



Publications

for HAAKE CaBER 1

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Optimization of the filling process of shampoo sachets with the HAAKE CaBER 1 Rheometer

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Key Words:

- Shampoo
- filling
- elongational viscosity
- stringiness
- HAAKE CaBER

Abstract

With certain shampoo formulations, 'strings' of shampoo are formed when filling sachets during production. This causes the product to spill across the sachet seam area. As a consequence, the sachet cannot be properly sealed. Using the HAAKE CaBER 1 extensional rheometer 'string forming' shampoo formulations were easily and quickly distinguished from 'well performing' samples. Rotational rheometers were not able to provide this information.

Introduction

While most commercial rheometers are capable of generating only shear flows, in many industrial processes and applications the flow is predominantly extensional in nature. Typical examples of this type of flow are fiber spinning, paper coating, extrusion and filling food or toiletries in bottles. This paper describes the optimization of filling shampoo into sachets. With certain shampoo formulations, 'strings' of shampoo are formed when filling the sachets, which causes the product to spill across the seam area. As a consequence, the sachet cannot be properly sealed. This failure is expensive as it will result in the disposal of many improperly sealed sachets.

Using classical rotational or oscillatory shear experiments, no discernible differences could be observed between the five shampoo formulations investigated. The use of the HAAKE CaBER 1 (Capillary Breakup Extensional Rheometer) however, allowed the characterization of the formulations' extensional properties in a quick and easy experiment, thus providing a solution to the problem.

Shampoos consist of 80 -90% water with more than 2% detergent, foaming agents and about 1% fragrances and preservatives [1]. Often

shampoos contain antistatic agents, thickeners and conditioners [2]. Current health and beauty trends make it important to stabilize special-effect particles in gels, body washes or shampoos, hence the addition of thickeners to prevent the sedimentation of these particulate phases [3]. A problem with thickeners, however, is that they can be the cause of unwanted extensional properties, i.e. they can cause string formation.

These unwanted rheological properties can manifest themselves in an unpleasant and "slimy" feeling while using the product. They can also cause string formation during the high speed filling of shampoo into sachets or bottles, resulting in improper sealing of the sachet or messy bottles. Slowing down the filling speed would solve the problem, but that has implications for the throughput capability of the production line. A far better solution would be to modify the formulation of the shampoo in such a way that the highest filling speed can be used.

In this investigation five shampoos with different formulations were tested to find out which formulation could be filled into the sachets successfully at a high filling speed. All formulations were previously

tested on a high speed packing line with differing degrees of success. Some exhibited the string formation problem that resulted in failure of the sachet seams.

Experimental

The measurements were carried out with the HAAKE CaBER 1 extensional rheometer. The CaBER experiment gives a quick insight into the material properties under an extensional deformation which occurs, for example, during the sachet filling. It is impossible to determine the extensional properties of a fluid using a traditional rotational rheometer.

In an extensional flow the streamlines converge and the velocity increase (i.e. the acceleration) is in the direction of the flow (Figure 1a). This is in contrast to the situation in a shear flow where the streamlines are parallel and the velocity increase is perpendicular to the direction of the flow (Figure 1b).

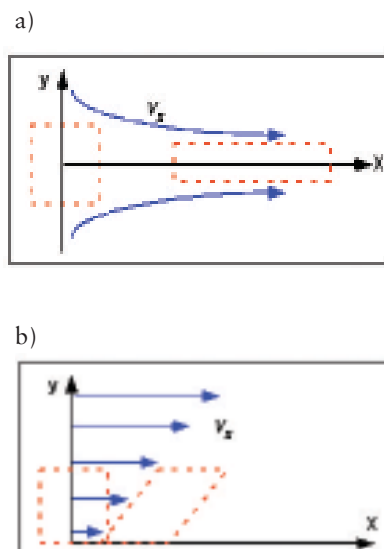


Figure 1: Comparison between extensional flow (a) and shear flow (b).

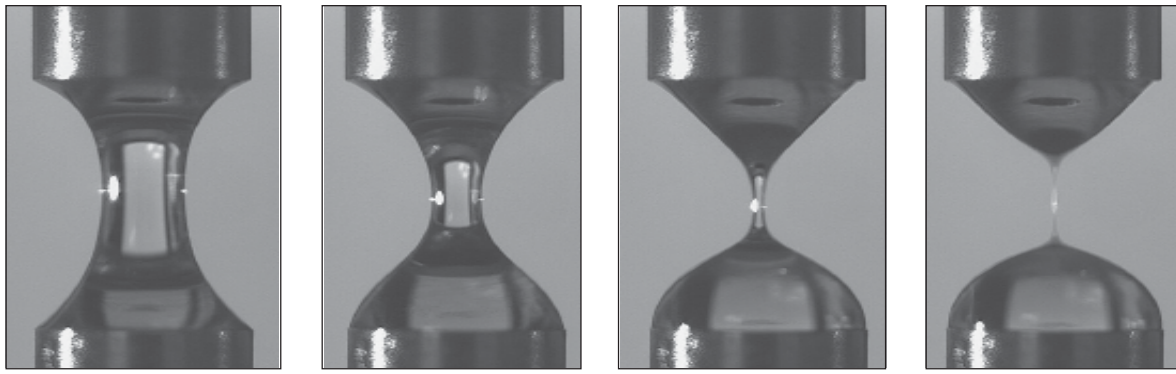


Figure 2: Sequence of a CaBER measurement.

The principle of the CaBER experiment is simple. A small quantity of sample (less than 0.2 ml) is placed between two parallel plates (diameter e.g. 6 mm). The fluid is then exposed to a rapid extensional step strain by moving the upper plate upwards, thereby forming a fluid filament (Figure 2).

The filament evolution as a function of time is controlled by the balance of the surface tension and the viscous and elastic forces. The surface tension is trying to “pinch off” the filament while the extensional rheological properties of the fluid are trying to prevent that. A laser micrometer measures the midpoint diameter of the gradually

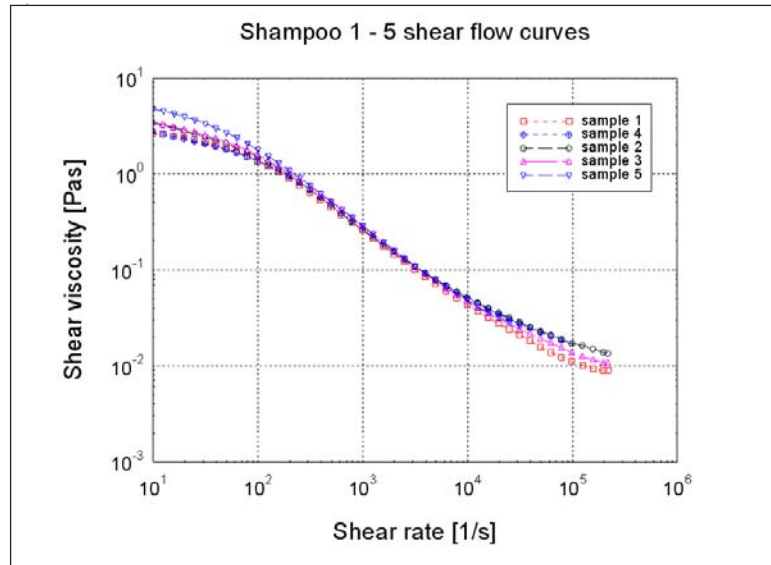


Figure 4: Shear viscosity curves of shampoos 1-5.

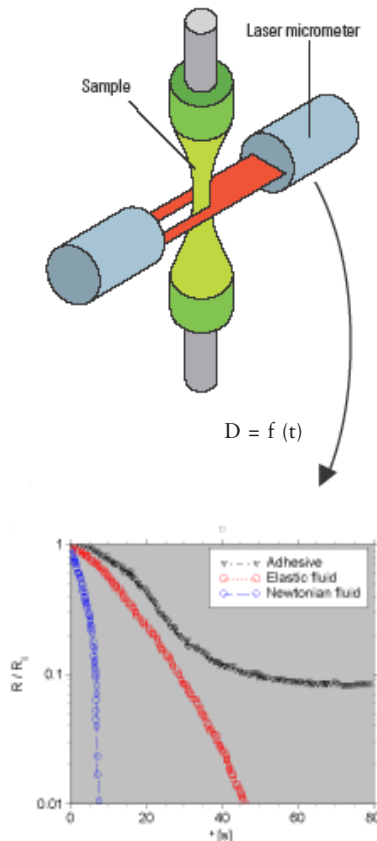


Figure 3: Principle of the CaBER experiment.

thinning fluid filament after the upper plate has reached its final position (Figure 3).

From the measured data, which describes the evolution of the filament diameter as a function of time (Figures 2a, 2b and 2c), the filament break-up time (Figure 2d), the extensional deformation and deformation rate and extensional viscosity can be calculated.

Results and Discussion

Five different shampoo samples were measured. Two of the samples (samples 1 and 2), performed well in the sachet filling equipment; the three other samples (samples 3, 4 and 5) did not perform well.

When measured in a rotational rheometer, the five samples did not show any differences in the flow curves that could explain their different during the filling of the sachets (Figure 4).

In contrast, when measured in an extensional flow using the

HAAKE CaBER 1 rheometer, the measured diameter versus time curves (see Figure 5) of the five samples nicely rank according to their filling behavior: the shorter the filament lifetime in the CaBER experiment, the better the filling properties.

The 5 samples clearly differentiated in extensional flow. The filament lifetimes of shampoos 1 and 2 are relatively short. These shampoos can be filled into sachets without any obvious problems. For shampoos 3, 4 and 5, the filament lifetimes are significantly longer, which leads to problems in sachet filling. String formations prevented the sachets sealing, a problem which can only be resolved by slowing down the filling process.

The graph of the extensional flow curves (see Figure 6) shows that the extensional viscosities of samples 1 and 2 (which performed well) are clearly lower than those of samples 3 and 5 (which did not perform well). The lower extensional

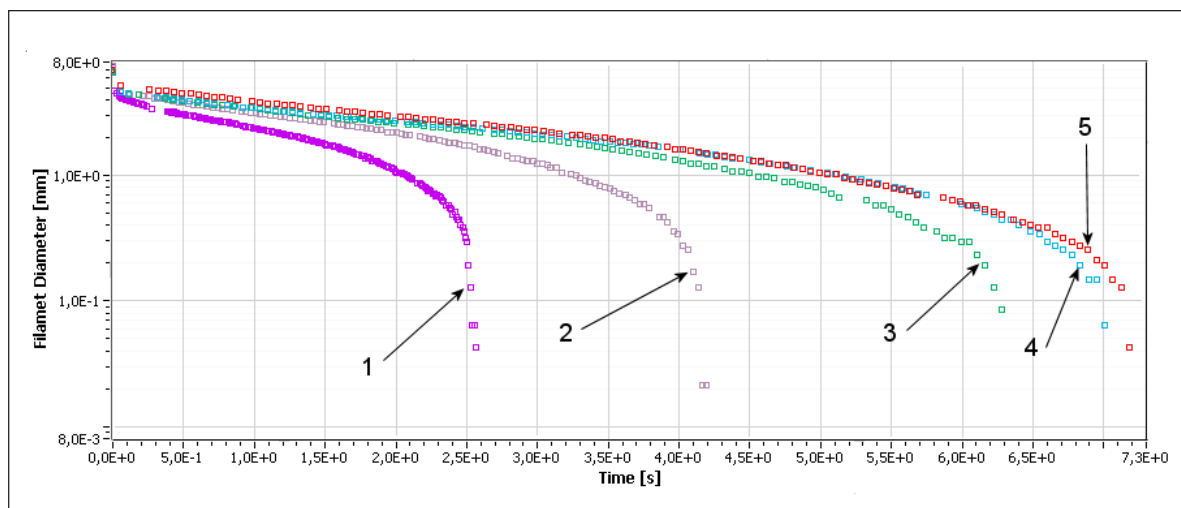


Figure 5: Filament diameter decay of shampoos in the CaBER experiment.

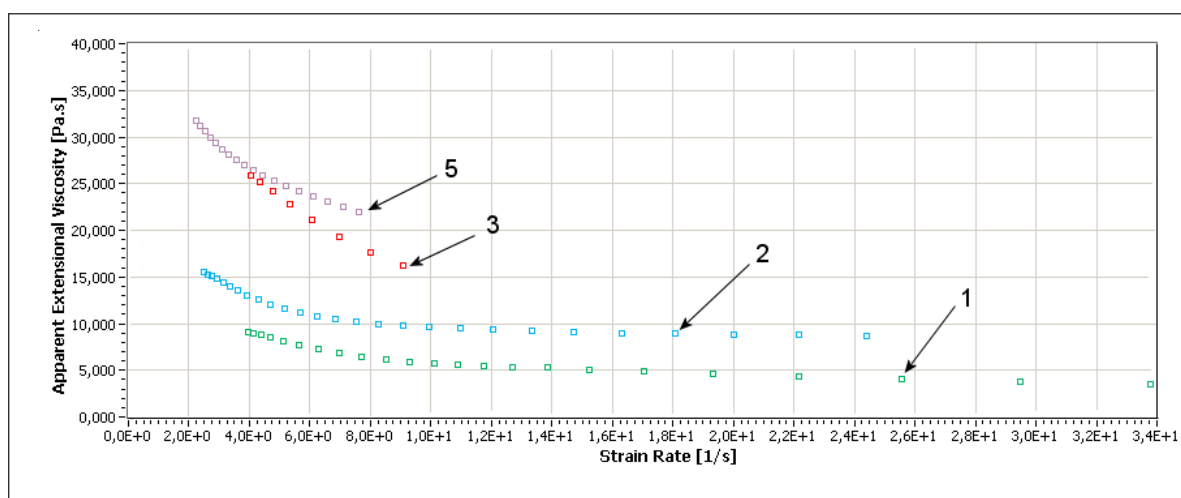


Figure 6: Extensional flow curves of shampoos 1-5.

viscosity leads to a higher strain rate and shorter break-up time (filament life time) in the CaBER experiment and in the filling equipment.

