INFLUENCE OF THE MOLAR MASS DISTRIBUTION ON THE ELONGATIONAL BEHAVIOUR OF POLYMER SOLUTIONS IN CAPILLARY BREAKUP

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ABSTRACT:
Commercially available, blended methylhydroxyethyl celluloses with similar weight-average molar masses but varying molar mass distributions were characterized by different techniques like steady shear flow and uniaxial elongation in capillary breakup experiments. The determined relaxation times τ were then correlated with the absolute molar mass distribution acquired via SEC/MALLS/DRI (combined methods of size-exclusion-chromatography, multi angle laser light scattering and differential refractometer). In order to describe the longest relaxation time of the polymers in uniaxial elongation via integral mean values of the molar mass distribution, defined blends of polystyrene standards with varying molar mass distributions were characterized. The obtained data was scaled via different moments of the molecular weight distribution and could be correlated with the results obtained for the methylhydroxyethyl celluloses.

ZUSAMMENFASSUNG:
Kommerziell erhältliche Methylhydroxyethylzelluloseblends mit ähnlichem gewichtsgemittelten Molekulargewicht aber unterschiedlicher Molekulargewichtsverteilung wurden mittels verschiedener Methoden wie stationäres Scherfliessen und uniaxialer Dehnung in Kapillaraufbruchexperimenten charakterisiert. Die ermittelte Relaxationszeit t wurde dann mit der absoluten Molekulargewichtsverteilung in Beziehung gesetzt, die durch SEC/MALLS/DRI (Kombination von Grössenausschluss-Chromatographie, Vielwinkellaserlichtstreuung und differentielle Refraktometrie) gemessen wurde. Um die längste Relaxationszeit der Polymere in uniaxialer Dehnung durch integrale Mittelwerte der Molekulargewichtsverteilung zu bestimmen, wurden defnierte Polystyrolblendstandards mit unterschiedlicher Molekulargewichtsverteilung charakterisiert. Die erhaltenen Daten wurden mit verschiedenen Momenten der Molekulargewichtsverteilung skaliert und konnten in Beziehung gesetzt werden mit den Ergebnissen für Methylhydroxyethylzellulose.

RÉSUMÉ:
Nous avons caractérisé des mélanges commerciaux de méthyle-hydroxyéthyle de cellulose possédant des poids moléculaires moyens identiques, mais dont les distributions en poids sont différentes, au moyen de différentes techniques comme l'écoulement en cisaillement constant et l'extension uniaxe obtenue à l'aide d'un capillaire à rupture de filament. Les temps de relaxation mesurés ont été corrélés avec les distributions en masses molaires obtenues par SEC/MALLS/DRI (méthodes combinées de chromatographie à exclusion de tailles, diffusion de lumière à angles multiples et réfractomètre différentiel). Dans le but de décrire les temps de relaxation les plus longs des polymères en élongation uniaxe à partir des valeurs moyennes intégrales de la distribution en poids molaires, des mélanges définis de polystyrènes standards possédant des distributions en poids molaires variées ont été caractérisés. Les données obtenues ont été quantifiées au moyen des différents moments de la distribution en poids moléculaires, et ont pu être corrélés avec les résultats obtenus pour les méthyle-hydroxyéthyles de cellulose.

KEY WORDS: Elongational rheology, polystyrene blends, MHEC, MWD

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1 INTRODUCTION

The influence of the molar mass distribution (usually referred to as MWD (molecular weight distribution) in literature) and the polydispersity, M_w/M_n, on the rheological properties of polymers is of great importance for diverse technical applications and polymer processing. The experimental detection of the discrete influence of the polydispersity on the rheological properties and also of the polydispersity itself is not easily to achieve quantitatively.

This applies particularly for cellulose 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 trials 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 breakup extensional rheometry, of blended polymers with the different moments of the MWD.

2 PROBLEM

For steady shear flows it has already been shown that the broadness of the transition area from Newtonian to the non-Newtonian flow regime is not a quantitative measure for the molecular weight distribution of a polymer [3]. The longest time of relaxation for shear flows τ_0, as the onset of non-Newtonian flow, is an integral property that depends on the MWD [3 - 5]. Therefore the (empirical) correlation of the parameters of constituive equations as the transition parameter b in the modified Carreau model [6] to the molecular weight distribution strongly depends on the limiting parameters of the fit and show only small changes over a wide range of distributions.

