12th Fall Rubber Colloquium

EVALUATION OF NONLINEAR DIFFERENTIAL MODELS FOR THE SIMULATION OF POLYMER MELTS

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Introduction and motivation

The goal of this work is to evaluate conceptual difficulties if differential equations based on the Upper Convected derivative (UCD) are used for the description of rubber melts with high relaxation times. To achieve this, three commercial polymers were investigated which cover all kinds of principle nonlinear dynamic behaviour: two polybutadien types (BR linear ARLANXEO BUNA CB22, BR highly branched CB1220) and one hydrogenated nitrile type (HNBR) of lower viscosity (ARLANXEO THERBAN 3404). All polymers provide nonlinear shear behaviour, i.e. shear thinning, where TH3404 is introduced to include a lower Mooney polymer providing smaller and thus more modelling friendly relaxation times. CB1220 and TH3404 show pronounced strain hardening where CB22 remains linear under uniaxial load.

The differential model regarded is the Giesekus constitutive equation

$$\frac{\partial \mathbf{T}_p}{\partial t} + (\mathbf{u}\cdot\nabla)\,\mathbf{T}_p - \mathbf{T}_p\cdot\nabla\mathbf{u} - \nabla\mathbf{u}^\top\cdot\mathbf{T}_p + \frac{1}{\Lambda}\mathbf{T}_p + \frac{\alpha}{\eta_p}\mathbf{T}_p\cdot\mathbf{T}_p \;=\; 2\frac{\eta_p}{\Lambda}\mathbf{D} \qquad (1)$$

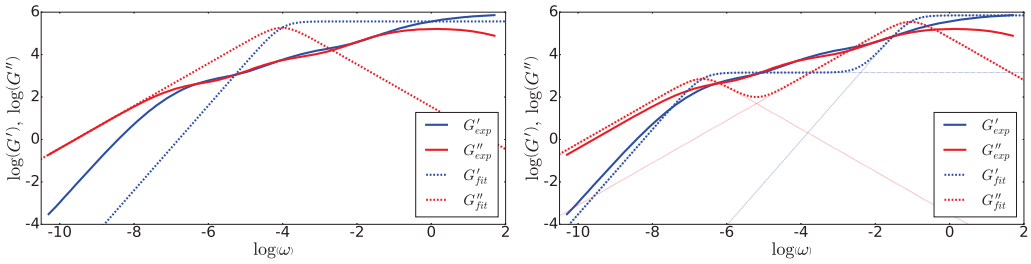
for the elastic stress tensor $\mathbf{T}_p$ (c.f. [5]), where Λ denotes the relaxation time of the fluid, $\alpha \in [0,1]$ the mobility factor and η_p the "polymer" viscosity. For the following evaluation, this model is chosen because it is able to predict both, shear thinning as well as elongational hardening. At the same time it is one of the most commonly used models to simulate the material behaviour of polymer melts. Additionally, the so-called multi-mode approach is applied, in which the extra stress tensor is regarded as a sum of $K > 1$ single stress tensors, i.e. $\mathbf{T}_p = \sum_{k=1}^{K} \mathbf{T}_{p,k}$, each satisfying a separate constitutive equation of the form (1) containing independent parameters Λ_k and $\eta_{p,k}$. Hence, in principle the Giesekus model – as well as most of the other differential models using UCD – is able to reproduce the nonlinear dynamic effects mentioned above.

This in turn induces the central questions tackled in the following: Basically, the capability of the differential constitutive equation (1) is evaluated with regard to the description of the experimentally determined linear and nonlinear behaviour of standard rheological flow quantities like storage and loss modulus or shear and elongational viscosity. At the same time it is investigated, if consideration of $K > 1$ modes in the extra stress tensor leads to an improvement of the previously achieved results. It turns out, that the modelling quality is very poor wherefore

the reasons will be traced back to principle problems of the approach. On the other hand, the considerations are extended to the comparison of experimental results (pressure drop in a slit die) with the data of finite element (FE) simulations. The analysis shows that the high relaxation times of rubber melts not only lead to a non-sufficient description of standard rheometry flows, but also make a simulation of "real" elastic flows almost impossible.

