikalisch-Technischen Bundesanstalt (PTB, The National Metrology Institute of Germany).



Determination of a small yield point of a waterborne system in the γ/τ diagram (left), conventional flow curve (right)

Fig. 1: Determination of the yield point

If a yield point is existing, a straight line can be observed in the range of low shear stress, shear stress τ and shear deformation/strain γ are then proportional at low values. The investigated material shows consequently a reversible linear-elastic deformation behaviour (Hooke's elasticity law). At higher stresses the structure at rest breaks down, the