Abstract

One of the major problems in cellulosic industry is to maintain a constant flow profile of a respective special product, tailored for a decisive application, because cellulose as a biopolymer shows a pronounced variation in its molar mass or its molar mass distribution due to varying growing conditions. To keep the product properties constant, it is common use to blend the raw cellulose, which is to be chemically converted to its final form, from different cellulose pulps. This blending results in a minimisation of the influence of the molar mass or the molar mass distributions (MMD) of the single cellulose pulp. Although this procedure ensures almost constant zero-shear rate viscosities $\eta_0$, interrelations in “real” flow fields are more complex than that. In complex flow fields simple shear is superposed by different kinds of elongational stresses resulting in flow anomalies like filament formation or die swell, therefore elongational viscosities or – stresses are particularly important. As flow phenomena like filament formation are surface tension controlled processes, only the longest modes of relaxation $\tau_0$ of a polymer are excited. Since the longest relaxation time increases with the broadness of the MMD at a constant weight-average molar mass the distribution has to be kept narrow for optimization of the filament formation behaviour. As light scattering methods are very expensive and labour-intensive, the main aim of this work is therefore to examine the possibility of a correlation of the MMD of a polymer with the rheological or better elongational material functions.

The first part of this work is dealing with the rheology of the polymer standard polystyrene dissolved in diethylphthalate (DEP) and styrene oligomere. This already in former works well characterized polymer [1] was consulted to record the possibilities of the relatively new method of capillary break-up with the uniaxial elongational rheometer CaBER in regards of its sensitivity to the molar mass or its distribution, concentration and quality of the solvent.

First of the concentration- and molar mass dependence of the material functions of steady shear flow (shear viscosity $\eta$, longest relaxation time $\tau_0$ and slope of the flow curve $n$), and oscillatory shear ($G'$ and $G''$) were investigated. To quantify the visco-elasticity of the system polystyrene (PS) in diethylphthalate (DEP) the structure-property-relationships of shear flow were established.

\[
\eta_0 - [\eta] - c \\
\eta_0 / (Pa \cdot s) = 1.10 \cdot 10^{-2} \left( c \cdot [\eta] + 0.368 \cdot c \cdot [\eta]^2 + 8.46 \cdot 10^{-3} \cdot c \cdot [\eta]^{4.82} + 1 \right)
\]

\[
\tau_0 - [\eta] - c \\
\tau_0 / s = 1.29 \cdot 10^{-10} \cdot c^{-2.423} \left( (c \cdot [\eta])^2 + 0.368 \cdot (c \cdot [\eta])^3 + 8.46 \cdot 10^{-3} \cdot (c \cdot [\eta])^{3.82} \right)
\]

\[
\eta - n - c \\\n0.82 + 0.65 \cdot 10^{0.079 \cdot [\eta]}
\]

With these structure-property-relationships one is able to describe the complete flow curve of polystyrene in diethylphthalate theoretically as a function of the concentration and the intrinsic viscosity $[\eta]$. To transfer these intrinsic viscosities $[\eta]$ to the weight-average molar mass $M_w$, the Kuhn-Mark-Houwink-Sakurada relationship was established via viscosimetry for this polymer-solvent-system:
\[ [\eta] = 8.23 \cdot 10^{-3} \cdot M_w^{0.702} \text{ [ml/g]} \]

For the same polystyrenes dissolved in DEP the elongational material functions were then determined over a wide range of concentrations in capillary break-up experiments. The transient elongational viscosity \( \eta_E \) reflected the Trouton ratio of uniaxial elongation in the Newtonian flow regime, resulting in trice the value of the zero-shear viscosity \( \eta_0 \) of steady shear. In the non-Newtonian flow regime transient elongational viscosities around a hundredfold the values of \( \eta_0 \) were determined according to the coil-stretch-transition. The longest relaxation times \( \tau_0 \) rose about to orders of magnitude for the different molar masses in the investigated concentration range. As the concentration dependence of the longest relaxation times \( \tau_0 \) of ultradilute solutions was discussed rather controversially in literature recently, polystyrene Boger fluids (polystyrene in styrene oligomer) at very high dilution were also investigated, since at concentrations in the ppm regime no reasonable data could be obtained for the polystyrene solutions in DEP as the relaxation processes were not detectable anymore in capillary break-up. It could be shown that the relaxation times \( \tau_0 \) show even below the most conservative definition of the critical concentration \( c^* \) a strong decrease with a decreasing concentration. This decrease of relaxation times ends below a concentration \( c^\$ \): 

\[
c^\$ < \frac{\nu}{2 \frac{1}{[\eta]} E^2 \zeta (3 \nu)}
\]

This is the lowest concentration for an observable polymer contribution to a capillary break-up experiment. It could be shown in contrast to the current interpretation, that below this concentration the longest relaxation times \( \tau_0 \) are equal to the Zimm relaxation times \( \tau_z \) and do not fall below that theoretical value.

To analyse the influence of the MMD in order to describe the longest relaxation time of the polymers in uniaxial elongation via integral mean values of the molar mass distribution, defined polystyrene blends in diethylphthalate were then prepared. This was done in a fashion that the weight-average molar masses \( M_w \) were kept constant at 5.8 Mg/mol with different MMDs varying in its polydispersity indices \( M_w/M_n \) from approx. 1.0 to 1.84. Whereas the methods steady shear flow and oscillatory shear were not able to detect these differences in the MMD even qualitatively, uniaxial elongation in capillary break-up yielded different longest relaxation times \( \tau_0 \) for the investigated blends. These longest relaxation times, reduced by the relaxation times of the mono disperse sample could be scaled via the \( z+2 \)-average and the weight-average molar mass:

\[
\frac{\tau_0}{\tau_{0,M}} = \left( \frac{M_{z+2}}{M_w} \right)^{1.22}
\]

The second part of this work is dealing with the rheology of the cellulosic derivatives methylhydroxyethyl cellulose (MHEC) and hydrophobically modified hydroxyethyl cellulose (hmHEC). These two hydrocolloids were also characterized rheologically in regards to the influence of the MMD on the flow behaviour.

As for the polystyrenes, first of all the concentration- and molar mass dependence of the material functions of steady shear flow and oscillatory shear were quantified in the solvents water and aqueous 2 wt\% sodium hydroxide. As the investigated MHEC samples were blended from different cellulose pulps, the influence of the MMD had to be clarified. Again only uniaxial elongation proved to be the right tool to correlate the rheological
behaviour in terms of the determined longest relaxation times $\tau_0$. It could be shown that the scaling law determined for the polystyrene blends could be directly assigned to the here investigated commercially available, blended cellulose ethers.

The results of uniaxial elongation could then be correlated directly with the absolute molar mass distributions obtained via means of SEC/MALLS/DRI (size-exclusion-chromatography, multi-angle laser light scattering and differential refractometer).

In addition to this, uniaxial elongation in capillary break-up proved to be a method allowing for a very sensitive detection of non molecularly dispersed fractions of the investigated native cellulosic derivatives (MHEC and hmHEC), because the non centrifuged sample solutions (even though they mostly appeared optically transparent) showed pronounced longer break-up times than the uncentrifuged ones.