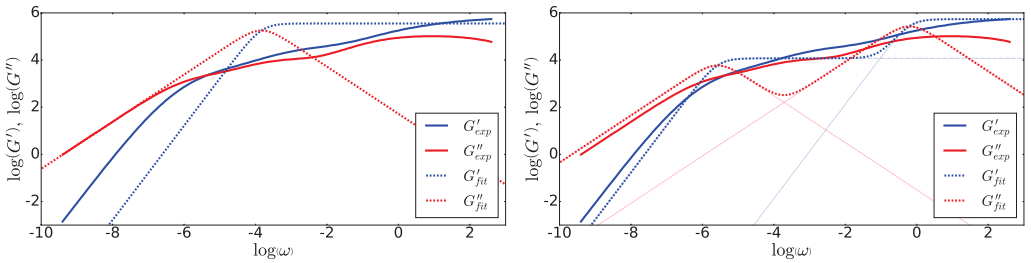
Analysis of modelling behaviour

One essential step of the modelling procedure is the determination of the material parameters provided by the models. Firstly this means to determine the linear viscoelastic dynamic behaviour, here in terms of Prony series parameters, by considering small oscillatory shear tests. Furthermore, the model parameters governing the nonlinear material behaviour provided by uniaxial and shear strain tests at higher deformation rates have to be fixed.



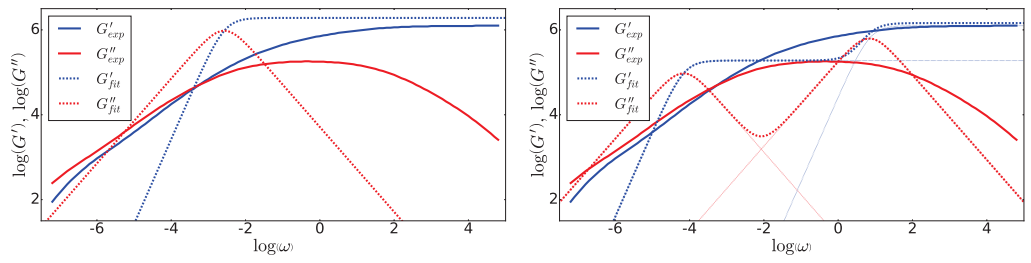
(a) CB22, $K = 1$

(b) CB22, $K = 2$



(c) CB1220, $K = 1$

(d) CB1220, $K = 2$



(e) TH3404, $K = 1$

(f) TH3404, $K = 2$

Figure 1: measured and calculated (Prony series with $K \in \{1, 2\}$ elements) storage and loss moduli

The parameter of the dynamic moduli identification is provided by minimizing the logarithmic deviation with respect to logarithmic equidistant spread frequencies. In all cases the fit range

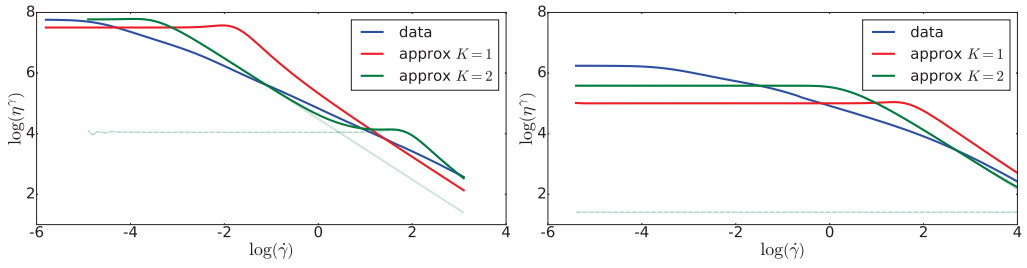
was chosen to cover the processing relevant regions from the flow regime up to the rubber plateau. The analysis shows, that the approximation quality is in the same range for all polymers and obviously improving when the number of modes is increased. Nevertheless, due to the wide range of relaxation times, even the use of two modes[1] provides a non-sufficient representation of the experimental data (c.f. table 1 and figure 1).

material	$K=1$			$K=2$		
	overall	G'	G''	overall	G'	G''
CB22	354.91	179.75	175.16	112.11	48.27	63.84
CB1220	332.28	139.10	193.17	112.15	42.88	69.27
TH3404	336.77	134.21	202.55	137.13	60.49	76.65

