Application Note
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The influence of thickeners on the application method of automotive coatings and paper coatings – rheological investigations with the HAAKE CaBER 1

Key words:

- Paper coatings
- Automotive coatings
- Misting
- Elongational viscosity
- Roller application
- HAAKE CaBER 1

Rheology Application Notes

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Abstract

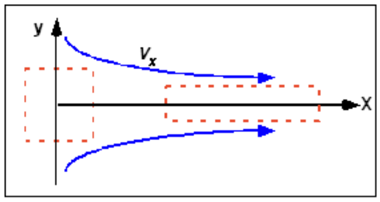
Spraying automotive coatings and the application of paper coatings are industrial processes, in which elongational flows play an important role. As a result, the application behaviour of these fluids often cannot be sufficiently characterised with traditional shear experiments. Products with similar shear viscosities can have very different elongation properties. With the HAAKE CaBER 1 extensional rheometer, a liquid filament is created that is stretched under the influence of surface tension. Using the decrease in the filament diameter as a function of time and the life of the filament, it is possible to characterise the elongational behaviour of low-viscosity to pasty liquids in a simple way. The rheological properties of typical water-based automotive coatings and paper coatings are determined by the thickeners used and their interactions with the other recipe components. In the CaBER experiment, different types of thickener display a characteristic decrease in the filament diameter as a function of time. Different break-up times are desirable, depending on the application. When automotive coatings are sprayed, short break-up times are advantageous in order to obtain the finest possible drop distribution. When paper coatings are applied with rollers, spraying and „misting“ should be prevented as much as possible, which means that formulations with long break-up times are advantageous.

Introduction

Elongation flows occur in many industrial production and working processes, especially where product flows experience cross section changes or are diverted, and determine these significantly. Spraying, coating, pumping or filling processes are typical examples that are relevant in almost all branches of industry. The characterisation of elongational properties in product development and quality assurance is therefore essential in order to optimise product properties or production processes.

In a shear flow, the flow lines run parallel – in an elongational flow they converge (figure 1). Elongational flows and elongation properties of substances therefore cannot be simulated and analysed with rotational rheometers. Materials that display a similar rheological behaviour in the shear experiment may display very different properties in elongational flows.
This article discusses the rheological results of elongational and shear experiments of various thickeners and formulations, to which such thickeners have been added.

a)



b)

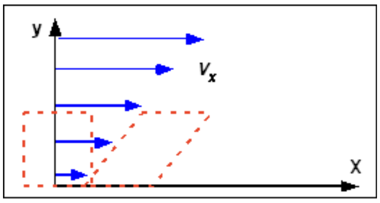


Figure 1: Comparison between extensional flow (a) and shear flow (b).

Material and Methods

With the HAAKE CaBER 1 extensional rheometer (**C**apillary **B**reak-up **E**xtensional **R**heometer) it is possible in a simple experiment to examine quickly and without complications the rheological properties of liquids in an elongation flow.

A drop of liquid is placed between two parallel plates in the HAAKE CaBER 1. The upper plate is then moved up very quickly (in 50 ms), during which the sample is elongated, producing a liquid filament. The necking and breakage of the liquid filament provides valuable information about the product and process properties of the substance being examined (Figure 2).
The measuring principle shown in Figure 3 is simple: A laser micrometer measures the decrease in the sample diameter D as a function of the time **t after** the upper plate has arrived in its final position. The relative elongational viscosity is calculated from the measurement result (D = f(t)).
If the surface tension of the sample is known, the absolute elongational viscosity can be determined. The decrease in the string diameter as a