A more accessible method for the detection of the MWD is via SAOS (small amplitude oscillatory shear). Here one can determine the spectrum of relaxation times for a polymer sample, which can be directly correlated with the modes of relaxation of a discrete molar mass [7, 8]. However this relaxation spectrum is superposed by the molecular weight distribution which leads to a complex correlation of the spectra to the molecular weight distribution, that is still discussed in literature [9 - 15].

A new method to determine the influence of the MWD on the rheological characteristics is via elongational flows. While the elongational investigation of polymer melts is established for quiet a while [16 - 18] the significantly lower viscous polymer solutions are still hard to characterize in their elongational behaviour. In the past years several methods for determination of the elongational profile of polymer solutions have been introduced. This can be done via pressure drop in porous media [19, 20], opposed jets [21], or via optical detection of the birefringence of a polymer in a planar elongational flow in a 4-roll apparatus [22, 23]. All these methods have serious drawbacks in terms of time intensitivity and complex experimental setups in case of opposed jets and 4-roll apparatus.

A new and fast method to determine the behaviour of polymer solutions in uniaxial elongational flows is the commercially available CaBER (Capillary Breakup Extensional Rheometer). Elongational strains of CaBER type experiments appeal to the longest relaxation time of a polymer coil due to the balanced stresses in a surface tension driven flow [24 - 26]. Therefore the problem simplifies again to a correlation of longest relaxation times to the molecular weight distribution. Though it is not yet clarified via which integral mean value of the MWD integral values of the distribution of relaxation times can be described.

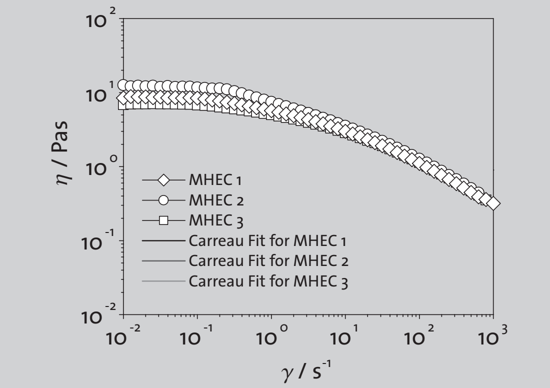
Hence the aim of this contribution is to determine this correlation between longest relaxation times of CaBER type experiments with the MWD of different polymers. This is to be done first via investigation of the behaviour of ideal blended polymer standards with a defined MWD in uniaxial elongational flow in the CaBER experiment and second for a set of commercially avail-

Table 1 (above): 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	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 cellulose samples in cm^3/g)

Figure 1 (below): Shear viscosity η versus shear rate $\dot{\gamma}$ for MHECs 1-3, 2 wt%, dissolved in aqueous NaOH (2 wt%) at 25°C.



able blended celluloseethers introduced in the introduction.

3 EXPERIMENTAL SECTION

The polystyrene standards used for this work were acquired from Polymer Labatories (PL) and Polymer Standard Sevices (PSS). 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 the accordant solvent. Homogenization was achieved by permanent agitation over a period of time not shorter than 3 days (MHEC in 2 wt% NaOH) at RT, at least 7 days (polystyrene in diethylphthalate) with alternating temperature for at least 60 days for Boger fluids (polystyrene in styrene oligomere). Intrinsic viscosities, [η], where determined with an Ubbelohde capillary IIc (polystyrene) or Ic (MHEC), in a watertub temperated at 25.0 ± 0.05°C. Steady shear flow and SAOS measurements where carried out on a rate controlled ARES rheometer (TA Instruments) with cone and plate geometries. Elongational characterization was done on a CaBER rheometer (ThermoHaake). 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).

4 RESULTS AND DISCUSSION

4.1 INFLUENCE OF THE MWD ON THE FLOW BEHAVIOUR OF MHEC

In the following chapter the influence of the MWD on the rheological behaviour of the MHECs is to be discussed. The investigated MHECs were specifically blended from three different celluloses with different intrinsic viscosities ($[\eta]_{cellulose3} < [\eta]_{cellulose2} < [\eta]_{cellulose1}$) by the producing company 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 Table 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 substitution) of the investigated MHECs are summarized. In addition to this the intrinsic viscosities of the pure cellulose samples are listed.

A general problem of native cellulose derivatives is that molecularaly disperse solutions are hard to obtain since the cellulose backbone tends to form aggregated clusters in solution via H-bonds of unsubstituted OH-groups. To supress this formation of aggregated structures all rheological measurements of the MHECs were accomplished in a solvent consisting of 2 wt% NaOH in water.