Table 1: deviation of calculated and experimental data

On the basis of the determined parameters Λ_k and G_k for $k \in \{1,2\}$, the viscosities are calculated by $\eta_{p,k} = \Lambda_k G_k$. In the following, these parameters are used to determine the mobility factors $\alpha_k \in [0,1]$ appearing in the Giesekus constitutive equation (1). Due to experimental reasons, the asymptotic shear viscosity $\eta^{\gamma}(\dot{\gamma})$ and the transient strain viscosity $\eta^{\varepsilon}(t,\dot{\gamma})$ were used for the procedure of the Giesekus parameters α^{ε} and α^{γ}. The latter saves an additional fit step since the transient viscosity function is analytically given in the Giesekus model (c.f. [4]). The individually determined mobility parameters are weighted equally to obtain the final value for α_k. In case of the linear polymer (i.e. no strain hardening), the transient strain viscosity is completely determined by the master curve. Because Giesekus models strain hardening for all α in the parameter range, the mobility parameters for this specific polymer were determined from the shear data only.

To check the influence of the temperature, the considerations were done at room temperature and at a typical processing temperature ($T = 140\,°C$).



(a) CB1220 (b) TH3404

Figure 2: shear viscosities at $T = 140\,°C$

Considering approximations of shear thinning data, as expected a more or less accurate reproduction is established by the Giesekus model for all materials which is no particular surprise

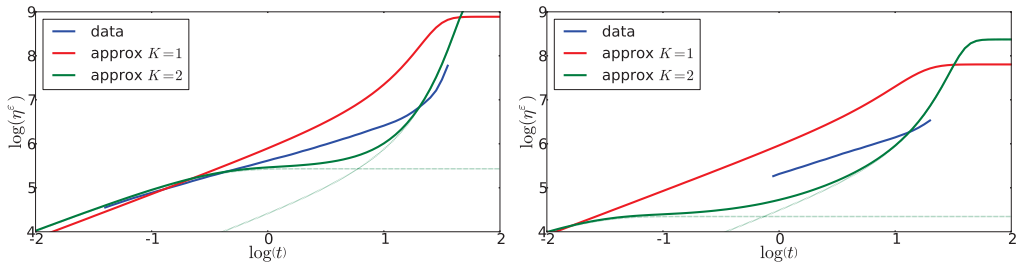
[1] An increase of the number of relaxation modes will evidently improve the approximation quality significantly. But FE simulations using three or more modes currently require inacceptable simulation times and costs and is thus not needed for this paricular investigation.

from a general modelling perspective. CB1220 and TH3404 indicate the typical behaviour: increase of the number of modes increases the approximation quality (c.f. figure 2(a) and table 2). But similar to the inadequate approximation of the linear modulus data due to the small mode number of Prony series, the modeled behaviour deviates from the measured data in a well-known oscillation-like way, the latter due to the singular (i.e. very small) Maxwell relaxation processes used for the Prony series.

	K	CB22	CB1220	TH3404
η^{ε}	1	-	27.86	27.29
	2	-	11.75	28.61
η^{γ}	1	57.12	44.28	64.13
	2	22.20	21.81	32.08

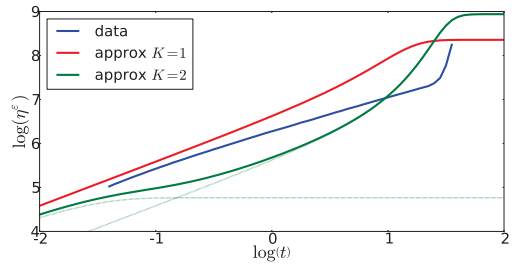
Table 2: deviation of experimental and calculated data at $T = 140\,°C$

Briefly speaking, modelling of shear thinning of polymers showing a broad transition into the flow regime (e.g. rubber melts) by use of a few singular relaxation modes leads to an in principle correct description with typical, spurious deviations. The approximation quality usually is inferior to those of generalized Newtonian models where the latter – of course – are of phenomenological nature and not part of a full modelling approach for nonlinear behaviour. The latter is the case for Giesekus since it provides the potential for the description of strain hardening. This will be briefly discussed in the following.