Conclusions

The HAAKE CaBER 1 extensional rheometer is capable of an easy-to-handle and quick way of distinguishing between different shampoos and of predicting filament lifetimes for production and quality control. Shampoos 3 - 5 will need to be reformulated to solve the serious filling problems. In this way it is possible to optimize the quality of the shampoos and the production process.

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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

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 coa-

tings 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.

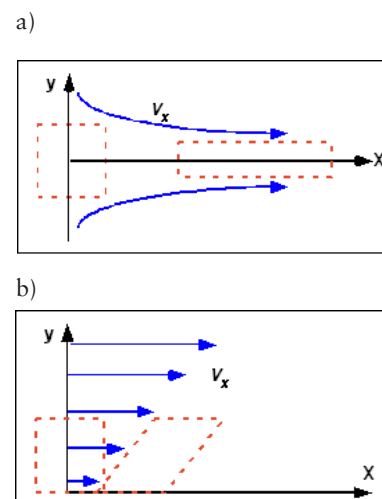


Figure 1: Comparison between extensional flow (a) and shear flow (b).

Material and Methods

With the HAAKE CaBER 1 extensional rheometer (Capillary Break-up Extensional Rheometer) 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



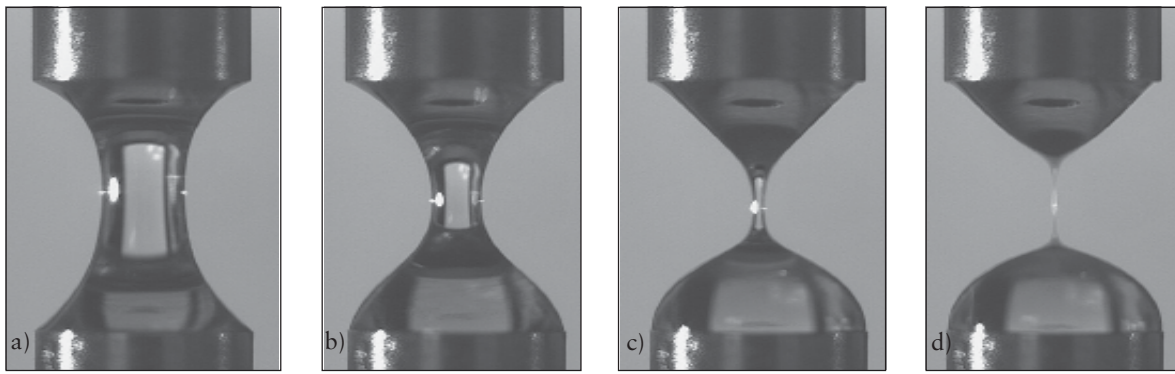


Fig. 2: Sequence of a CaBER measurement: filament formation (a), filament necking (b,c) and filament break-up (d)

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

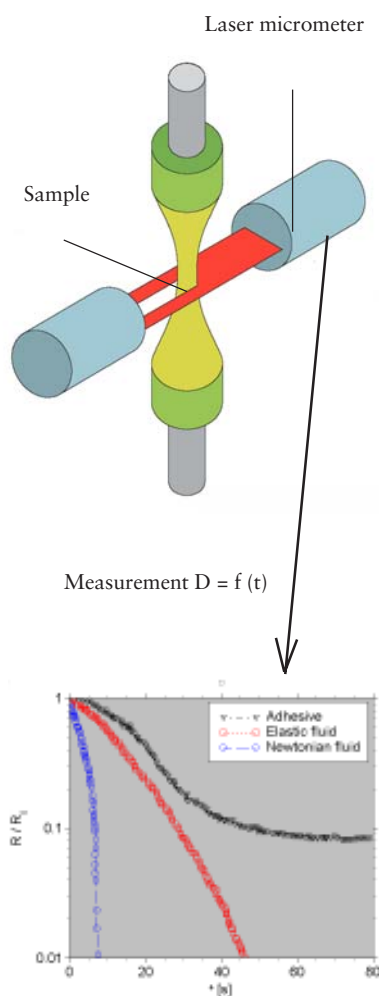


Figure 3: Functional principle of the HAAKE CaBER 1

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 character-

istic 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

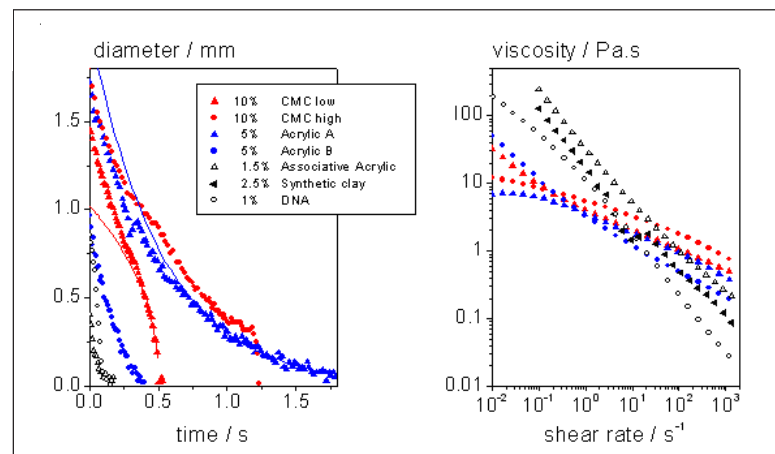


Figure 4: Comparison of CaBER experiment (a) and shear experiment of different aqueous thickeners

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).

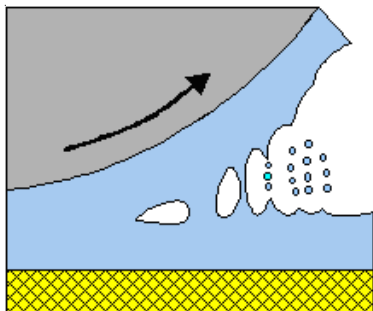


Figure 5: Schematic depiction of the filament and droplet formation when applying paper coatings via rollers.

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

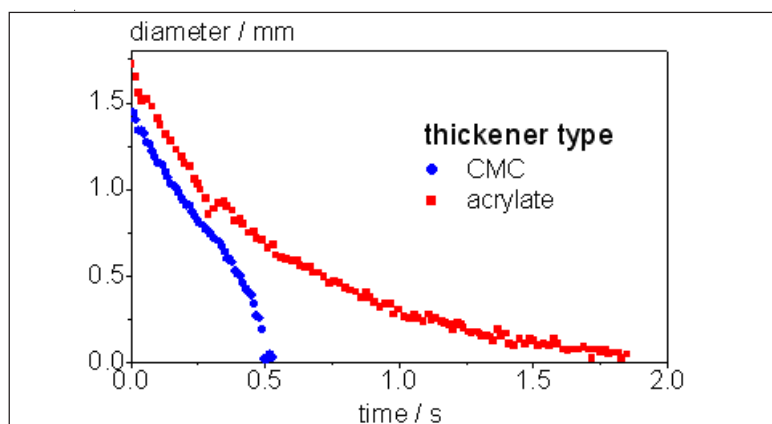


Figure 6: Comparison of two differently thickened coatings

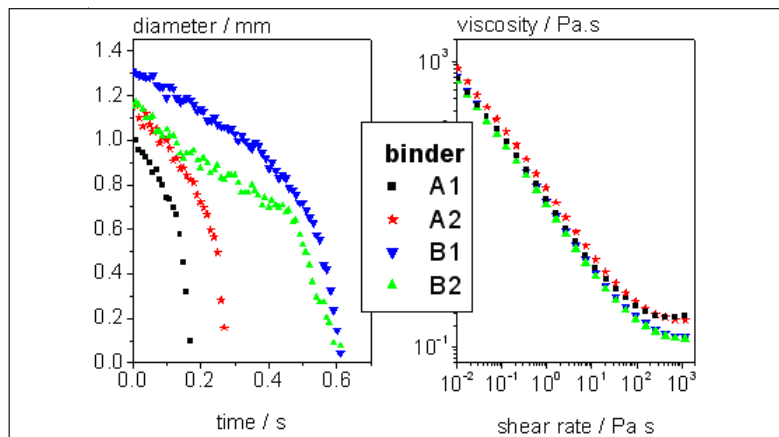


Figure 7: Comparison of CaBER experiment (a) and shear experiment (b) of different paper coatings

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).

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 automotive 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 thickener 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

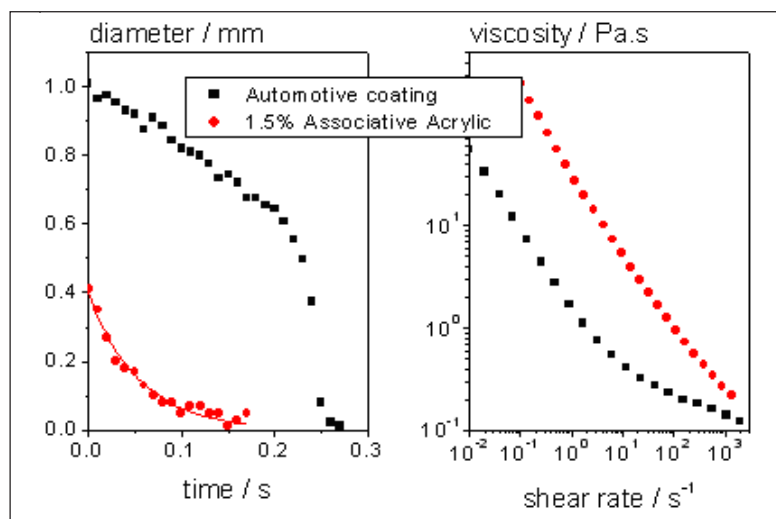


Figure 8: Comparison of the CaBER experiment (a) and shear experiment (b) of a pure thickener (red circles) and an automotive coating (black squares) containing this thickener

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.

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Correlation of misting during printing with extensional rheological investigations on offset printing inks with the HAAKE CaBER 1

Key words:

- Coating
- Elongational viscosity
- Misting
- Offset printing ink
- HAAKE CaBER 1

Rheology Application Notes

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Abstract

The tendency for misting on offset printing inks was examined on two samples using the rotational rheometer HAAKE RheoStress 600 and the extensional rheometer HAAKE CaBER 1.

The results for the amplitude and frequency curve, the creep and recovery test and the flow curve measurement with the rotational rheometer do not correlate with misting during printing.

With the rotational rheometer, it was possible with the aid of the filament break-up time to easily and quickly draw distinctions between different tendencies for misting with offset printing inks.

Introduction

Offset printing is the most widely used method in the printing industry. A thin film of printing ink is applied onto the printing form via a system of rollers. In one hour, it is possible to print approximately 10,000 sheets using this method. Factors that are crucial to printing quality include the printing inks used with regard to their wettability, gradation, sheen and drying.

Offset printing ink consists of the 3 components pigment, binding agent and additives. It is a suspension with complex rheological properties that are influenced by the components used.

In the printing process, it is required that smooth and sharply defined tear-off edges are obtained and that scumming (misting) of the ink is avoided. When the ink is transferred

to the printing plate and when the latter is moistened, water droplets are formed in the printing ink. When there are such droplets in an ink string that forms in the gap between the printing roller and the rubber blanket, the ink can spray. In practice, relative terms such as stickiness (short, long) and rigidity are often used to describe the properties of a printing ink. In addition, besides rheological variables the tack value (stickiness) is defined as a relative value. A forecast regarding the tendency of printing inks to foam and to spray is desirable for ink development and for their use in the printing machine.

Material and methods

Two offset printing inks were examined at a temperature of 40°C with regard to their tendency to mist. The inks were available in their unmodified (sample A) and modified

form (sample B). The rotational rheometer HAAKE RheoStress 600 with air bearings permits all the usual rheological examinations such as flow curve measurements, flow limit measurements, creep and recovery, deformation jump and oscillation tests, as well as normal force measurements.