Figure 1 shows that the investigated MHECs do not show significant differences in terms of their shear viscosity, 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_O of steady shear flow.

$$\eta=\eta_o\left[1+\left(\tau_o\gamma\right)^b\right]^{n/b} \tag{1}$$

with *b* being a transition parameter and *n* being the slope of the flow curve. These calculated relaxation times, listed in Table 2, show no quantitative differences.

Still these samples show a different behaviour in the practical application as in droplet breakup, filament formation and nozzle extrusion. A method to quantitatively access

Polymer	η_0 / Pas	τ_0 Carreau / s	b	n	τ_0 CaBER / s
MHEC 3	7.9	0.17	0.53	-0.61	1.85
MHEC 2	12.8	0.18	0.53	-0.70	0.92
MHEC 1	9.3	0.17	0.53	-0.65	1.12

Table 2 (above): Longest relaxation times of steady shear flow and CaBER experiments for the investigated MHECs 1-3.

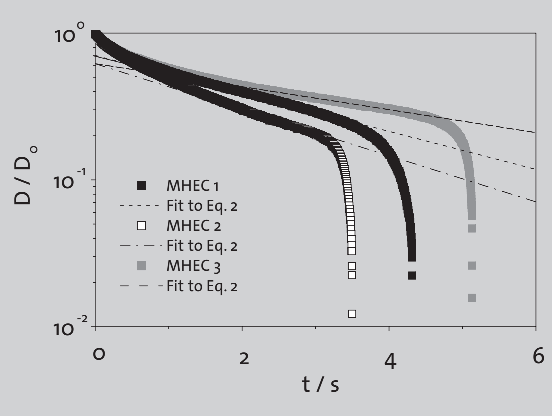


Figure 2 (below): Filament diameter versus time for the MHECs 1-3, 2 wt% in NaOH at 25°C.

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 elongational flow field has a different effect on the MHECs. The MHEC solutions show pronounced differences in filament breakup. The sample MHEC 3 shows a considerably higher breakup time then the blending composition of this sample would suggest, since its MWD is the most narrow over all. Via the time dependent decrease of the filament diameter one can directly evaluate the longest relaxation time, τ_O. According to Anna and McKinley in the spectrum of relaxation times of the elasticity modulus

$$G(t)=\sum_{i=0}^{N_{modes}} G_i \cdot e^{\frac{-t}{\tau_i}} \tag{2}$$

in CaBER like experiments only the longest relaxation time is excited [26]. For this reason only the moldulus of the longest relaxation time, G_O, has to be taken into account for further considerations. For the time dependent filament diameter at intermediate times one comes to the following, in regards to Entov and Hinch, slightly corrected expression [27]

$$D=\left(\frac{G_o D_o}{4\sigma}\right)^{1/3} D_o e^{\frac{-t}{3\cdot\tau_o}} \tag{3}$$

with σ being the surface tension of the investigated fluid. The decrease of the filament diameter for a viscoelastic fluid therefore depends only on the elastic modulus, G_O, the initial filament diameter, D_O, and the longest relaxation time, τ_O. The arising question is which mean average mode of the relaxation time resp. the MWD is appealed to by uniaxial elongation. To approach this problem, defined polystyrene blends were firstly investigated to quantify the influence of the molar mass respectively the MWD on the elongational flow behaviour.

4.2 *Influence of the MWD on the flow behaviour of polystyrene*

The polystyrene solutions investigated were blended from different narrowly distributed polystyrene standards with varying molar masses to achieve an approx. constant molar mass M_w of $4.7 \cdot 10^6$ g/mol with different MWDs varying in M_w/M_n from approximately 1 to 1.84 (manufacturers specifications were used for primary evaluation of molar mass distribution). The true molar masses of the polystyrene standards were acquired via viscosimetry and the Mark-Houwink-Sakurada equation [28]

$$[\eta]=K_\eta M^a \tag{4}$$

with $K_\eta = 8.62 \cdot 10^{-3}$ cm^3/g and a = 0.736, and are listed together with the intrinsic viscosities of the polystyrenes in Tab. 3. In Table 4 the absolute composition of the investigated polystyrene blends are listed together with the width of the MWD. The flow curves shown in Fig 3 for these

Table 3: Molecular parameters of the investigated polystyrene standards.