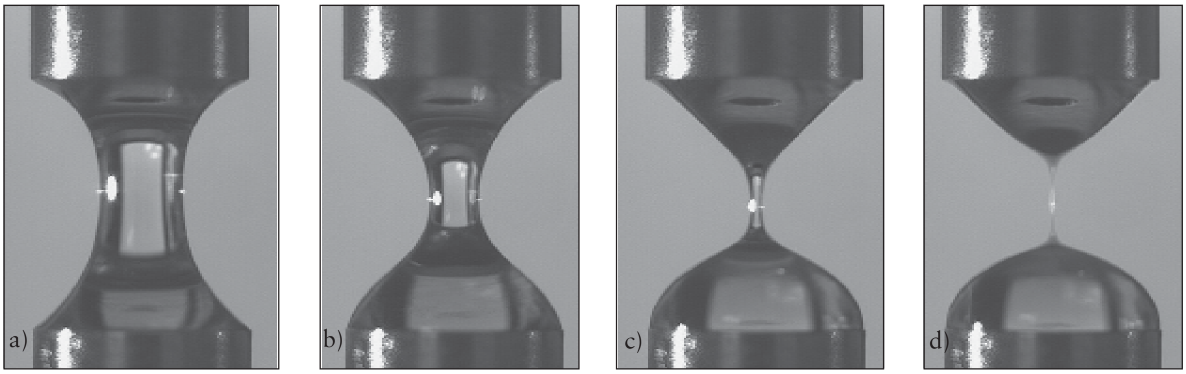


Fig. 2: Sequence of a CaBER measurement: filament formation (a), filament necking (b,c) and filament break-up (d)

function of time is determined by the competing physical effects of surface tension, viscosity, elasticity and mass transfer.

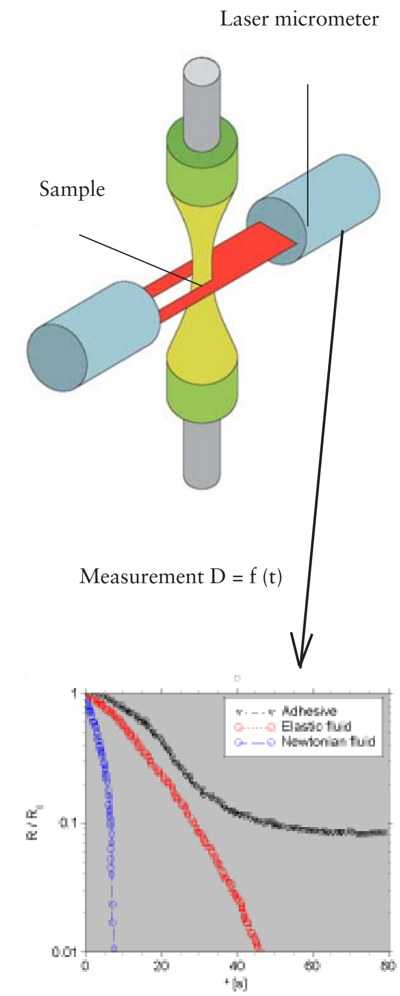


Figure 3: Functional principle of the HAAKE CaBER 1

Results of aqueous thickener solutions and correlation with the application process

Three different classes of thickeners were examined with the HAAKE CaBER 1 and a rotational rheometer:

- CMC thickener (CarboxyMethylCellulose)
- Acrylate thickener
- Associative thickener

In addition to the traditional acrylate-based synthetic products, the associative thickeners include clay mineral suspensions and DNA solutions. The former because of their associative house of cards structure, the latter because of the strong intermolecular interactions. CMC and acrylate thickeners are widely used in the paper industry. Associative thickeners are used in areas such as formulations of cosmetics and automotive coatings. Figure 4 shows the result of the elongational and shear experiments with these thickeners.

The viscosity curve in the shear speed range of 10^{-2} to 10^{3} s^{-1} was measured with the rotational rheometer. Figure 4b shows a log-log depiction of the relationship between the viscosity and the shear speed. The shear-thinning behaviour (decrease in viscosity as the shear speed increases) is at its most pronounced in the case of the associative thickeners; the viscosity curves of the acrylate and CMC thickeners both display a significantly lower decrease in viscosity.

In elongation experiments, the various thickeners displayed characteristic differences. The filament break-up time is very short in the case of the associative thickeners. The reason for this is that the pronounced network structure is destroyed very quickly in the elongational experiment and cannot rebuild itself during the elongation experiment.

The acrylate thickeners and associative thickeners (Figure 4a) display an exponential decrease in the filament diameter as a function of time, and thereby the typical elongational behaviour of an elastic fluid. The CMC solutions display the elongational behaviour of a more viscous fluid, i.e. the filament diameter decreases according to a power law.

The thickeners that have zero viscosity in the shear experiment display a longer string life than the associative thickeners, the shear viscosity of which increases in the low-shear range.

The differences in the CaBER experiment that were found for associative and non-associative thickeners correlate with the spray coating properties of water-based automotive coatings: Smaller droplets are formed in the case of the formulations containing associative thickeners.