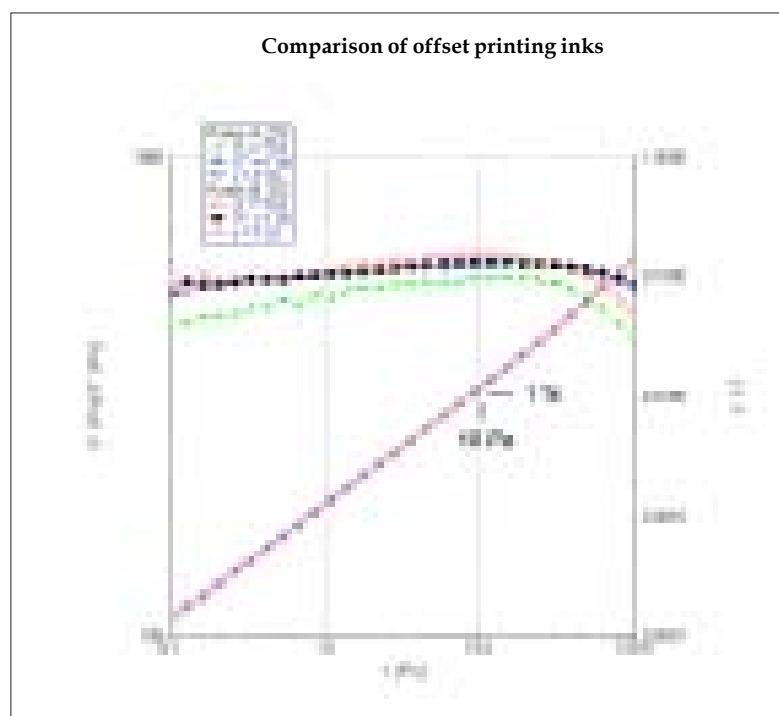


Figure 1: Amplitude curve in CS mode

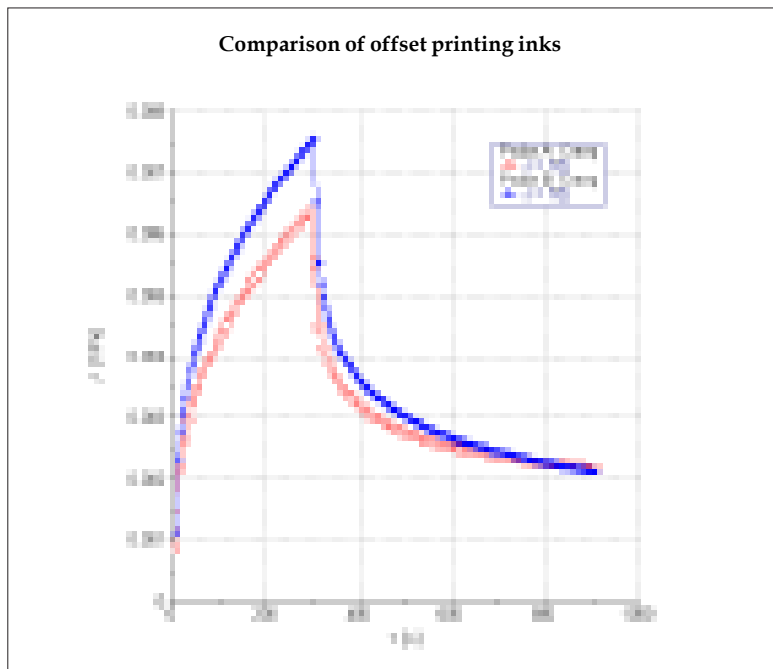


Figure 2: Creep test curve of the compliance $J(t)$ in the creepage phase ($t = 1 \text{ Pa}$) and in the recovery phase ($t = 0 \text{ Pa}$)

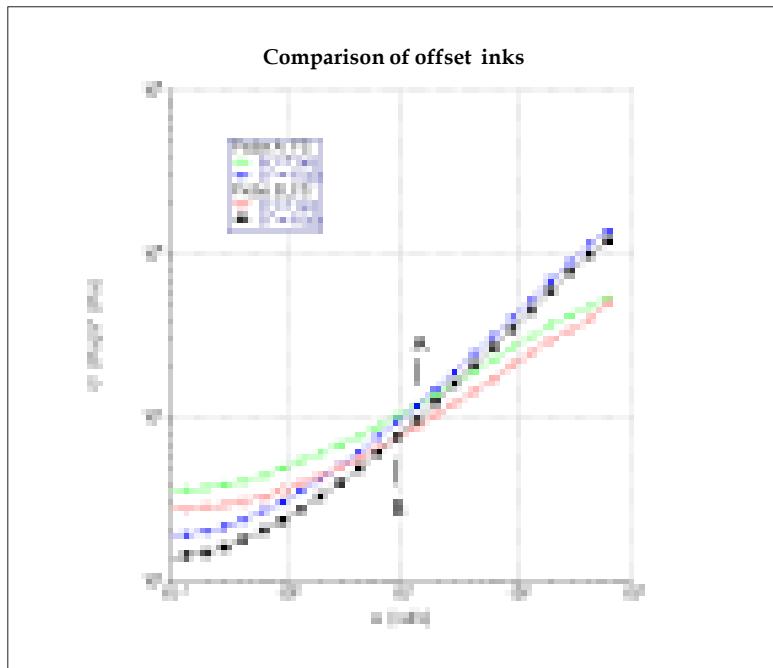


Figure 3: Frequency curves of the storage modulus (open symbols) and loss modulus (closed symbols)

A cone/plate measuring unit consisting of a Peltier temperature control unit and measuring cone C35/1° was used. Rheometer control and evaluation of the measured data were performed with the software HAAKE RheoWin.

Using the extensional rheometer HAAKE CaBER 1, a low sample volume of 6 mm diameter and 3 mm height was extended to a height of 10 mm by way of abrupt extension (50 ms). An extension flow formed for a short time in a liquid. The reduction in the filament diameter up until the point of breakage was measured as a function of the time (1, 2).

Rotational rheometer results

An amplitude sweep measurement was carried out first in the oscillation mode with a defined shear stress (CS) in order to determine the linear-visco-elastic range (LVB). Two minutes was selected as the temperature adjustment time. There was no noticeable difference between the two samples (Figure 1). For measurements within the LVB, a shear stress of 10 Pa and a deformation of 1% should not be exceeded. The slight rise in the storage and loss module indicates that the sample was still relaxing during the measurement.

A creep and recovery test was carried out in the next step. The temperature equilibration time was two minutes. The applied shear stress of 1 Pa was held for a period of 300 s and the recovery was observed. Clear differences were apparent between the two samples (Figure 2; Table 1).

The modified sample B has a greater elastic deformation and recovery at low shear stresses. The zero viscosity η_0 is almost the same on both samples. However, there are different retardation times λ_r . These results are relevant to all stages in the printing process that occur at low shear stresses, for example the gradation of the ink after printing. In addition, the necessary information is obtained about how long it is necessary to wait after the sample filling until the start of the measurement, and also the necessary measurement time for the creepage and recovery phase. Three times the recovery time – in this case approx. 20 to 30 minutes – applies as a rule of thumb.

In another measurement, the reaction to different excitation frequencies was examined with a frequency sweep for both samples. This measurement was performed in the linear visco-elastic range (LVB) with a deformation of 1%.

The curves for both samples are similar (Figure 3). They show the typical pattern for offset printing inks. For slow stresses, the storage modulus G' is much bigger than the loss modulus G'' , and in this range the samples are extremely elastic. The loss modulus G'' predominates for rapid stresses, and the viscous component prevails. The intersection point of $G'(\omega)$ and $G''(\omega)$ – also designated as the crossover point – represents a characteristic variable in the frequency curve (Table 1).

For sample B, the crossover point is at a lower cycle frequency ω and the module values are lower. The sample is „softer“. This could be an indication of reduced mist formation.

Table 1: Zero viscosity η_0 , retardation time λ_r , crossover modulus and crossover frequency

	Probe A	Probe B
η_0 [Pas]	118.000	117.000
λ_r [s]	460	590
$G'_c = G''_c$ [Pa]	1194	731
ω_c [rad/s]	13.8	8.5

However, the deformations occur in the roller gap outside the LVB, while the measurement was made inside this range.

In the rotation test, the flow curves of both samples were measured (Figure 4). Here, problems arose through

the gap emptying at high shear speeds and through shear heating at high shear speeds. At a shear speed of 140 s^{-1} , the viscosity curves display only a slight difference. For sample A, the interpolation provides with 14.3 Pas a slightly higher (dynamic)

viscosity than for sample B at 12.7 Pas . This means that no clear sample differentiation is possible with regard to the question „misting during printing“.

Extensional rheometer results

Figure 5 shows semi-logarithmically the decrease in the thread diameter referred to the starting diameter for sample A and sample B over the period up until breakage. Three repeat measurements were performed in each case, with a slight scatter in the filament break-up times. The reason for this was the type of sample filling and different waiting times up until the measurement. However, great differences can be found in the average thread breakage time between sample A at 148 seconds and sample B at 33 seconds. Due to the significantly longer thread breakage time, sample A tends to mist formation, while sample B displays this tendency less.

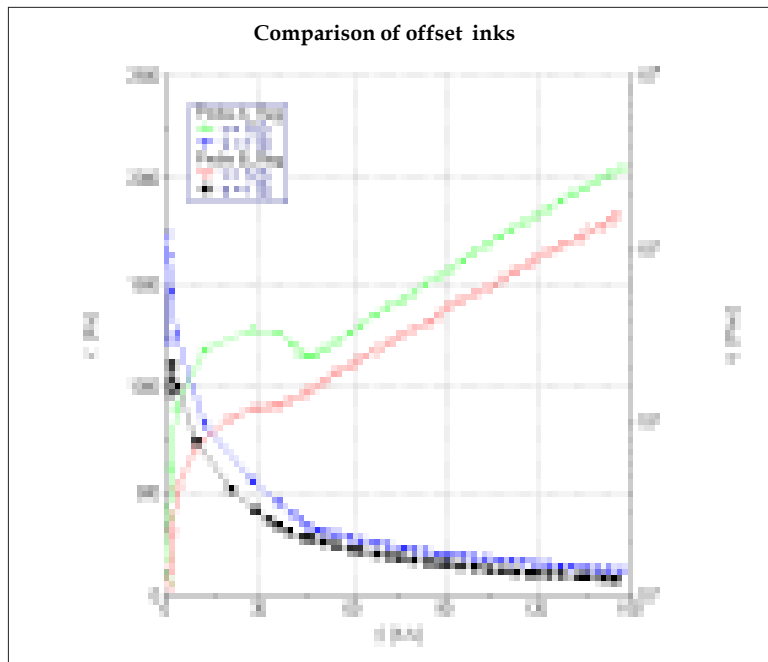


Fig. 4: Rotation test-breakage curve (open symbols) and viscosity curve (closed symbols)

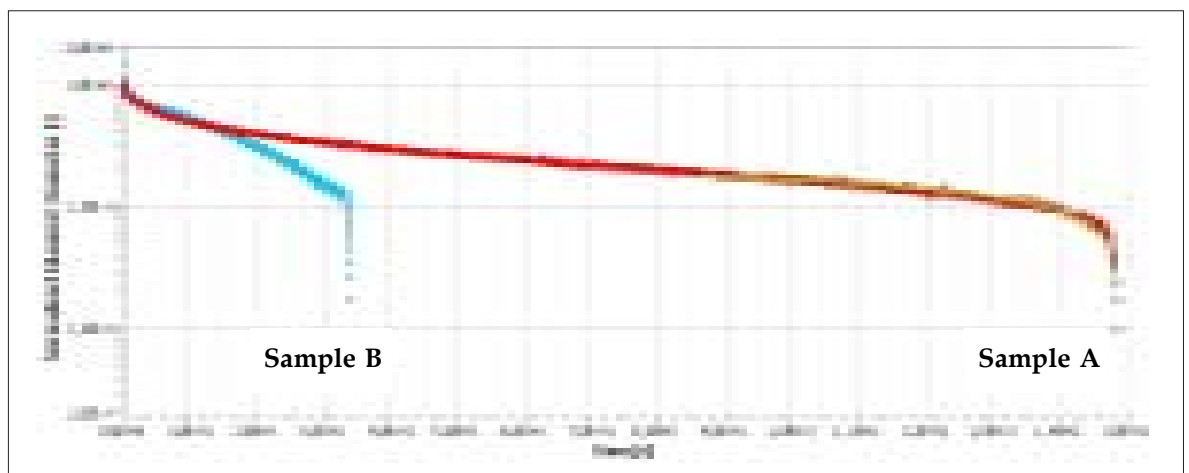


Figure 5: Decrease in the relative filament diameter

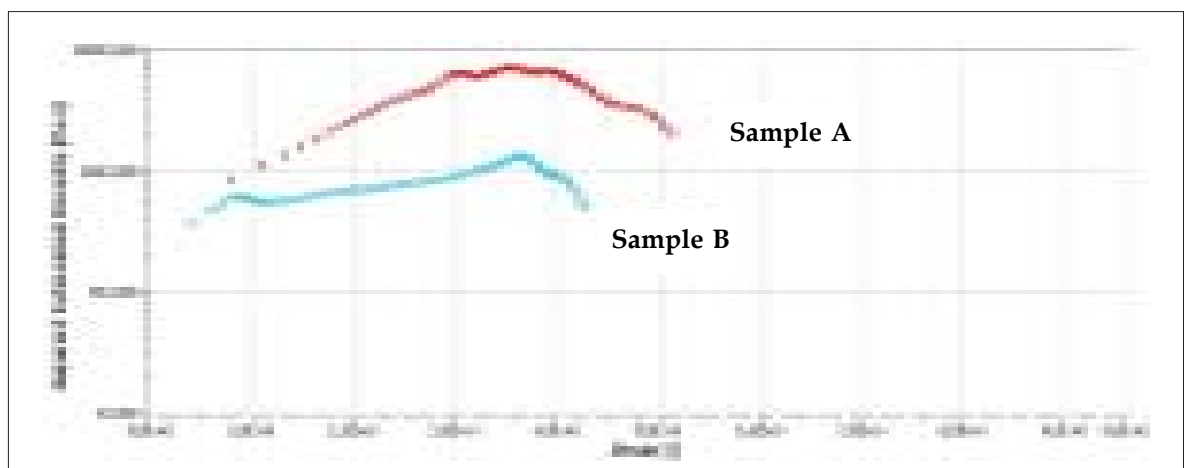


Figure 6: Apparent extensional viscosity as a function of the extension

A great difference between both samples can also be found in the apparent elongational viscosity that can be calculated with the aid of model assumptions (Figure 6)., where sample A displays a value up to 10 times greater than sample B.