Polymer	$[\eta]$ cm^3/g	M_w 10^6 g/mol	M_w / M_n
PS 1$^+$	200	0.85	1.00-1.05
PS 2$^+$	513	3.09	1.00-1.05
PS 3$^+$	701	4.70	1.00-1.05
PS 6$^+$	715	4.82	1.00-1.05
PS 5$^+$	917	6.76	1.00-1.05
PS 4$^+$	996	8.17	1.00-1.05

($^+$measured in Toluene)

Blend	Blend Composition / wt.%						M_w / M_n
	PS 1	PS 2	PS 3	PS 4	PS 5	PS 6	
1.0	-	-	100	-	-	-	1.00 - 1.05
1.1	-	22.2	66.0	9.8	2.0	-	1.06
1.2	0.3	34.0	46.6	13.5	5.3	0.3	1.11
1.5	7.7	37.3	32.2	13.7	7.8	1.3	1.36
2.0	18.9	33.7	25.0	12.3	7.7	2.4	1.66
3.0	27.6	30.3	20.6	10.6	7.5	3.5	1.84

Table 4 (left above): Blend composition and values of polydispersity M_w / M_n for investigated polystyrene blends.

Blend	τ_0 CaBER
1.0	0.062
1.1	0.076
1.2	0.083
1.5	0.098
2.0	0.104
3.0	0.12

Table 5 (right above): Longest relaxation times of uniaxial elongation for investigated polystyrene blends.

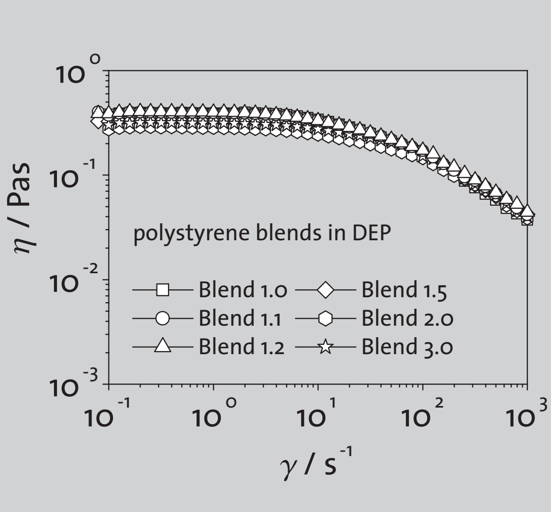


Figure 3 (left middle): Shear viscosity η versus shear rate γ for polystyrene blends, 1.0 wt% in diethylphthalate at 25°C.

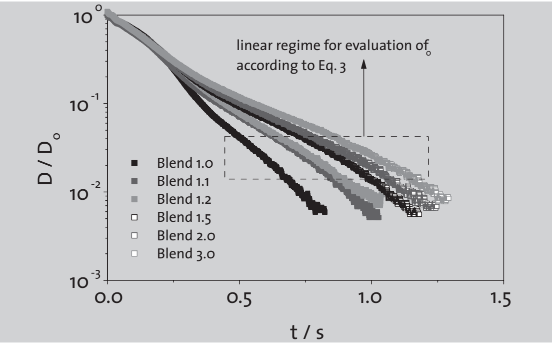


Figure 4 (right middle): Filament diameter versus time for polystyrene blends, 1.0 wt% in diethylphthalate at 25°C.

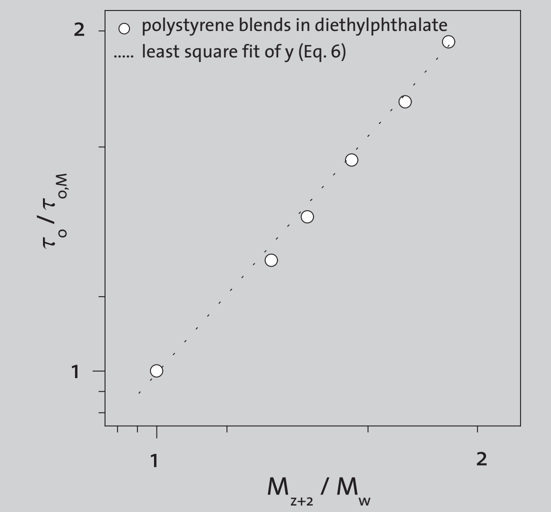


Figure 5 (below): Least square fit of parameters c and y to M_{z+2}/M_w for polystyrene blends in diethylphthalate.

blends (1 wt% in diethylphthalate) show approximately the same flow characteristics. In contrast to this the results of uniaxial elongation in a CaBER experiment are shown in Fig. 4 for the same polystyrene blends.