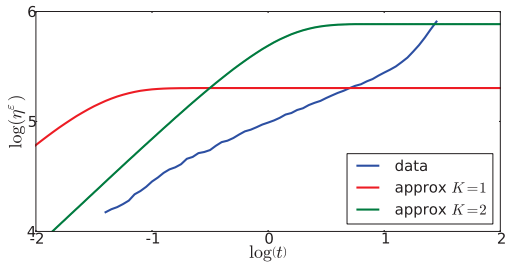


(a) CB1220, $T = 23\,°C$

(b) CB1220, $T = 140\,°C$, $\log(\dot{\varepsilon}) = -2$



(c) TH3404, $T = 23\,°C$



(d) TH3404, $T = 140\,°C$

Figure 3: elongational viscosities for Hencky strain rate $\dot{\varepsilon} = 0.01$

Figures 3 exemplarily show the transient viscosity of the strain hardening polymers (CB1220, TH3404) for the strain rate $\dot{\varepsilon} = 0.01$ and two temperatures. The mobility factors α_k were

determined by an averaging procedure over an optimized approximation of five different strain rates (from 0.001 to 10 1/s). For $\alpha > 0$ finite asymptotic strain viscosity is modeled (which is obviously necessary from the physical point of view, but was never observed in a transient strain experiment). The approximation quality is not only very poor (see table 2), but also principally wrong especially regarding the onset of strain hardening.

This points at a principle shortcoming of the Giesekus approach: strain hardening is modeled if the rate of deformation is greater than the reciprocal of the maximum relaxation time. Furthermore, the onset of strain hardening is quasi fixed by the relaxation times determined by linear viscoelasticity. Thus the deviations observed are of rather principle nature. This might be underlined by the fact that the high relaxation time of CB22, showing completely linear strain behaviour (at the rates considered), can not be described at all because the Giesekus model predicts strain hardening in all cases. CB22 is thus not further analyzed regarding its strain behaviour.

In the following section it will be discussed how the insufficient modelling of basic rheometric flows will influence the simulations of a step-slit die flow.

Simulation of a step-slit die flow

To simulate a polymer flow in a die the constitutive equation (1) is coupled with the well-known Stokes equations. The considered step-slit die, which was inserted into a high pressure capillary rheometer (Göttfert Rheotester 2000), is of length $100.2\mathrm{mm}$ and possesses a contraction from heigth $1\mathrm{mm}$ to $0.25\mathrm{mm}$ realized by two quadrants with radius $0.3\mathrm{mm}$. By assuming a die of infinite width where transverse effects are neglected, two-dimensional simulations are applied which will still provide a sufficient approximation quality of the actual slit geometry (1:10). The resulting pressure drops are compared to the measured values (4 points, see figure 4).

The simulations use the parameters previously determined by the basic flow experiments. Unfortunately, due to the "High Weissenberg Number Problem" (HWNP, c.f. [3]), not every set $(\Lambda, \eta_p, \alpha)$ of determined parameters can be applied in simulations. This problem arises from numerical reasons, because for high relaxation times Λ, being proportional to the so-called "Weissenberg Number" We, large gradients occur in the flow variables and cause a breakdown of the simulations. So it turns out that TH3404 with its relatively small relaxation times at $T = 140℃$ provides the only parameter set accessible for a numeric simulation. Thus, the parameter set used was

$$\Lambda^{\mathsf{sim}} = 0.0269, \quad \eta^{\mathsf{sim}} = 51.2861, \quad \alpha = 0.745$$

in case of $K = 1$ and

$$\Lambda_1^{\mathsf{sim}} = 1.0471,\ \eta_1^{\mathsf{sim}} = 199.5262,\ \alpha_1 = 0.745,\ \ \Lambda_2^{\mathsf{sim}} = 1.05e-5,\ \eta_2^{\mathsf{sim}} = 0.0129,\ \alpha_2 = 0.485$$

for $K = 2$ (with units: $[\Lambda] = 1\mathrm{s}$ and $[\eta] = [\Lambda][G] = 1\frac{\mathrm{kg}}{\mathrm{mm \cdot s}}$). Additionally, the density of the melt takes the value $\rho = 0.91 \cdot 10^{-6}\frac{\mathrm{kg}}{\mathrm{mm}^3}$.