Summary

The tendency towards misting with offset printing inks could be differentiated quickly and easily by measuring the filament break-up time on two samples with the extensional rheometer HAAKE CaBER 1. With a high-performance rotational rheometer, a differentiation with regard to this criterion was not possible with any clarity, even with comprehensive rheological measurements.

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Optimizing and forecasting the filling behavior of coatings with the HAAKE CaBER 1

Dr. Dirk Eidam; Jint Nijman, Thermo Fisher Scientific, Process Instruments, Karlsruhe, Germany

Keywords:

- Coatings
- Filling Process
- Extensional Viscosity
- Filament Lifetime
- Temperature Dependence
- Stringiness
- HAAKE CaBER 1

Abstract

Two coatings, which showed different stringing behavior when filled into containers during a production process, have been investigated with the HAAKE CaBER 1 extensional rheometer. It was shown that the filament lifetime as measured by the CaBER corresponds directly with the behavior seen in the production process. By changing the processing temperature, the behavior of the problematic sample could be optimized.

Introduction

When filling coatings into containers in industrial processes, the stringiness of the product may cause problems by leaving excess material on the packaging. In the filling process considered here, the process temperature is 60°C. At this temperature product A can be filled into the containers without problems, whereas during the filling of product B the fluid jet will not break-up quickly enough after the filling has stopped. This slow break-up causes strings of coating material spill over the container.

This phenomenon, which is caused by the extensional properties of the samples, can be monitored with the HAAKE CaBER 1 (Capillary Breakup Extensional Rheometer) instrument.

Figure 1 shows the results of two filament break-up experiments. Product A has a filament lifetime of 0.62 s whereas product B needs 0.8 s before breaking up. This time is obviously too long for the process considered here.

Experimental

The principle of the CaBER measurement is simple. A small quantity of sample (less than 0.2 ml) is placed between two parallel plates (diameter 6 mm). The fluid is then exposed to a rapid extensional step strain by moving the upper plate upwards, thereby forming a fluid filament (Figure 2). The filament evolution as a function of time is controlled by the balance of the surface tension and the viscous and elastic forces. The surface tension is trying to „pinch off“ the filament while the extensional rheological properties of the fluid are trying to prevent this process. A laser micrometer measures the midpoint diameter of the gradually thinning fluid filament after the upper plate has reached its final position.

From the measured data, which describe the evolution of the filament diameter as a function of time, the filament break-up time, the extensional deformation, the deformation rate and the extensional viscosity can be calculated (2).



The temperature of the samples can be controlled with an accuracy of ± 0.1 K using a circulator (in this case a HAAKE Phoenix).

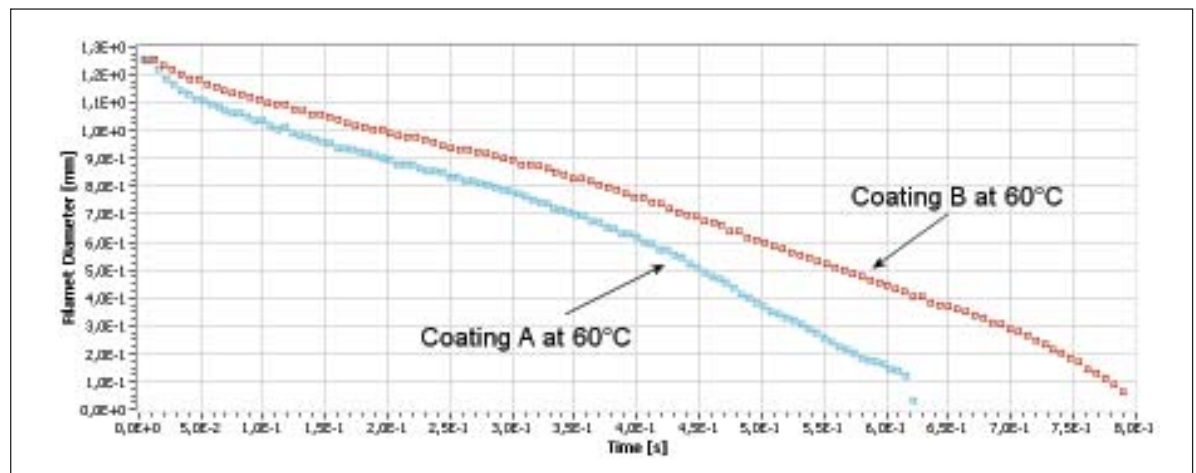


Figure 1: Filament diameter as a function of time for products A and B at a temperature of 60°C.

Results and Discussion

In order to optimize the filling process of product B, it was measured in the HAAKE CaBER 1 at different temperatures. Figure 3 shows that the filament lifetime decreases with increasing temperature.

At a temperature of 80°C, the filament lifetime is reduced to 25% of the original value. The filament lifetime of sample B at a temperature of 65°C is 0.66 s. For sample B, a temperature increase to 65°C would be sufficient to make it perform like sample A at 60°C, thereby solving the filling problems.

Conclusion

With the CaBER experiment the properties of coatings that are important during the filling of the coating in containers can be analyzed quantitatively. The filament life time is a direct measure of the stringiness of the product, as observed in the filling process. By changing the processing temperature the behavior of the problematic sample could be optimized. The capillary break-up experiment is a valuable tool for forecasting the behavior of the investigated coatings in the filling procedure.



Figure 2: Sequence of a CaBER measurement [1].

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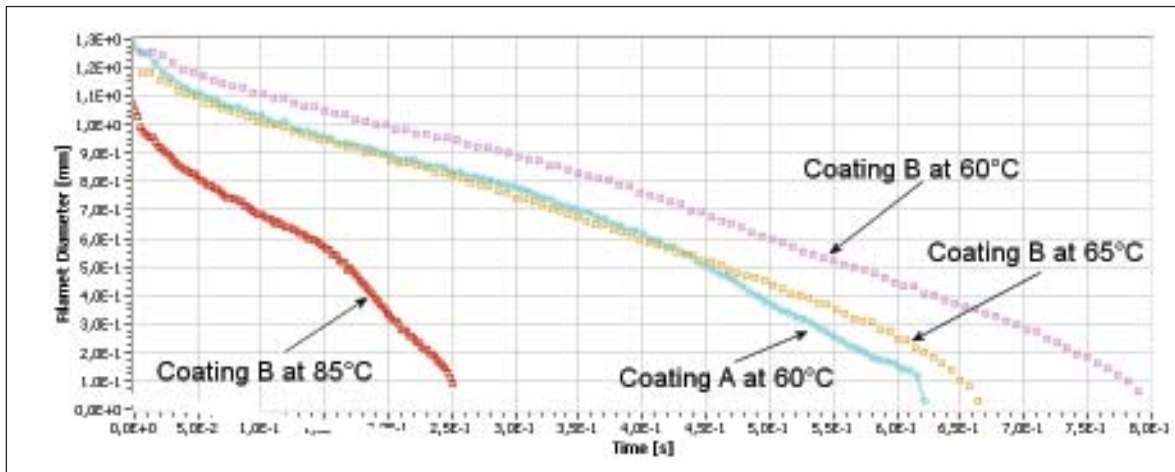


Figure 3: Filament diameter as a function of time at different temperatures for product B at $T = 60^{\circ}\text{C}$, 65°C and 80°C and product A at $T = 60^{\circ}\text{C}$.

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HAAKE CaBER 1 – molecular weight distribution

Polystyrene, blends of standards, same MW, different MWD

Rheology Application Notes

CaBER test result

In extensional flow differences in molecular weight distribution (MWD) can be differentiated.

In shear flow differences in MWD cannot be detected.

Conclusion

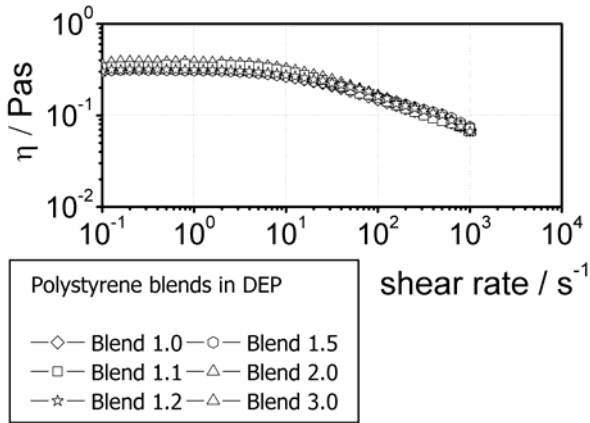
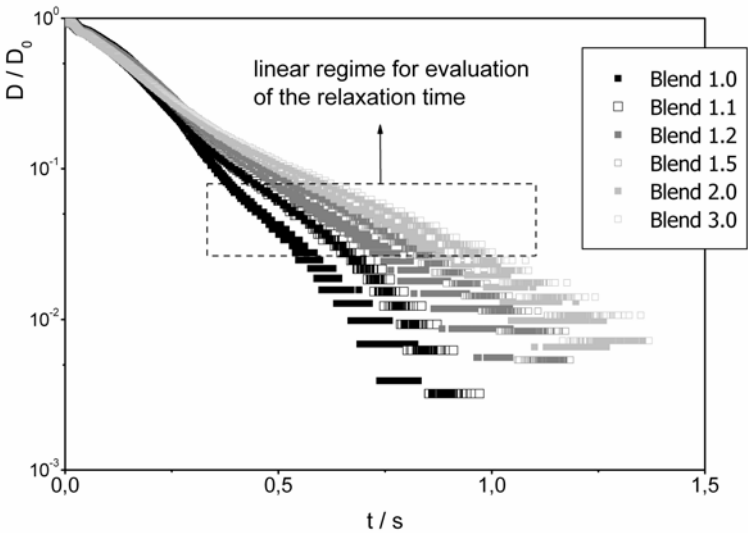
The CaBER measurement is highly sensitive towards high molecular components in mixtures.

Practical applications

Industrial processes where high molecular polymer fractions influence application behaviour.

References

Clasen/ University of Hamburg
RheoFuture 2004



Blends ($M_w = \text{const}$)	(M_w/M_n)
1.0	1.00 - 1.05
1.1	1.06
1.2	1.11
1.5	1.36
2.0	1.66
3.0	1.84

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HAAKE CaBER 1 – polymer solutions

Polystyrene, $M_w = 1.8$ Mio g/mol in styrene oligomers at very low concentrations

Rheology Application Notes

CaBER test result

In extensional flow the effect of smallest concentrations of polymers (ppm range) can be measured quantitatively.

In shear flow differences between small concentrations cannot be detected.

Conclusion

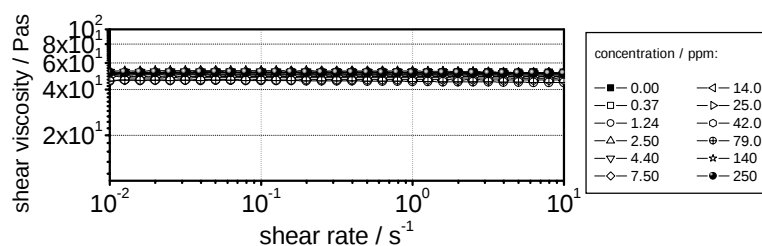
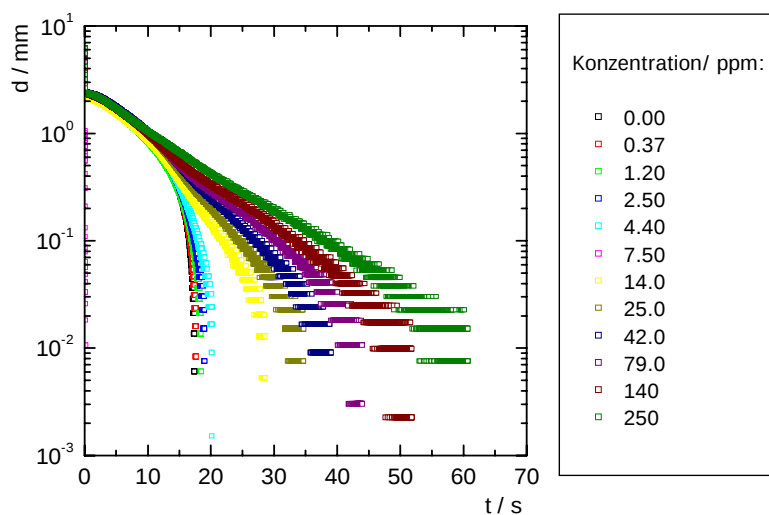
CaBER measurement detects small amounts of polymers in extensional flow.

Practical applications

Industrial polymer systems where extensional flow appears
(Filling, spraying, coating, ...)

References

Clasen/ University of Hamburg
RheoFuture 2004



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HAAKE CaBER 1 – binary polymer mixtures

Polystyrene, blends of standards, $M_w = 1.8 \text{ Mio g/mol} + M_w = 13 \text{ Mio g/mol}$

Rheology Application Notes

CaBER test result

At a constant concentration of 250 ppm in Boger fluids binary mixtures can be differentiated in extensional flow.

In shear flow differences between in mixing ratio cannot be detected.