Fig. 4 shows, that in contrast to steady shear flow experiments one can determine pronounced differences in the capillary thinning behaviour for the investigated polystyrene blends. In the linear regime of this semi-logarithmic plot one can evaluate longest relaxation times according to Eq. 3. The longest relaxation time in uniaxial elongation increases with a factor 2 from blend 1 to blend 3. For a correlation of linear viscoelastic terms like η_0 and J_0 with the MWD of a polymer, different approaches have been made in literature [29 - 31] with the general form

$$\hat{a} = \hat{a}_M P \tag{5}$$

with P being a correction term that depends on different modes of the MWD and $\hat{a}$ and $\hat{a}_M$ being a viscoelastic characteristic value of the distributed and the mondisperse sample. To correlate the relaxation behaviour of the polystyrene blends with the MWD, a model equation was searched for, that directly relates the ratio of relaxation times of monodisperse (blend 1) and polydisperse samples with the MWD. The factor P in the majority of approaches is of the form

$$P = \left(\frac{M_x}{M_w^y} \right)^c \tag{6}$$

with M_x being the x-mean molar mass

$$M_x = \frac{\sum n_i M_i^x}{\sum n_i M_i^{x-1}} \tag{6a}$$

and y and c being empirical or theoretical predicted parameters. Least square fits of the experimentally obtained values of τ_O and $\tau_{O,M}$ as our characteristic viscoelastic properties as a function of P (Eq. 6) for several different x-mean distributions and c and y as fitting parameters were accomplished to determine the best suited M_x. As shown in Fig. 5, the best correlation could be obtained for M_x as the z + 2 average molar mass.

The least square fit of the data in Fig. 5 gave the following equation to describe the

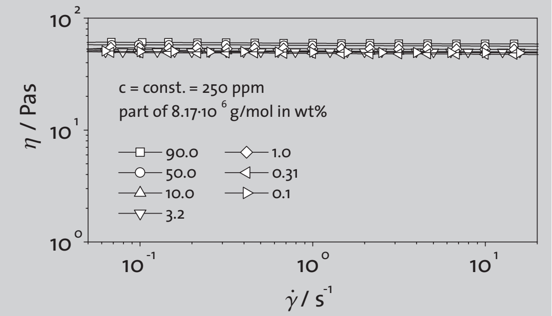


Figure 6 (above): Shear viscosity η versus shear rate $\dot{\gamma}$ for investigated polystyrene Boger fluids, 0.025 wt% at 25°C.

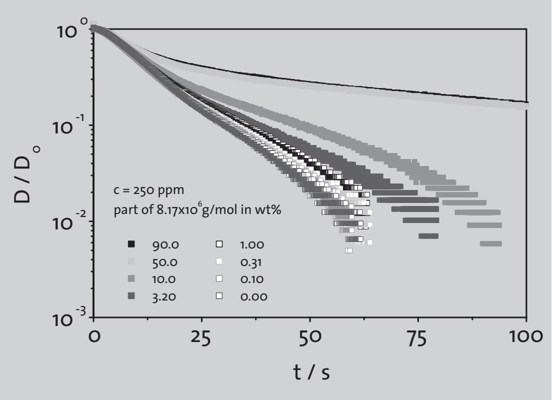


Figure 7 (below): Filament diameter versus time for the investigated polystyrene Boger fluids, 0.025 wt% at 25°C.

dependency of the relaxation times from the width of the MWD

$$\frac{\tau_o}{\tau_{o,M}} = \left(\frac{M_{z+2}}{M_w}\right)^{1.22} \tag{7}$$

with

$$M_{z+2} = \frac{\sum n_i M_i^5}{\sum n_i M_i^4}$$

The integraly determined longest relaxation time of uniaxial elongation in CaBER like experiments of a distributed sample is hence mainly influenced by the M_{z+2} mean molar mass of the MWD. However, one has to keep in mind, that the correlation in Eq. 7 to the M_{z+2} mean molar mass and the values of c and y are so far purely empirical.

To point out the influence of a high-molecular fraction on the flow behaviour in capillary breakup, two polystyrene standards ($2.8 \cdot 10^6$ g/mol and $8.17 \cdot 10^6$ g/mol) were blended at a constant concentration of 250 ppm in styrene oligomer as the solvent. The resulting zero shear viscosity of these Boger fluids [32] is very high compared to a solution in DEP, so that relaxation actions of the polymer coils are slowed down to a high degree which therefore leads to an improved detectability even at concentrations below c^* (critical overlap concentration). The results of steady shear flow measurements for these Boger fluids are shown in Fig. 6.