These display a lower elongational viscosity than formulations based

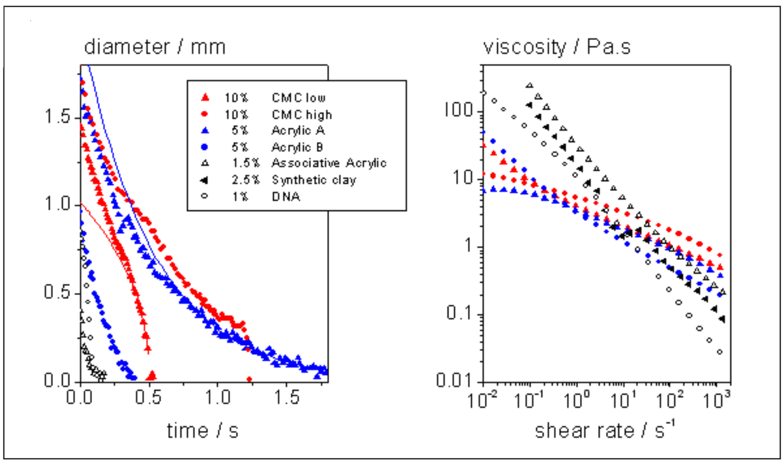


Figure 4: Comparison of CaBER experiment (a) and shear experiment of different aqueous thickeners

on non-associative thickeners, even when the shear viscosity functions are almost identical in a wide shear rate range (1).
In the case of paper finishing, the coating is in most cases applied via rollers. When the coating is transferred to the raw paper, unwanted drop formation can occur, the so-called „misting“. In case of this phenomenon, the elongational viscosity also plays a decisive role (Fig. 5).

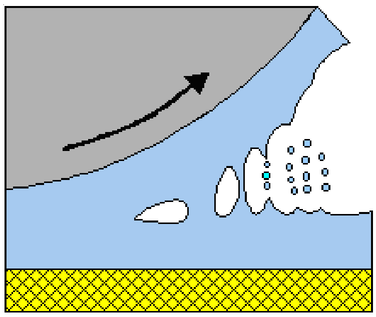


Figure 5: Schematic depiction of the filament and droplet formation when applying paper coatings via rollers.

The time curve for the filament diameter in the CaBER experiment for two paper coatings that differ only by the addition of a thickener is shown in Figure 6. It is apparent here that the filament break-up times of the coating with acrylate thickener is significantly longer than in the case of the recipe containing CMC. This correlates with practical experience in machine experiments. Coatings thickened with acrylate tend to spray and mist more rarely than those containing CMC.

Results of aqueous thickener solutions and correlation with the application process

An acrylate thickener was used to make different paper coatings with the same mixture of clay mineral

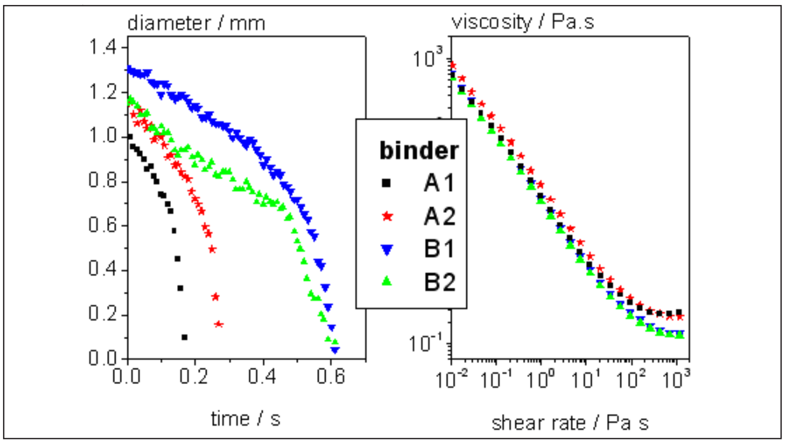


Figure 7: Comparison of CaBER experiment (a) and shear experiment (b) of different paper coatings

and calcium carbonate pigments, but with different binding agents.

In the CaBER experiment, it was apparent that the pure thickener has a clear tendency to form filament. The filament break-up time varies between 0.5 s and 100 s, depending on the polymer concentration.

The results from elongational and shear experiments on the investigated paper coatings are shown in Figure 7.

The coating formulations without thickener display no filament formation at all. However, if the formulation contains only 0.35% of this acrylate thickener, string formation could be observed in the experiment. This is related to the interaction between the dissolved thickener molecules, pigments and binder particles. Type A binders have a different particle surface (charge, steric stabilising groups and tensides) and therefore a different affinity to the thickener than the Type B binders.

It can be seen that the filament diameter for all paper coating compounds decreases by mathematical power quantities (Figure 4a). In contrast, the pure thickener displays an exponential decrease in the filament diameter (Figure 7a).