Conclusion

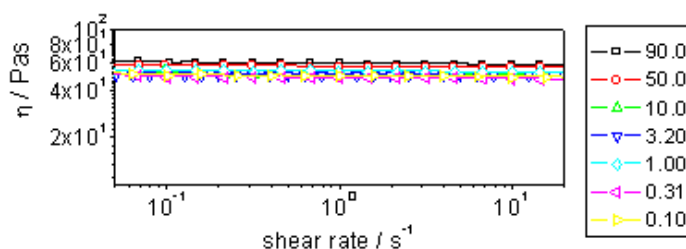
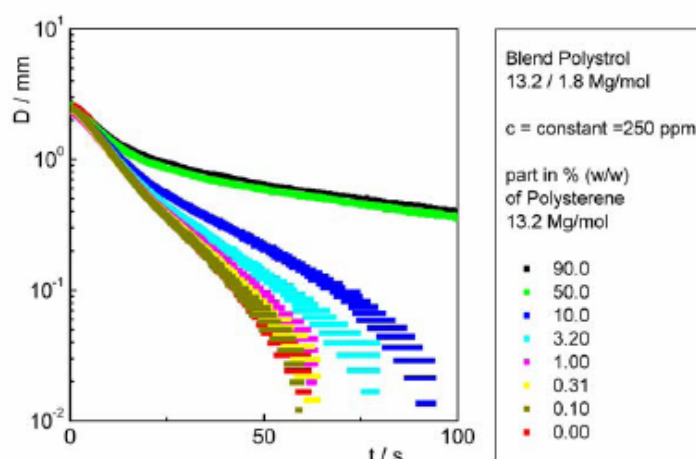
The influence of molecular weight of polymers is more sensitive in the CaBER measurement.

Practical applications

Industrial processes where small changes in polymerization process or recipe may influence application behaviour.

References

Clasen/ University of Hamburg
RheoFuture 2004



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HAAKE CaBER 1 – reproducibility

Newtonian Test fluids E6000 and E40000

Rheology Application Notes

Test fluids

Newtonian Standard fluids
E6000 ($\eta = 6000$ mPas, 20 °C)
E40000 ($\eta = 40000$ mPas, 20 °C)

CaBER test results

	Break up time/ s
E6000 #1	2.08
E6000 #2	2.09
E6000 #3	2.09
E40000 #1	13.4
E40000 #2	13.0

1. CaBER data (break up times) can be measured with high reproducibility
2. Extensional viscosity of Newtonian Standard fluids follows Trouton ratio (= 3x shear viscosity value)

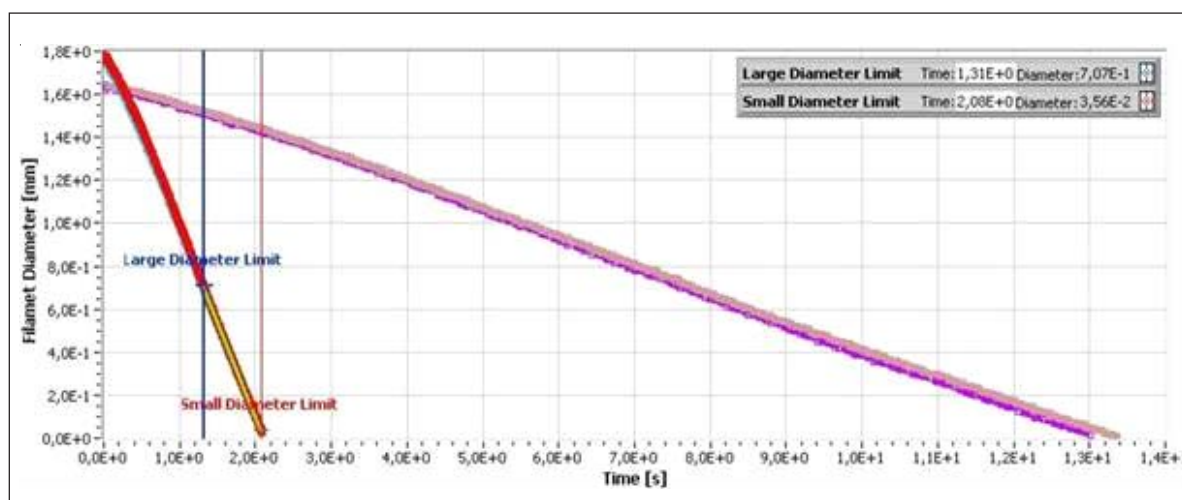


Fig. 1: Diameter as a function of time (break up time) for 2 different Newtonian fluids E6000 and E40000 (multiple measurements with new filling)

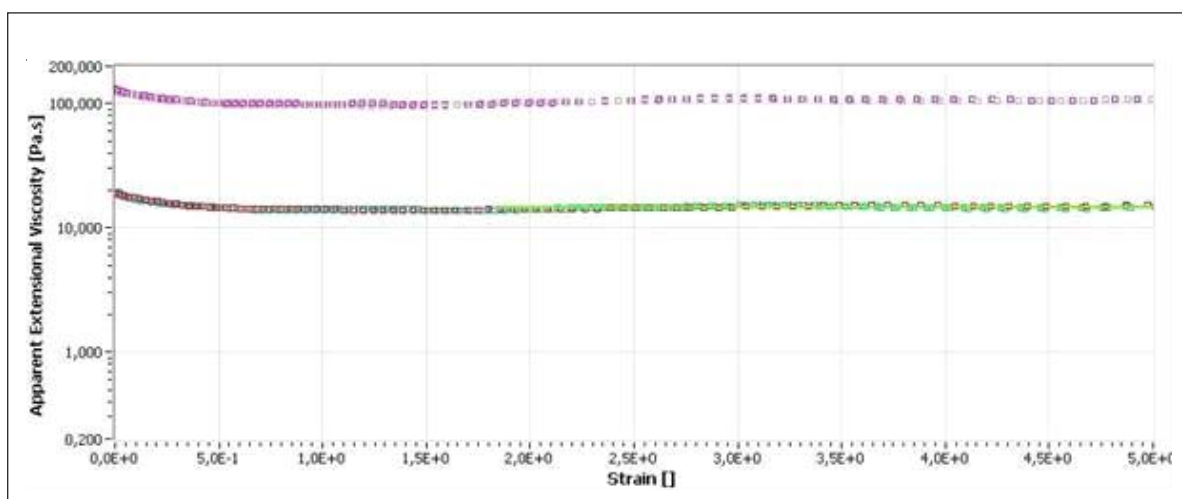


Fig. 2: Extensional viscosity as a function of deformation for 2 different Newtonian fluids (calculated from data shown in fig. 1)

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Cellulosic Derivatives in Capillary Break-up - Influence of the MWD and Gel Particles

Key words:

- HAAKE CaBER1
- Elongational Rheology
- Cellulosic Derivatives
- Thickeners
- Polymer Solutions
- MWD

Rheology Application Notes

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Abstract

Application note V-219 showed that the CaBER1 extensional rheometer is able to detect slight differences in the MWD (molecular weight distribution) of blended polystyrene standards. However, the question remains if these results obtained on a standard system can be transferred to more complex polymers in solution like cellulosic derivatives?

In order to control the adaptability of this method, commercially available, blended methylhydroxyethyl celluloses (MHEC, e.g. used as thickener agent in construction materials) were characterized by uniaxial elongation in capillary break-up experiments with the CaBER1 extensional rheometer. The determined break-up and relaxation times t resp. τ were then correlated with the blending composition of the methylhydroxyethyl celluloses and hence with the high molar mass fraction of the sample.

Introduction

The MHECs characterized here are amongst other applications utilized as thickening- and water retention agents in plasters. As plasters are more than often applied by spraying, strong elongational forces are implied. These elongational forces again may induce flow anomalies like spattering (or misting, roping in other applications), which are directly related to the elasticity of the polymer and hence the high molar mass fraction of the incorporated polymer.

To describe the high molar mass fraction of a polymer, the weight-average molar mass M_w alone

is not satisfactory; the molecular weight distribution and hence the polydispersity has to be taken into account also. However, the detection of the influence of the polydispersity on the rheological properties is not easily to achieve quantitatively.

This applies particularly for cellulosic derivatives, because native polymers naturally show very broad molar mass distributions. The processability of these cellulose derivatives depend strongly on their MWD, which in turn depends on the origin of the specific cellulose [1]. Therefore in technical applications cellulose samples are usually blended to broaden the MWD and hence minimize the effect of the MWD of a single sample. However, already the initial molar mass distribution of the sample that is to be blended is not easy accessible and the “right” mixing ratio is often chosen on empirical tryouts of the material properties of the different mixing ratios [1,2].

Aim of this contribution is therefore to correlate the relaxation times, determined via capillary break-up extensional rheometry with a Haake CaBER1, of blended methylhydroxyethyl celluloses with the MWD of the samples.

Materials and Methods

The methylhydroxyethyl celluloses (MHEC) used were made available from a company involved in MHEC chemistry.

Preparation of the samples was achieved by solving the respective amount of polymer in 2 wt% NaOH. Homogenization was achieved by permanent agitation over a period of time not shorter than 3 days at RT.

Filtrating of this solvent was achieved with a cellulosic filter of a pore size of 0.1 μm (Sartorius GmbH, Germany)

Elongational characterization was achieved on a Haake CaBER1 extensional rheometer.

Determination of the molar mass and its distribution of the MHECs was achieved using a combined method of size exclusion chromatography (SEC), multi-angle laser light scattering



(MALLS) and differential refractometer (DRI).

Results and Discussion

The investigated MHECs were specifically blended from 3 different celluloses with different intrinsic viscosities ($[\eta]_{\text{cellulose3}} < [\eta]_{\text{cellulose2}} < [\eta]_{\text{cellulose1}}$) by the supplier to obtain different MWDs but almost the same M_w . This is usually done to tune the flow properties of a specific sample to a specific application. The blended samples were hydroxyethylated afterwards.

In Tab. 1 the different blending ratios and the DS (degree of substitution for the methyl group at one glucose monomer unit) and MS (molar degree of substitution for the hydroxyethyl group because of multiple substitutions) of the investigated MHECs are summarized. In addition to this the intrinsic viscosities of the pure cellulose samples are listed.

Polymer	Cellulose 1 1738*	Cellulose 2 925*	Cellulose 3 356*	M_w / M_n	DS_M	MS_{HE}
MHEC 1	50	-	50	broad	1.78	0.33
MHEC 2	37.5	25	37.5	intermediate	1.75	0.31
MHEC 3	25	50	25	narrow	1.76	0.30

(*Intrinsic viscosities of the raw cellulose samples in cm^3/g as provided by manufacturer)

Table 1: Blending composition, DS (degree of substitution for the methyl-group) and MS (molar degree of substitution for the hydroxyethyl-group) of the investigated MHECs 1-3.

Polymer	M_w 10^5 g/mol	M_w / M_n	M_z 10^5 g/mol	Recovery Rate / %
MHEC 1	3.41	3.5	7.38	74
MHEC 2	3.23	2.9	6.55	79
MHEC 3	2.94	2.5	5.77	72

Table 2: Molecular parameters of investigated MHECs 1-3, determined via combined methods of SEC/MALLS/DRI.

The determined mean values for the distribution and the polydispersities for the MHECs are listed in Table 2 together with the recovery rates of the SEC. The recovery rate is the fraction of polymer that reaches the differential refractometer based on the amount of polymer that was originally injected.

Figure 1 shows that the investigated MHECs do not show significant differences in terms of their shear viscosity, as required by the producer; only the sample MHEC 2 gives a slightly higher zero shear viscosity than the other two samples. Via fitting of the experimental data to the modified Carreau model one can determine the longest relaxation time τ_0 of steady shear flow.

$$\eta = \eta_0 \left[1 + (\tau_0 \cdot \dot{\gamma})^b \right]^{-1/b} \quad (1)$$

with b being a transition parameter and n being the slope of the flow curve. These calculated relaxation times, listed in table 3, show no quantitative differences.

Still these samples show a different behaviour in the practical application as in droplet break-up, filament formation and nozzle extrusion. A method to quantitatively access these properties is via extensional flow. Figure 2 shows the results for uniaxial elongation determined with the CaBER experiment for the same MHEC solutions shown in Fig. 1.

From Fig. 2 one can see very clearly that the MHEC solutions show pronounced differences in filament break-up.

The sample MHEC 3 shows a considerably higher break-up time then the blending composition of this sample would suggest, since its MWD is the narrowest over all.

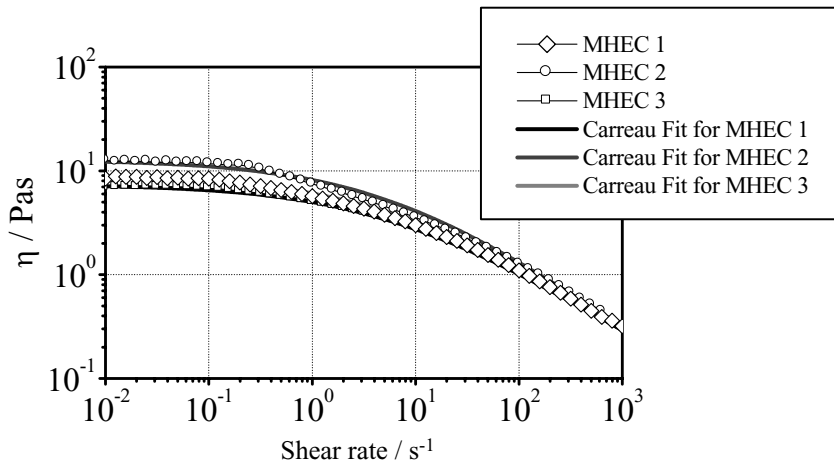


Fig. 1: Filament diameter versus time for the MHECs 1-3, 2 wt% in NaOH (2 wt %) at 25°C.