Fig. 6 shows that almost no differences in zero shear viscosity can be detected for the set of investigated binary Boger blends as expected for a mainly solvent dominated shear flow in a dilute solution. In contrast to this, the results of uniaxial elongation for this set of Boger blends are shown in Fig. 7.

As shown in Fig. 7 a fraction of 0.31 wt% of the high-molecular species already results in measureable longer breakup times. Since the CaBER experiment reacts very sensitive to the longest relaxation time of the high-moleclar edge of the MWD according to Eq. 3 tiny amounts of high-molecular species already lead to a pronounced influence on the elongational behaviour. However, one has to keep in mind that in contrast to the blends in Fig. 4 these binary blends do not have a constant weight average molar mass but rather an increasing M_w with an increasing part of the high molecular weight species. Therefore, one would naturally expect the relaxation time to rise with increasing part of high molecular weight species. A better way to observe the influence of the distribution is again to plot a reduced $\tau_o/\tau_{o,M}$. The required $\tau_{o,M}$ can be obtained from the pure low and high molar mass solutions, since the relaxation time dependence scales with $M_w{}^{3\nu}$ for narrow distributions [9, 26], with ν being the excluded volume coefficient

$$\tau_{o,M} = (2.3 \pm 1.7) \cdot 10^{-10}_{w} M^{(1.62 \pm 0.05)} \tag{8}$$

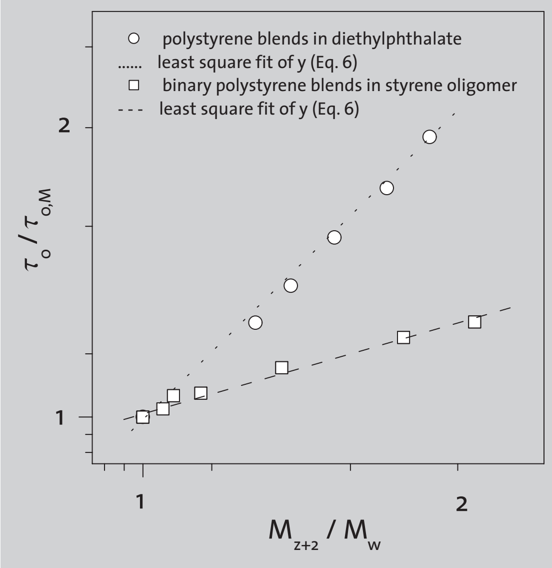
We obtain

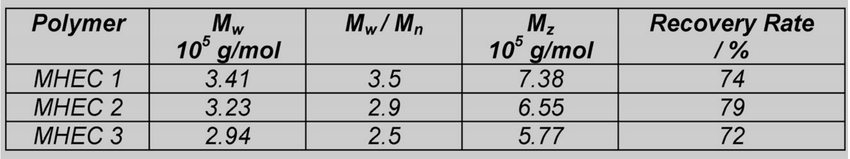
$$\tau_{o,M} = 1.6 \cdot 10^{-10} M_w{}^{1.62}$$

in good agreement with Anna and McKinley and can therefore plot

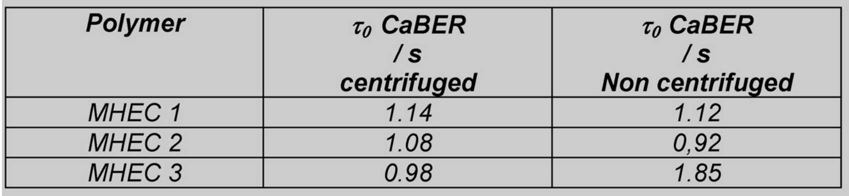
$$\frac{\tau_o}{\tau_{o,M}} = f\left(\frac{M_{z+2}}{M_w}\right)$$

The results are shown in Fig 8. From Fig. 8 one can see that the relaxation times of the binary blends do not scale with the same exponent c as the polystyrene blends in DEP (Eq. 7). Still, linear fitting of the data works out quiet well, as shown





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



Polymer	τ_0 CaBER / s centrifuged	τ_0 CaBER / s Non centrifuged
MHEC 1	1.14	1.12
MHEC 2	1.08	0,92
MHEC 3	0.98	1.85

Figure 8 (left above): Least square fit of parameters c and y to M_{z+2}/M_w for polystyrene blends in diethylphthalate and binary polystyrene blends in styrene oligomer.

Figure 9 (right above): Differential molecular weight distributions (MWD) of the investigated MHECs 1-3.

Figure 10 (right middle): Filament diameter versus time for the centrifuged MHECs 1-3 at 25°C.