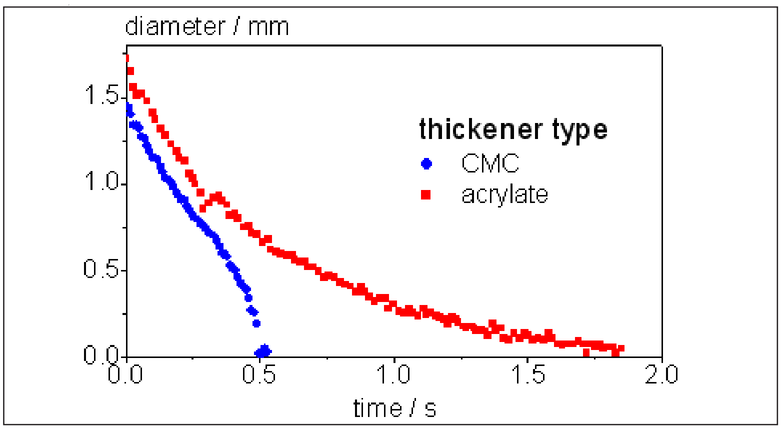


Figure 6: Comparison of two differently thickened coatings

In the shear experiment, it was barely possible to differentiate between the different mixtures of the paper coatings (Figure 7b), which means that it is not possible to draw conclusions from this data about the application behaviour during the coating process.

A water-based automotive coating and an aqueous solution of an associative thickener used in this formulation as a rheological additive were examined in the elongational and shear experiment. The results of these measurements are compared in Figure 8.

In the elongational experiment, the decrease in the filament diameter as a function of time again as expected displays the exponential curve for the pure thickener, while the complete formulation follows the pattern of the power law function.
Surprisingly however, the filament break-up time for the auto-motive coating is significantly longer than for the pure thickener, even though the shear viscosity of the pure thickener up to a speed of 100 s^{-1} is approximately one decade above that of the automotive coating.

Summary

In the CaBER experiment, the acrylate thickeners display an exponential decrease in the filament diameter as a function of time, while the CMC solutions display power law behaviour. The thicke-ner solutions examined have similar shear viscosities but in the elongation experiment it was apparent that the filament break-up time for the CMC thickener is shorter than for the acrylate thickener.
The long filament break-up time correlates with the reduced misting

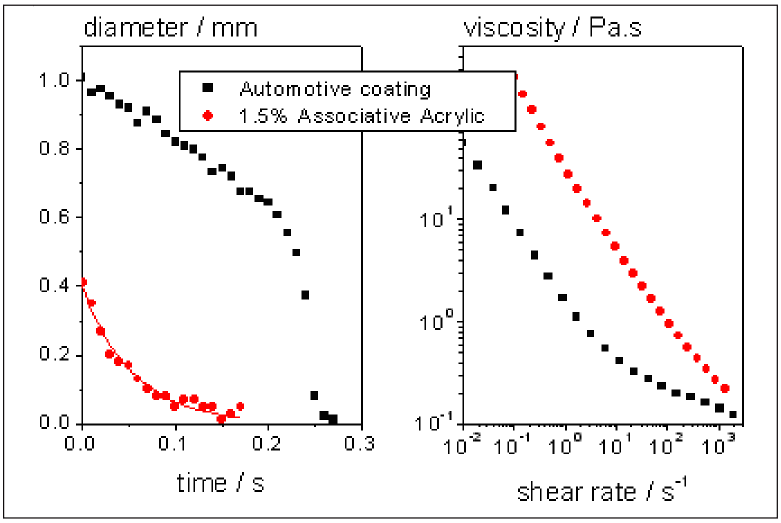


Figure 8: Comparison of the CaBER experiment (a) and shear experiment (b) of a pure thickener (red circles) and an automotive coating (black squares) containing this thickener

during roller application, e.g. of paper coatings. On the other hand, very short filament break-up times indicate excellent properties for spraying, e.g. automotive coatings.

The elongational and shear experiments on paper coatings and automotive coatings indicate that the behaviour of these substances cannot be predicted by the simple characterisation of the pure thickener. The properties of these complex formulations are controlled by the balance of the interactions between the dissolved thickener polymers and the pigments or the binder.

The shear viscosities often do not permit any clear conclusions to be drawn about the application behaviour. Elongational experiments can often better differentiate between various products and allow correlations with the process behaviour with regard to the coating processes described above.

References

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