Polymer	η / Pas	τ_0 Carreau / s	b	n	τ_0 CaBER / s <i>centrifuged</i>	τ_0 CaBER / s <i>Non centrifuged</i>
MHEC 3	7.9	0.17	0.53	-0.61	1.14	1.12
MHEC 2	12.8	0.18	0.53	-0.70	1.08	0.92
MHEC 1	9.3	0.17	0.53	-0.65	0.98	1.85

Table 3: Carreau parameters and longest relaxation times of elongation for the investigated MHECs 1-3.

As shown in table 2, the ratios of recovery for the light scattering experiments indicate a rather large amount of not molecularly dispersed sample that is separated

sample preparation for the light scattering measurements the MHEC solutions were centrifuged and again examined via CaBER measurements. The results are shown in Fig. 3.

with light scattering. Sample MHEC 1 with the broadest MWD shows the longest break-up time sample MHEC 3 with the narrowest MWD the shortest break-up time. The results of the CaBER experiments and the results of light scattering can thus be correlated with the same sample preparation, because in both cases only the molecularly dispersed fraction of the sample is characterized.

The relaxation times evaluated from Fig. 3 via

$$D = \left(\frac{G_0 \cdot D_0}{4 \cdot \sigma} \right)^{\frac{1}{3}} D_0 \cdot e^{\frac{-t}{\tau_0}} \quad (2)$$

[3] are also listed together with the relaxation times of the non-centrifuged samples in Table 3. As the concentrations used for the MHEC solutions are relatively high (2 wt%) structure buildup via hydrogen bonding is an issue. These aggregates may have great influence on the elongational behaviour of the MHEC solutions even in the centrifuged state and superpose the results obtained for the single polymer coil.

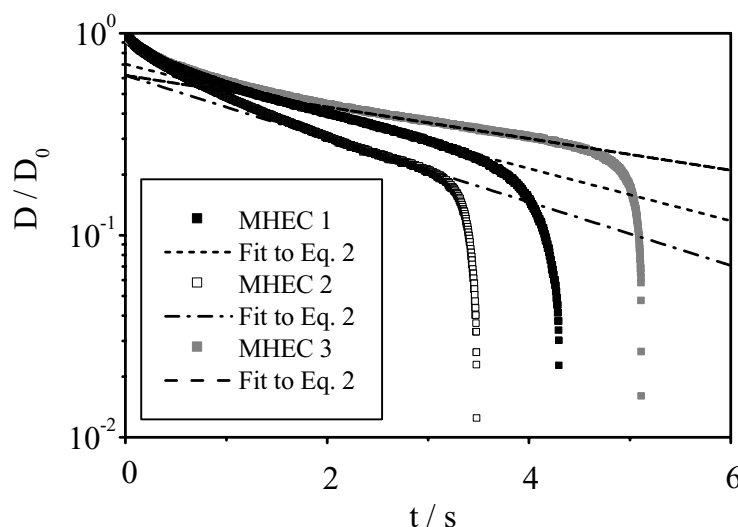


Fig. 2: Filament diameter versus time for the samples MHECs 1-3, 2 wt% in NaOH (2 wt %) at 25°C.

from the solution by filtration and the following pre-columns. To adjust the sample preparation for the CaBER experiments to the

In contrast to Fig. 2 the centrifuged samples show the order in break-up times expected from the distributions determined

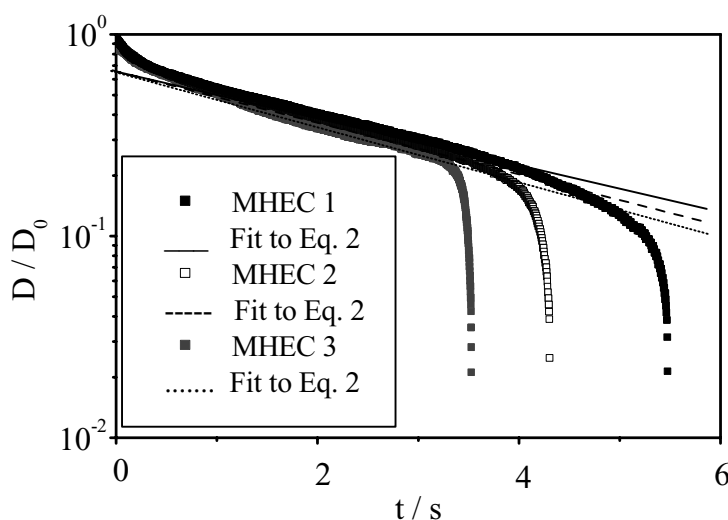


Fig. 3: Filament diameter versus time for the centrifuged samples MHECs 1-3, 2 wt% in NaOH (2 wt %) at 25°C.

Summary

The longest relaxation times τ_0 obtained by CaBER experiments for blended celluloseethers yield information on the MWD of these polymers. In comparison to shear tests this method is faster and more sensitive.

The results could then be correlated with the absolute molar mass distributions obtained via means of SEC/ MALLS/ DRI.

Uniaxial elongation in CaBER experiments is a more sensitive method for the detection of the molecular weight distribution then steady shear flow for samples with similar weight-average molar mass and

therefore similar flow properties in steady shear flow experiments. CaBER experiments also allows for a sensitive detection of non molecularly dispersed fractions of the investigated native cellulose derivative and can thus predict the processability of these polymers in elongational flows.

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Investigating the processing properties of instant release film-coating polymers in aqueous solutions by means of extensional rheology

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Purpose

The application of an instant release film-coating polymer onto the surface of a substrate such as a tablet or a pellet is a standard process in the pharmaceutical industry. In this realm, recent polymers such as polyvinyl alcohol (PVA) and in particular Kollicoat® IR (PVA-PEG graft copolymer) offer low viscosities of their aqueous solutions. This property enables high solid matter contents leading to short and economical film-coating processes [1, 2].

Furthermore, high solid matter contents influences the rheological characteristics of an aqueous polymer solution. Even if the resulting dynamic shear viscosity is found to be low, poor extensional rheological properties can cause severe problems during the atomisation of the film-coating dispersion (Fig. 1).

This work was intended to investigate the extensional rheological properties of several instant release film-coating polymers and to deduce a recommendation for their processability (the influence of colouring agents was studied separately [3]).

Materials and Methods

Materials

The following instant release polymers were investigated: Kollicoat® IR and Kollicoat® Protect – both BASF SE, Ludwigshafen Germany; Pharmacoat® 603 (HPMC 3 mPas) and Pharmacoat® 606 (HPMC 6 mPas) – both Shin-Etsu Chemical Co. Ltd., Tokyo, Japan; Klucel® EF (HPC EF) – Ashland Aqualon, Wilmington, U.S.A.

Methods

Aqueous polymer solutions of various concentrations (concentrations are indicated in Table 1 and the different charts respectively) were prepared. Both extensional properties and dynamic shear viscosity were measured at a temperature of 25 °C.

Extensional viscosity

For extensional testing, the Thermo Scientific HAAKE CaBER 1 (Thermo



Fig. 1: "Cobweb" caused by filament formation.

Fisher Scientific, Karlsruhe, Germany) was used. This equipment determines the capillary break-up time (filament life-time) as a measure for the extensional viscosity.

Dynamic shear viscosity

In order to measure the dynamic shear viscosity, the Thermo Scientific HAAKE RotoVisco 1 rotational rheometer (Thermo Fisher Scientific, Karlsruhe, Germany) with liquid temperature control for concentric cylinder measuring geometries was used.

Results and Discussion

In a coating process, a film forming polymer or a coating formulation (additionally holding pigments, colorants and further additives) is applied onto a substrate. In order to do this, the spraying dispersion is atomised into small droplets. This is typically done by using dispersion and compressed air with a two-component nozzle.

Important for a smooth and homogeneous appearance of the final coat is: firstly, the droplet formation during atomisation and secondly, the spreading of the droplets on the surface of the substrate. Hereby, the actual droplet formation is described by extensional rheology, the spreading is mainly influenced by dynamic shear viscosity.

The filament life-time (FLT) – which is actually measured in the extensional experiment – indicates the quality of the atomisation process. As long as the FLT is in a specific range, good results can be expected, whereas very long FLTs may result in a spray drying effect as shown in Fig. 1. Hereby, both droplets and filaments are formed. The ratio of surface to volume is much higher for a filament leading to an instant drying. Finally the dried filaments are deposited on mounting parts such as nozzles or the nozzle-arm – which looks like a cobweb.

Systematic investigations showed that the basis for an appropriate comparison of instant release film coating polymers is the same dynamic shear viscosity [4]. For the first set of measurements, a viscosity of about 50 mPas was adjusted for all solutions (Table 1). Hereby, Kollicoat® IR was found with the highest solid matter content – about three times higher than the two cellulose derivatives HPC EF and HPMC 6 mPas.

	Viscosity [mPas]	Polymer content [%]
Kollicoat® IR	51.7	17
Kollicoat® Protect	52.6	14
HPMC 3 mPas	51.0	10
PVA	47.5	11
HPMC 6 mPas	45.5	6
HPC EF	61.7	6

Tab. 1: Dynamic shear viscosity of polymer solutions and corresponding polymer contents.

It was found that the various solutions resulted in markedly different FLTs (Fig. 2). Even though, one might expect that a high polymer concentration results in a long FLT, the sample with the highest content showed the shortest FLT. This suggests the lowest risk of a cobweb-effect for Kollicoat® IR.

PVA on the other hand, showed a very pronounced filament formation with a FLT four times longer than the one for Kollicoat® IR. Hence, PVA bears a distinctively higher risk for the cobweb-effect.

In the second set of experiments, solutions with various polymer concentrations were tested (Fig. 3, Fig. 4). Comparing the two HPMC grades, a similar FLT was determined with the polymer concentrations of 10% HPMC 3 mPas and 5% HPMC 6 mPas (Fig. 3). When increasing the polymer concentration, a higher impact on FLT could be found for the 6 mPas grade.

A similar effect could be seen for 17% Kollicoat® IR and 14% PVA, for both polymers FLT was found to be similar, whereas at a concentration of 20% PVA yielded a much longer FLT (Fig. 4).

After describing the atomisation characteristics via FLT, the actual spreading of the dispersion can be described by dynamic shear viscosity (Fig. 5). Generally, higher polymer contents led to a distinctive increase in viscosity. The lowest values could be found for Kollicoat® IR resulting in the highest processible polymer concentrations which still leads to smoothly coated surfaces.

Conclusion

Two rheological characteristics are of utmost importance for developing a spraying dispersion properly:

- Filament life-time is responsible for the atomisation characteristics and consequently for process safety.
- Dynamic shear viscosity is describing the spreading and stands for coat quality and process efficiency.

Therefore, the best coating processes are achievable with a low viscous polymer solution allowing for high solid matter contents and still yielding short filament life-times. The Kollicoat® products were found to match all these requirements best. The results for the cellulosic derivatives revealed that their application lead to a less economical process.

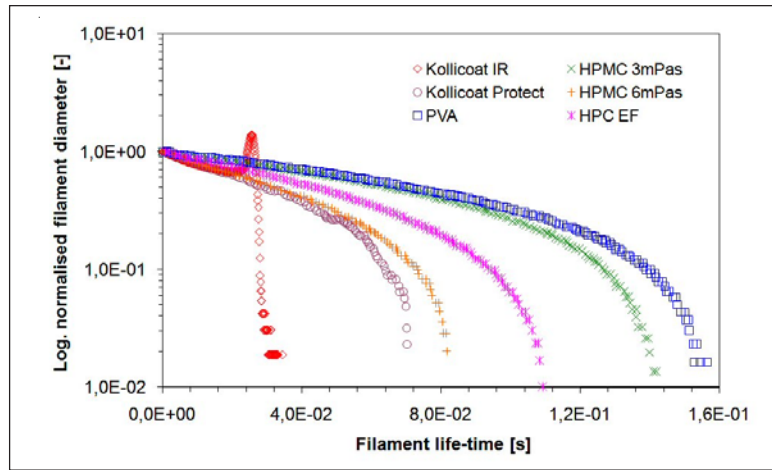


Fig. 2: Filament life-time of various polymer solutions holding a dynamic shear viscosity of about 50 mPas.

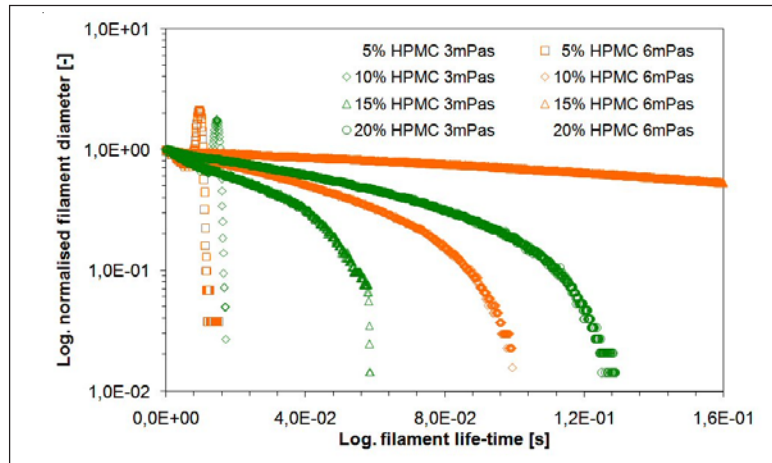


Fig. 3: Filament life-time of various concentrations of HPMC type 3 and 6 mPas.