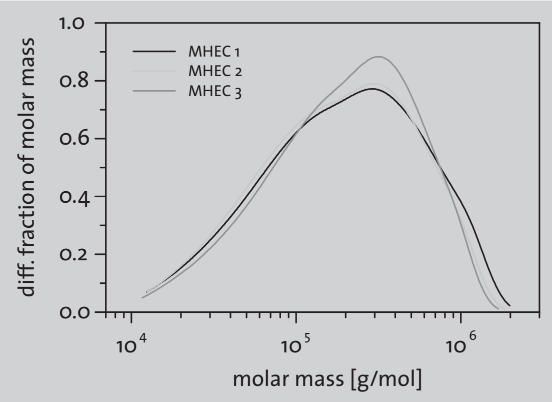
Table 6 (left middle): Molecular parameters of investigated MHECs 1-3, determined via combined methods of SEC/MALLS/DRI.

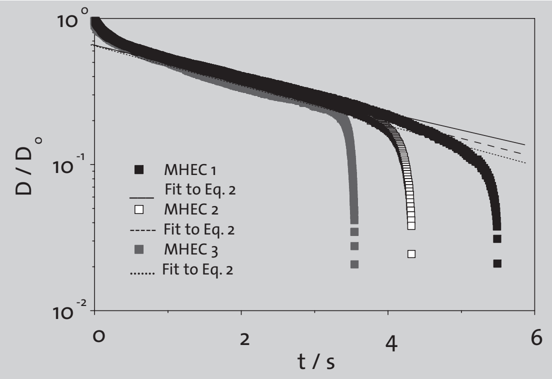
Table 7 (left below): Longest relaxation times of uniaxial elongation for the investigated centrifuged and non-centrifuged MHECs 1-3.

in Fig. 8. However, we should keep in mind, that we are dealing not with a flory distribution, but a bimodal distribution of the molar mass. In addition to this the styrene oligomers are a worse solvent than diethylphtalate and close to theta conditions. We therefore refrain from comparing *c* for diethylphthalate and Boger fluid.

4.3 Influence of the MWD on the elongational behaviour of MHECs

Since the influence of the width of the MWD on the elongational behaviour of polymer fluids was investigated on polystyrene standards, the absolute molar masses and their distributions were determined for the investigated commercial MHECs 1-3 to correlate the results with the elongational behaviour shown in Fig. 2 in form of the thread thinning behaviour. Determination of the absolute molar masses and the molar mass distributions was achieved via coupled methods of size exclusion chromatography (SEC), multi angle laser light scattering (MALLS), and differential refractometer (DRI) [33]. The results of the light scattering experiments for the three different MHECs are shown in Fig. 9 in terms of the differential molar mass distribution.





As shown in Fig. 9 the sample MHEC 1 exhibits the broadest distribution of the molar mass that also is close to being bimodular. The other two samples MHEC 2 and MHEC 3 follow up with MHEC 2 having a broader distribution than MHEC 3. All three samples have very similar weight average molar masses. The determined mean values for the distribution and the polydispersities for the MHECs are listed in Table 6 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.

However the determined MWDs do not correlate with the results for uniaxial elongation for the MHECs shown in Fig. 2 because sample MHEC 1 with the broadest distribution and hence the highest ratio of high molecular weight polymer does not show the longest breakup time. Instead, as shown in Fig. 2 the sample MHEC 3 with the narrowest distribution shows the longest breakup time. As shown in table 6, the ratios of recovery for the light scattering experiments indicate a rather large amount of not molecularly dispersed sample that is seperated from the solution by filtration and the following pre-columns. To adjust the sample preparation for the CaBER experiments to the sample preparation for the light scattering measurements the MHEC solutions were centrifuged and again examined via CaBER measurements. The results are shown in Fig. 10.

In contrast to Fig. 2 the centrifuged samples show the order in breakup times expected

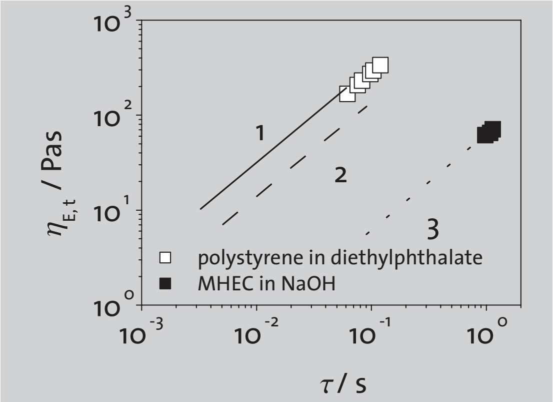


Fig. 11 (above): Comparison of two distinct $\eta_{E,t}/\tau_0$ dependencies for flexible (1) resp. rigid like behaviour (2) according to Stelter et al. to experimental data.