The numerical simulations – resulting in the pressure drops listed in table 3 – are realized within the software package FEATFLOW using the corresponding numerical method presented in [2]. Notice, that the calculated pressure drops are taken from steady-state simulations.

Figure 4: points of measurement in the die

data	K	$\Delta p_1 = p(x_2) - p(x_1)$	$\Delta p_2 = p(x_3) - p(x_2)$	$\Delta p_3 = p(x_4) - p(x_3)$
sim	1	2.256	60.614	118.372
	2	8.420	205.711	350.697
exp		111.847	260.853	397.747

Table 3: pressure drops in bar

If only one mode is used in the modelling approach, the simulated pressure drops do not match the experimental data at all. The value with minimal deviation is obtained for Δp_3, where the pressure drops take roughly the same magnitude. But still, the approximation does not show an acceptable quality. The experimental data is reproduced in a superior way if two modes are considered. Beside the third pressure drop, in this case also the pressure drop between x_2 and x_3 shows a good accordance. In either case, the results for Δp_1 show a huge discrepancy to the experimental data, probably due to inappropriate boundary conditions applied at the inflow.

On the basis of the pressure drops listed in table 3, the same observations can be made as in the previous section. The quality of the approximations is improved if $K = 2$ is chosen instead of $K = 1$, because in this case the pressure drops Δp_2 and Δp_3 show a higher accordance to the experimental values. At a first glance, the simulation results seem to be acceptable but it has to be emphasized, that the generation of those only worked for the low relaxation time case at high temperatures. In all other cases the simulations broke down (it should be mentioned that an experimental realization was possible at finite pressure drops)! And as in the case of the rheometry flows, the simulation strategies stumble over the high relaxation times.

Conclusion

Approximations of nonlinear dynamic materials by differential models based on a multi-mode approach in combination with an Upper Convected time derivative seem to be not adequate for the description of rubber melt flows. This is mainly due to the fact that the (usually high) relaxation times, determined by the linear visoelastic behaviour, fix even the nonlinear behavior in terms of onsetting strain hardening and spurious shear oscillations. This is the case for the Giesekus model considered, being the most popular approach for modelling rubber, but also holds for other differential models using relaxation modes and UCD (like PTT or White-Metzner, c.f. [6], [7]). It should be emphasized that the preceding statements hold for long chain polymer

melts like rubber. In contrast, differential modelling approaches are very successfully applied for the description of nonlinear thermoplastic flows. An alternative strategy may be provided by constitutive equations of integral type as e.g. mentioned in [1]. The basic ideas will be shortly outlined in the following.

The proposed so-called "Deformation fields method" (DFM) considers a system of equations of the form

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho\left(\mathbf{u}\cdot\nabla\right)\mathbf{u} = -\nabla p + \eta_s\Delta\mathbf{u} + \nabla\cdot\boldsymbol{\tau} \tag{2a}$$

$$\nabla\cdot\mathbf{u} = 0 \tag{2b}$$

$$\frac{\partial \mathbf{B}}{\partial t} + \left(\mathbf{u}\cdot\nabla\right)\mathbf{B} - \nabla\mathbf{u}\cdot\mathbf{B} - \mathbf{B}\cdot\nabla\mathbf{u}^{\top} = \mathbf{0} \tag{2c}$$

$$\boldsymbol{\tau} = \int_{-\infty}^{t} M\left(t-t'\right) f\left(\mathbf{B}\left(t,t'\right)\right)\,\mathrm{d}t', \tag{2d}$$

in which the extra stress tensor $\boldsymbol{\tau}$ is expressed by an integral formulation containing a memory function M, which decays with time, and a function f of the Finger tensor $\mathbf{B}$. A specification of these functions leads to well-known models like Kaye-BKZ or DOI-Edwards. One principal advantage of these integral constitutive equations is the possibility to flexibly incorporate a continuous relaxation spectrum. The preceding discussion suggests that this might provide significant advantages over the restrictions of a differential approach. But at present integral models have not been analyzed well-grounded from a numerical point of view. This is necessary because the memory term in (2d) gives rise to difficulties, e.g. due to the infinite length of the integration interval which would require huge storage capacities. Thus a detailed analysis of such time-deformation factoring integral approaches containing non-singular memory functions will be subject of further works.

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