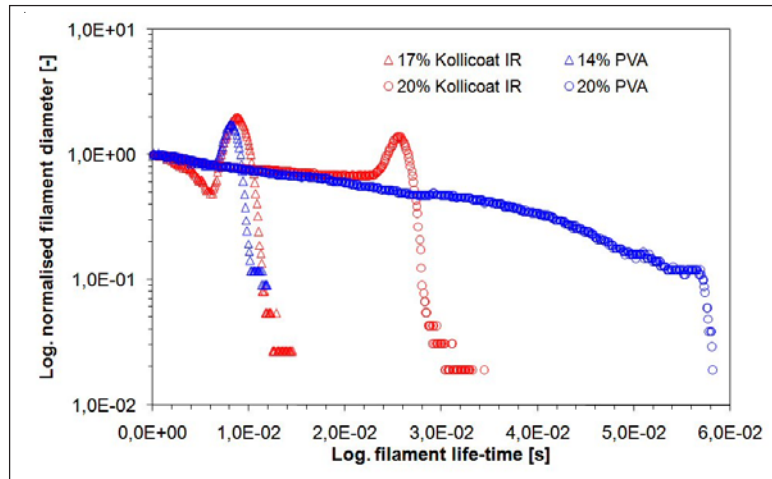


Fig. 4: Filament life-time of different concentrations of Kollicoat® IR and PVA.

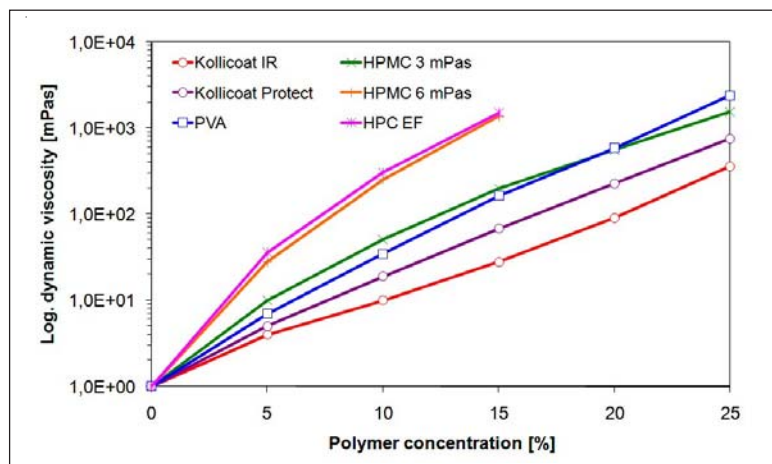


Fig. 5: Dynamic viscosity of various instant release polymers as function of polymer content in an aqueous media.

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Presented at the 3rd PharmSciFair; June 13-17, 2011; Prague, Czech Republic

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Investigating the influence of colouring agents on the rheological characteristics of a film-coating dispersion

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Purpose

Coating a tablet with a non-functional but coloured film is a standard procedure in the pharmaceutical industry. During the development and validation of such a film-coating process, a huge variety of data about the processability and applicability has to be gathered.

Hereby, the focus is typically set on the film forming polymer and its concentration which are known to have a strong impact on the coating result [1, 2, 3]. However, further excipients are involved which might influence the processability as well. The intention of this work was to investigate the influence of colouring agents on the rheological characteristics of a ready-to-use film coating system.

Materials and Methods

Materials

The polymers Kollicoat® IR and Kollidon® VA64 as well as the ready-to-use coatings Kollicoat® IR White II, Kollicoat® IR Sunset Yellow, Kollicoat® IR Carmine and Kollicoat® IR Red (all BASF SE, Ludwigshafen, Germany) were used.

All ready-to-use formulations contain Kollicoat® IR and Kollidon® VA64 as film-formers and the pigments kaolin and titanium dioxide. The individual colours are obtained by adding either an aluminium lake (sunset yellow, carmine) or an iron oxide (red) to the formulation.

Methods

Aqueous dispersions of these products were prepared in different concentrations to determine their individual rheological characteristics.

Extensional viscosity

For extensional testing, the Thermo Scientific HAAKE CaBER 1 (Thermo Fisher Scientific, Karlsruhe, Germany) was used. This equipment determines the capillary break-up time (filament life-time) as a measure for the extensional viscosity.

Dynamic shear viscosity

In order to measure the dynamic shear

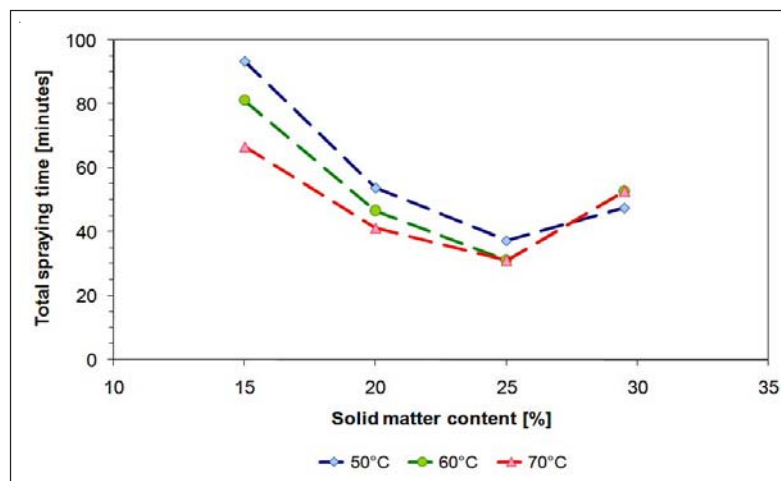


Fig. 1: Determination of the optimal solid matter content for a film-coating process resulting in the shortest possible spraying time (Kollicoat® IR Carmine) at three different inlet air temperatures [4].

viscosity, the Thermo Scientific HAAKE RotoVisco 1 rotational rheometer (Thermo Fisher Scientific, Karlsruhe, Germany) with liquid temperature control for concentric cylinder measuring geometries was used.

Results and Discussion

When optimising a film-coating process in regard to efficiency, the shortest possible time for applying the required weight gain homogeneously onto the cores has to be determined. The main influencing parameters are spray rate and solid matter content of the film-coating dispersion, whereas an increase of one of these parameters already leads to a shorter processing time.

By varying the inlet air temperature (50, 60, 70 °C) and spray rate, the shortest total spraying time for different solid matter contents was determined (Fig. 1). It was found that the spraying dispersion holding 30% solids showed distinctively different coating properties resulting in lower possible spray rates. This could be explained by a decisive change of the dispersions' viscosity. It was suggested that the results could only be transferred to formulations showing the same rheological characteristics [4].

Dynamic shear viscosity

Dynamic shear viscosity is an indicator for the spreading behaviour

of the droplets on the core surface. Hence, this value is to be used for estimating the final coat quality in regard to smoothness.

All formulations showed a shear viscosity clearly depending on solid matter content (Fig. 2). However, there was hardly any difference between the dispersions up to a concentration of 25%. At 30% and especially 35%, the flow properties differed markedly. The highest increase was found for Kollicoat® IR Sunset Yellow. The second ready-to-use coating containing an aluminium lake (Kollicoat® IR Carmine), yielded a low increase in shear viscosity. Interestingly, Kollicoat® IR Carmine and Kollicoat® IR Red (which holds an iron oxide) were found with the same viscosity curves.

Extensional viscosity

Extensional viscosity is an indicator for droplet formation as well as for the risk of spray drying. In a first test, the general effect of pigments on the extensional parameter filament life-time (FLT) was investigated. In order to do this, Kollicoat® IR White II dispersions (25, 30, 35%) were compared to polymer solutions containing Kollicoat® IR and Kollidon® VA64 in exactly the ratio and quantity as they are present in the dispersion (16.6, 19.9, 23.2%).

At 25% solids, there was hardly any difference between the polymer solu-

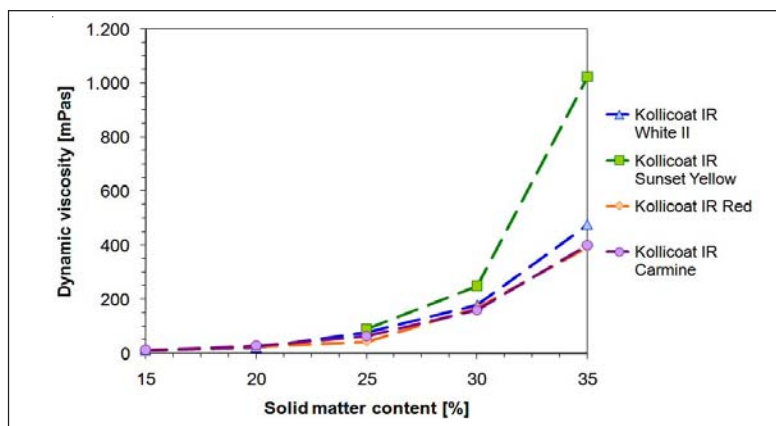


Fig. 2: Dynamic shear viscosity of different Kollicoat® IR based film-coating dispersions as function of solid matter content measured at 25 °C.

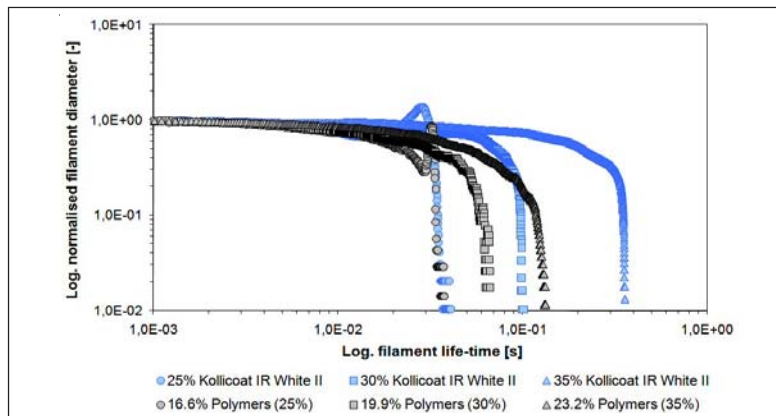


Fig. 3: Filament life-time of polymer solutions in comparison to dispersions of Kollicoat® IR White II.

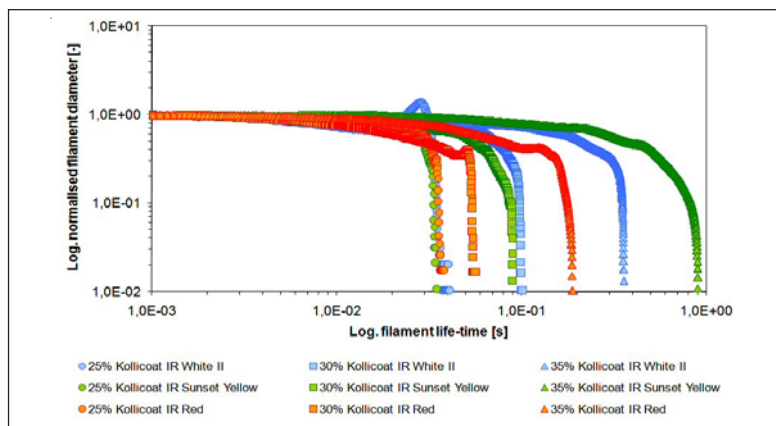


Fig. 4: Filament life-time of different Kollicoat® IR based film-coating dispersions holding different colorants as function of solid matter content.

tion and Kollicoat® IR White II dispersion (Fig. 3). Increasing the solid matter content resulted in a longer FLT for both formulations. However, the pigments present in Kollicoat® IR White II pronounced this effect leading to longer FLT for the dispersion compared to the equivalent polymer solution. After considering the general effects of pigments on FLT, the impact of different colorants was investigated in a second set of experiments (Fig. 4). When comparing the three different colours White II, Sunset Yellow and Red a similar FLT could be found for

solid matter contents of 25%. However, at higher concentrations markedly different FLT were found for the different formulations. This suggests that surface effects caused by the individual colorants affected the rheological properties of the spraying dispersion at higher solid matter contents.

Both investigations (shear and extensional viscosity) showed that the colouring agents did not influence the rheological properties at solid matter contents of 25%. As soon as the solid matter content was increased

to 30% or above, a pronounced effect of the colorant was observed. This suggests that coating parameters can be transferred from one formulation to another for spraying dispersions not higher concentrated than 25%.

Conclusion

Dynamic and extensional viscosity were found to be dependent on the solid matter content of the spraying dispersion. As soon as a concentration of 25% was exceeded the colouring agent had a distinctive influence on both rheological characteristics. This suggested that coating parameters can be used universally and independently of the colorant as long as the basic formulation (in regard to the kind and amount of polymers) is equivalent and a solid matter content of 25% is not exceeded. In regard to higher concentrations, the pigments influence the coating properties and parameters have to be gathered separately for each individual colour.

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Enhanced Oil Recovery and Elongational Flow – The Thermo Scientific HAAKE CaBER1

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Introduction

When a new oilfield starts producing oil, the oil is driven up the well by the internal pressure of the oil deposit. Unfortunately only about 10 % of the oil in place can be recovered like this (primary production). With supporting technical methods like e.g. pumping water into the oilfield to push the crude oil out of the porous stone or sand layer towards the production well, oil production can be increased up to approximately 20 – 40 % of the oil in place (secondary production). Due to the viscosity difference between water and oil sooner or later so-called fingering will occur, where the water injected will break through the oil instead of pushing the oil towards the production well.

To push the total recovery up to 30 – 60 %, so-called enhanced oil recovery (EOR) techniques are utilized (tertiary production). One of these techniques is polymer flooding. Here polymers are used to increase the viscosity of the injection fluid to suppress the fingering. Unfortunately the standard oilfield does not exist. Every oil deposit has its individual characteristics depending on a large number of parameters like for example temperature, pressure, crude oil viscosity, crude oil composition, salinity, and pore size distribution. Consequently, the polymers used for flooding have to be selected or even tailored to perform effectively under the conditions of the individual oil deposit.

