Prediction of the non-linear rheological properties of polymer solutions by means of the Rouse-Zimm model with slippage

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Abstract: The non-affine deformation of macromolecules and the slippage function are discussed. In case of polymer solutions with moderate concentration the slippage function is determined by means of the Cox-Merz rule. The non-linear viscoelasticity of these solutions is described with the aid of the Rouse-Zimm model with slippage function. The theoretical predictions show good agreement with published experimental data.

Key words: Slippage; Rouse-Zimm model; polymer solution; Cox-Merz rule; non-linear viscoelasticity

1. The rheological model with slippage function

Many constitutive equations have been presented to treat non-linear viscoelasticity of polymer fluids. A famous equation arose from the Rouse-Zimm model to deal with dilute polymer solutions [1]:

\[ T = \sum_{p=1}^{N} T_p, \]

\[ T_p + \tau_p \left[ \frac{D}{Dt} T_p - (\nabla v)^T \cdot T_p - T_p \cdot \nabla v \right] = n k T I , \]

where \( T \) is the extra stress tensor due to polymer molecules added into the solvent, \( T_p \) is the contribution to \( T \) by the \( p \)th motion mode of the Rouse molecular chain; the \( \tau_p \) are the relaxation times, which are given by a material time \( \tau_0 \), a measure of hydrodynamic interaction and the number of modes (segments) \( N \); \( \nabla v \) is the measurable velocity gradient of solution, \( n \) is the number concentration, \( k \) is the Boltzmann constant, \( T \) is absolute temperature, \( I \) is the unit tensor, and \( D/Dt \) is the material derivative.

The equivalent material integral constitutive equation is

\[ T(x, t) = \int_{-\infty}^{t} \int \mu(t-t') \left[ \mathbf{C}^{-1}(x,t,t') \right] dt' \]  

(3)

where

\[ \mu(t-t') = nkT \sum_{p=1}^{N} \frac{e^{-(t-t')/\tau_p}}{\tau_p} \]

(4)

is the memory function and \( \mathbf{C}^{-1} \) is the Finger tensor.

The equation above expands the linear viscoelasticity theory of polymers. But as to the typical non-linearity of shear-thinning and stress-overshoot, no qualitative explanation is possible; therefore the physical meaning of each assumption in the theory has to be rechecked.

One of the examinations lays emphasis on non-affine deformation. Johnson and Segalman pointed out that, assuming that macro and micro strain fields do not conform to each other and that non-affinity is described by a slippage factor \( a \), the forecasting ability of theory will be appreciably improved. The relationship given by them is [2]

\[ \nabla v^* = \frac{a+1}{2} \nabla v + \frac{a-1}{2} \nabla v^T , \]

(5)

where \( \nabla v^* \) has to be used in relation (2) instead of \( \nabla v \).

Xu and Schümm [3] considered that, with regard to a higher shear rate, the strong deformation of the
polymer coil in solution will disturb the velocity gradient field of solvent, leading to kinematic slipping in the related macroscopic homogeneous continuum. This slipping is a function of the deformation rate tensor $D$:

$$\nabla v^* = \nabla v - (1 - a) \cdot D \quad \text{with} \quad a \to 1 \quad \text{for} \quad D \to 0 .$$

From invariance of the state equation, Schütz and Otten [4] derived a slippage function, which is expressed as

$$\nabla v^* = \nabla v - f(D) ,$$

$$f(D) = \alpha' D + \Pi D \cdot \alpha' \cdot (D^2 + \frac{2}{3} \Pi D) ,$$

where $\Pi$ and $\Pi D$ are the second and third invariants of $D$, respectively, and $\alpha = \alpha(\Pi)$ and $\alpha' = \alpha'(\Pi D)$ are scalar slippage functions which have to be determined.

Although the functions mentioned above are in different forms, they have the same relationships in viscometric flow:

$$D^* = a(\nabla v) D ,$$

$$W^* = W .$$

Namely, the antisymmetric parts ($W$) of the velocity gradient tensors are equal (co-rotational), thus “slipping” occurs in the deformation rate tensors $D^*$ and $D$. Here, $a(\nabla v)$ is a slippage function in dependence on macro velocity gradient.

Based on this, the differential constitutive equation can be rewritten as

$$T_p + \tau_p \dot{T}_p = n k T I ,$$

where

$$\dot{T}_p = \frac{D}{D t} T_p - (\nabla v)^T \cdot T_p - T_p \cdot \nabla v$$

is the contravariant convected derivative of $T_p$ and

$$\dot{T}_p = \frac{D}{D t} T_p - (\nabla v)^T \cdot T_p - T_p \cdot \nabla v$$

is the contravariant convected derivative of $T_p$. The equivalent integral constitutive equation is [4]

$$T(x, t) = \int_{-\infty}^{t} \mu(t - t') [(C^*)^{-1}(t, t')] dt' ,$$

where the memory function is identical to the previous one; it does not depend on “slipping”. $(C^*)^{-1}(t, t')$ is called generalized Finger tensor, which is defined as

$$(C^*)^{-1}(t, t') = E^*(t, t') \cdot [E^*(t, t')]^T .$$

$E^*(t, t')$ can be obtained by solving the initial value problem below:

$$D \frac{D}{D t'} E^*(t, t') = -E^*(t, t') \cdot (\nabla v^*)^T$$

$$E^*(t, t) = I .$$

The advantage of the new constitutive equation does not only consist in qualitatively explaining phenomena of shear-thinning, stress-overshoot, and existence of the second normal stress difference, but also in quantitatively dealing with non-linear viscoelasticity of polymers by determining the slippage function. Its physical meaning is clearer than introducing a strain-dependent memory function.

A similar approach has been developed by Tschoegel et al. [5] and Doi-Edwards [6] who proposed single-integral equations of state comparable with Eq. (13). There are several theoretical concepts for closing the problem, i.e., by determining the slippage function. A widely used empirical rule, the Cox-Merz rule, is applied to the definition of slippage function for some polymer solutions with moderate concentration; it also deals with the concept of non-affine deformation and slippage function.

2. Theoretical calculation of slippage function

Equation (13) is taken as the basic state equation and memory function assumes the form as in the usual Rouse-Zimm model:

$$\mu_p(t - t') = \frac{n k T}{\tau_p} e^{-(t - t')/\tau_p} .$$

$N$ motion modes are superposed and partially integrated, resulting in

$$T = 2 n k T \int_{-\infty}^{t} \sum_{p=1}^{N} e^{-(t - t')/\tau_p}$$

$$\times E^* \cdot D^* \cdot (E^*)^T dt' + n k T N I .$$