Table 8 (below): Longest relaxation times evaluated according to Eq.7 for the investigated MHECs 1-3.

Polymer	$\tau_{0,M}$ theor. / s
MHEC 1	0.140
MHEC 2	0.136
MHEC 3	0.134

from the distributions determined with light scattering. Sample MHEC 1 with the broadest MWD shows the longest breakup time sample MHEC 3 with the narrowest MWD the shortest breakup 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. 10 via Eq. 3 are listed together with the relaxation times of the non-centrifuged samples in Table 7.

Comparing the breakup behaviour of the molecularly dispersed samples of MHEC to the polystyrene blends one can observe differences in the shape of the curves. Whereas the polystyrene blends show a steady thinning in the semi-log plot of Fig. 4 in accordance with Eq. 4, for late times the MHECs show a sudden increase in the thinning rate and a fast breakup. Stelter et al. [34] showed that the elongational behaviour of polymer solutions differs for ionic resp. non-ionic polymers. The main reason for this is that ionic polymers form more rigid and therefore more expanded polymer coils than non-ionic polymers of the same molar mass. This results in shorter breakup-times because the coils are closer to their finite extensibility. This effect results qualitativly in different shapes of the curves shown in Fig. 2 and Fig. 10 for the rigid MHECs and in Fig. 4 and Fig. 7 for the more flexible polystyrenes. Stelter et al. also showed that this effect quantitativly results in two distinct $\eta_{E,t}/\tau_0$ dependencies for flexible resp. rigid like behaviour where $\eta_{E,t}$ refers to the terminal elongational viscosity that is obtained once the polymer chains have reached their finite extensibility limit [34]. In Fig. 11 the steady terminal elongational viscosity is ploted versus the relaxation times for the investigated polymers. The terminal elongational viscosity $\eta_{E,t}$ has been determined from the general transient elongational viscosity

$$\eta_E = \frac{-\sigma}{dD_{mid}/dt}$$

that has been extrapolated at late times to its time independent limit.

Fig. 11 shows that the polystyrene blends in diethylphthalate correspond well to the behaviour of flexible polymers in extensional flows observed by Stelter et al. (line 1). In comparison to this the MHECs in NaOH show the expected lower values for $\eta_{E,t}/\tau_0$ since they are much more rigid. However, these values do not fit the trend for rigid like behaviour found by Stelter et al. which is diagrammed by line 2 in Fig. 11, but even lower values. Nevertheless a linear trend can be observed for the relaxation times of the MHEC solutions (line 3 in Fig. 11). The shift of the linear trend to higher relaxation times is probably due to higher concentrations used in this work and an even greater expansion due to the ionization by the NaOH. As the concentrations used for the MHEC solutions are relativly high (2 wt%) a structure buildup via hydrogen bonding may be 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.

However, the absolute measured MWDs of the MHECs can be consulted to evaluate the ratio $\tau_0/\tau_{0,M}$ qualitatively according to Eq. 7. With the CaBER relaxation times (see table 7) uniform values for $\tau_{0,M}$ should be the result if Eq. 7 is also valid for the MHECs. The evaluated values for $\tau_{0,M}$ are listed in Table 8 for the MHECs 1-3. As Table 8 shows, the theoretical predicted longest relaxation times for a hypothetical monodisperse MHEC sample are in good agreement with each other. In addition to this the calculated longest relaxation time $\tau_{0,M}$ is in fairly good agreement with the longest relaxation times for shear flow predicted by the modified Carreau model as shown in Fig. 1 and Tab. 2.

4 CONCLUSIONS

The longest relaxation times, τ_0, obtained by CaBER like experiments for defined blends of polystyrene standards with a normal molecular weight distribution can be scaled into an expression that correlates directly with specific moments of the molecular weight distribution. This determined scaling law (see Eq. 7) can be directly assigned to blends of commercially available, blended celluloseethers to obtain information on the MWD of these polymers. In comparison to small amplitude oscillatory shear 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 (see Fig. 8). It could be shown in this paper that uniaxial elongation in CaBER like 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 (see Figs. 1 and 3). Uniaxial elongation in CaBER like experiments also allows for a sensitive detection of non molecularly dispersed fractions of the investigated native cellulose derivative (see Figs. 2 and 9) and can thus predict the processability of these polymers in elongational flows.

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