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

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 methylhydroxy-ethyl 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 methylhyroxyethyl 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 refracto-meter (DRI).

Results and Discussion

The investigated MHECs were specifically blended from 3 different celluloses with different intrinsic viscosities ($[\eta]_{cellulose3}$ < $[\eta]_{cellulose2}$ < $[\eta]_{cellulose1}$) 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.

$$\eta = \eta_0 \left[1 + \left(\tau_o \cdot \dot{\gamma} \right)^b \right]^{n/b} \qquad (1)$$

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.
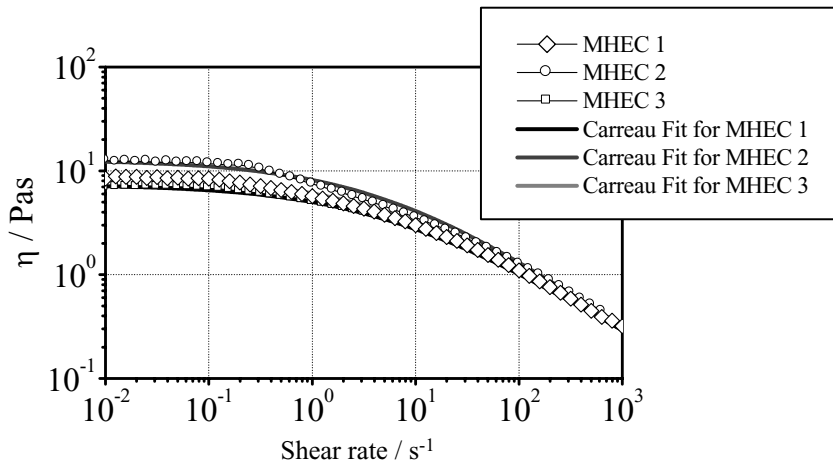

Fig. 1: Filament diameter versus time for the MHECs 1-3, 2 wt% in NaOH (2 wt %) at 25°C.

Polymer	η / Pas	τ_0 Carreau / s	b	n	τ_0 CaBER / s centrifuged	τ_0 CaBER / s Non centrifuged
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.
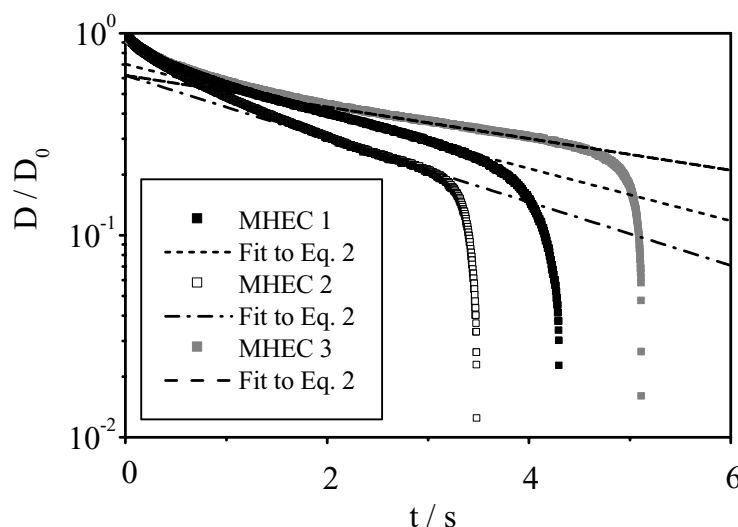

Fig. 2: Filament diameter versus time for the samples MHECs 1-3, 2 wt% in NaOH (2 wt %) at 25°C.

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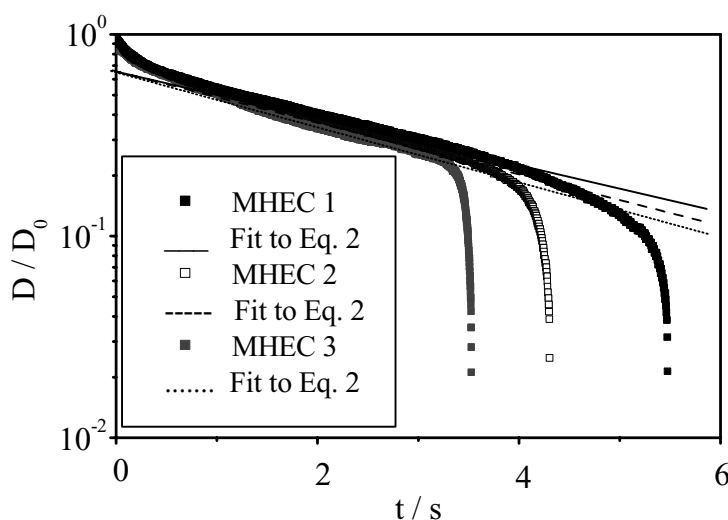
with light scattering. Sample MHEC 1 with the broadest MWD shows the longest break-up time sample MHEC 3 with the narrowest MWD the shortest break-up time. The results of the CaBER experiments and the results of light scattering can thus be correlated with the same sample preparation, because in both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

The relaxation times evaluated from Fig. 3 via

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

[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 relativly 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.

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

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

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.

References

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