Already several decades ago it has been observed that the flow of polymer solution through a porous medium cannot be described based on shear flow alone [1]. Instead of a continuous viscosity drop with increasing flow rate, polymer solutions can show an increase in viscosity above a characteristic flow rate. This effect has been called “shear thickening“

in earlier works. Currently it is commonly accepted that extensional effects (Fig. 1) are the cause for the viscosity increase observed [2]. In some cases it is even suspected to be the key factor to the effectiveness of polymer solutions in EOR [3].

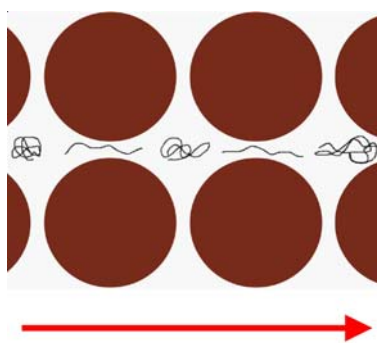


Fig. 1: Schematic illustration of the elongation and relaxation of a polymer coil during its flow through a porous medium. The red arrow indicates the direction of flow from the injection well to the production well.

As a consequence there is an increasing demand for analytical techniques capable of characterizing the extensional properties of low viscous polymer solutions used in polymer flooding.

Experimental

Classical studies have mostly been done via flooding real rock material retrieved from the well or synthetic porous media made of sand or similar materials. These porous media are difficult to make, difficult to characterize and difficult to maintain due to absorption of the polymers.

For a systematic characterization it is much easier to expose polymer solutions to an extensional field directly. The most convenient and time efficient approach is using the Thermo Scientific HAAKE CaBER 1, the only commercially available extensional rheometer for low viscous fluids (Fig. 2).

This Capillary Breakup Extensional Rheometer quickly pulls a small volume of a liquid apart to form a liquid filament. It measures the thickness of this filament (Fig. 3a) or, more precisely, how quickly this filament collapses. The thickness of the collapsing filament is measured at the mid-point between the two plates and plotted as a function of time (Fig. 3b).

In total, the collapse of the filament happens because the liquid flows away from the centre of the filament towards the upper and the lower plate, which causes its diameter to shrink until it breaks. The central point of the filament is located between two opposing flows, a so-called stagnation point where the flow speed is zero. Therefore the central volume element is exposed to a uniaxial elongational strain (Fig. 4).



Fig. 2: The HAAKE CaBER1, the only commercially available elongational rheometer for liquids.

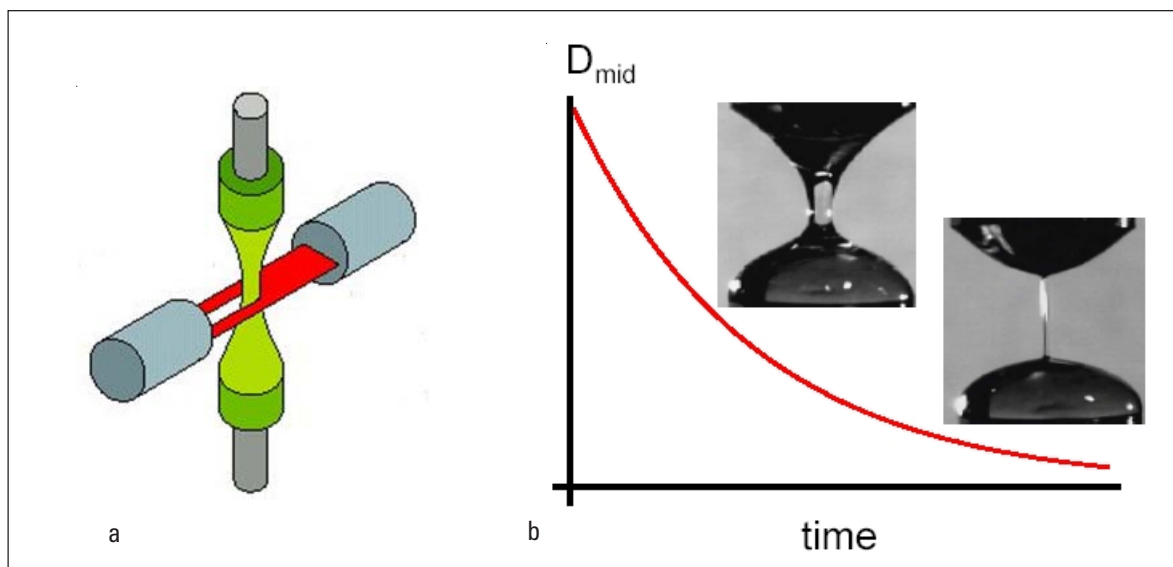


Fig. 3 a: Simplified principle of the HAAKE CaBER 1. The liquid sample is pulled upwards to form a filament (light green). The thickness of the filament is measured at its thinnest point with a laser micrometer.

b: Schematic depiction of the raw data from a CaBER test. The diameter of the liquid filament is measured in the middle between the two plates and plotted as a function of the time.

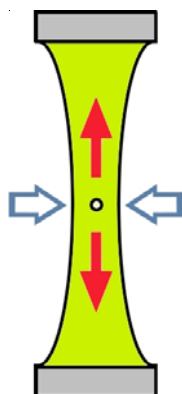


Fig. 4: During the collapse of the filament the liquid flows away from the centre point of the filament (red arrows) leaving a central volume element where the speed is zero. At this so-called stagnation point the liquid is exposed to a uniaxial elongational strain.

From a variety of powder polyacrylamides for polymer flooding, 2 different samples have been selected. According to the chemical characteristics of the oilfield, the tests were done for, a salt solution containing CaCl_2 and NaCl that was prepared to simulate the real-life chemical conditions in the field. A 5000 ppm polymer solution has been prepared from both polymer samples. To prepare each solution, a measured amount of the salt water has been filled into a glass container with a screw-on lid. A stirring magnet has been added and the polymer was introduced into the vortex of the stirred salt water. The glass was closed with its lid and carefully sealed with a flexible sealing tape to avoid any changes in concentration due to evaporation.

After some hours of slow stirring, the polymer solutions have been tested with the HAAKE CaBER 1. Due to

the low viscosity of the samples the 4 mm plates have been selected. Using a small syringe without needle (!) the samples have been filled into a 2 mm gap between the plates of the HAAKE CaBER 1 at 20 °C. Within 50 ms the upper plate was lifted to 6.5 mm above the lower plate, which equals a Hencky Strain of 1.2.

Under these test conditions the 2 polyacrylamides showed a significant difference in break-up time. The filament formed by Polymer 1 was less stable collapsing after approx. 0.01 s whereas the filament of Polymer 2 lasted for 1.1 s (Fig. 5).

Regarding the curves shown in Fig. 5 shows that both collapses happen abruptly. The plot shows the normalized filament diameter (D_N = actual diameter divided by initial diameter) as a function of time. Both polymer solutions start with D_N -values around 0.3, which stay almost constant until the break-up occurs. This behaviour indicates that both polymers have an extended coil structure in this kind of solvent. The results from the CaBER tests give an insight into the polymer/solvent interaction and the rigidity of the polymer coil in solution [4]. Based on the raw data the HAAKE CaBER 1 software calculates the apparent extensional viscosity, shown in Fig. 6 plotted against the elongational strain. Again the behaviour of the two polymers differs significantly. While Polymer 1 shows an almost constant viscosity, Polymer 2 exhibits a strong viscosity increase around a strain of 3. For flooding projects a rather constant viscosity has the advantage of a more uniform

behaviour independent of the actual strain, which depends on pore diameter and flow speed.

Summary

With the HAAKE CaBER 1 it is possible to test the elongational behaviour of even low viscous liquids like the flooding solutions tested for this report. Since the elongational viscosity of liquids is not accessible using a rotational viscometer or rheometer, this elongational rheometer is the perfect complement to get the full information needed to understand applications, which are clearly influenced or even dominated by elongational flow effects.

Especially when the real application cannot be accessed directly and any error could cause costly consequences, a reliable lab test, which can be performed quickly, is highly recommended. Polymer flooding of an oilfield is one of those applications where it is essential to gather as much relevant information as possible in the lab before trying something out in the oilfield deep underground. Regarding the costs involved in a flooding project and the financial benefit every improvement of the flooding efficiency yields, the investment in a HAAKE CaBER 1 is a very reasonable and foremost profitable one.

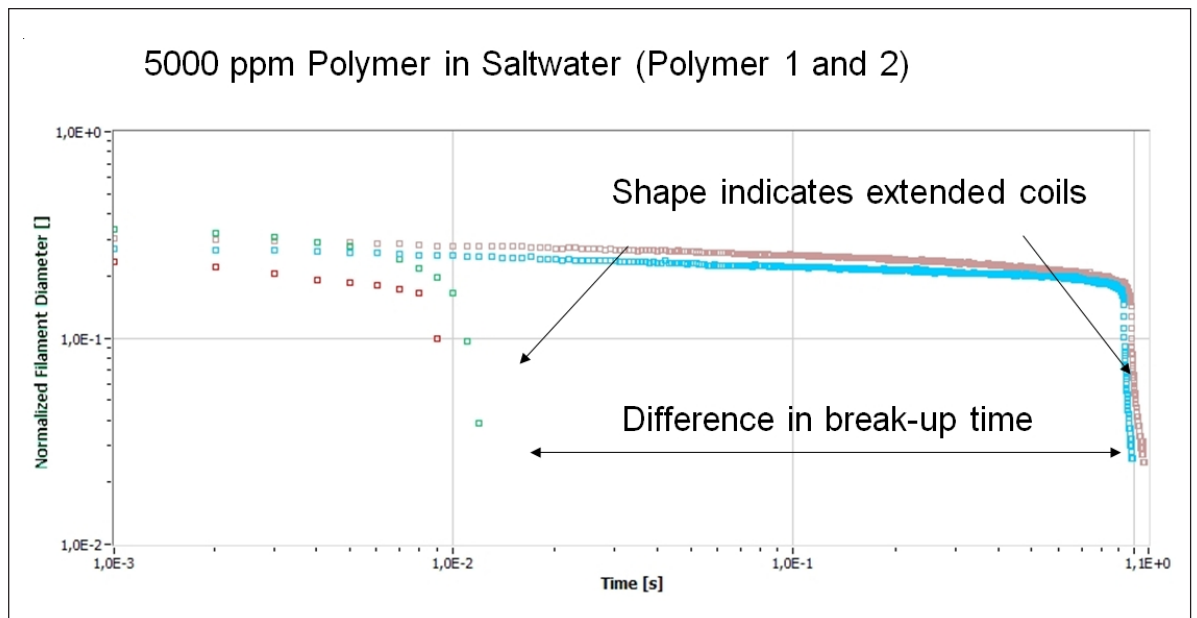


Fig. 5: Decrease of the normalized filament diameter over time for the solutions of 2 different polyacrylamides in saltwater. Although having the same concentration both solutions show different break-up times and different curve shapes.

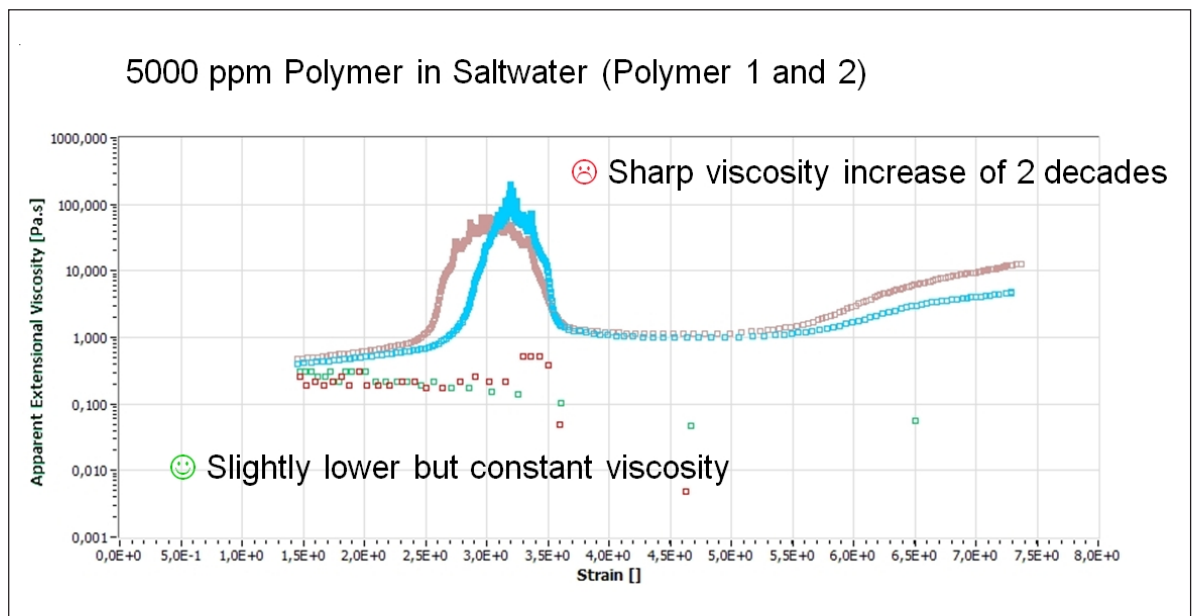


Fig. 6: Apparent elongational viscosities as a function of the elongational strain of 2 different polyacrylamides in salt water. One polymer shows a rather constant viscosity, the other one shows a sharp increase of viscosity by a factor of one hundred.

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Material Characterization

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