VISCOELASTIC CONSTITUTIVE EQUATIONS IN MODELING OF POLYMER PROCESSING

(Aplikace viskoelastických konstitučních rovnic při modelování polymerních procesů)

Short version of PhD thesis

by

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ABSTRACT

This PhD thesis overview concentrates on the description and applications of the most realistic constitutive equations (CEs) for polymer melts, which can be used in complicated non-isothermal modeling with an aim to correlate calculated and experimental data, as well as to explain flow phenomena still not understood. For this purpose, equations of fluid dynamic, including realistic CEs, are solved through finite element method (FEM).

A simple method is presented for the estimation of the linear viscoelastic relaxation spectrum from capillary steady shear and extensional viscosities data. For this aim a modified Leonov model is employed, and the spectra and model parameters are calculated through non-linear regression.

Specific attention is paid to the interfacial instability phenomenon in coextrusion flows. Both, the distribution of polymer melt stream from the extruder into an annular flow channel within flat spiral distribution system and merging area at which coextruded materials combine first time have been investigated.

The flow in a flat spiral distribution system, used mainly in the ‘stacked’ type of annular coextrusion dies, has been investigated through 3D FEM non-isothermal viscoelastic simulation. It was revealed that for a particular flat spiral die, viscous dissipation is extremely important and it may lead to generation of hot spots and to increased flow variation.

The coextrusion flow in the merging area has been investigated through 2D FEM non-isothermal viscoelastic simulation. The results indicate that the wave instabilities are related to varying amounts of material stretching across the interface. It has been found that a heuristic criterion based on the difference of the first normal stress differences across the layer interface may be used to detect a potential onset of interfacial instabilities. These instabilities are strongly influenced by both the die geometry and elongational strain hardening.

Keywords: constitutive equations, relaxation spectra, interfacial instabilities, coextrusion flow, viscoelastic stress calculation, extensional viscosity, FEM simulation, flat spiral die.
LIST OF PAPERS

This dissertation includes the following papers, referred to by Roman numerals:

I  “Computation of the Linear Viscoelastic Relaxation Spectrum from Capillary Viscosity Data”
   M. Zatloukal, C. Tzoganakis, J. Vlček, T. Dobbie
   accepted for publication in Advances in Polymer Technology

II “Numerical Simulations of Polymer Flows in Flat Spiral Dies”
   M. Zatloukal, C. Tzoganakis, J. Perdikoulias, P. Sáha
   submitted for publication to Polymer Engineering and Science

   M. Zatloukal, C. Tzoganakis, J. Vlček, P. Sáha
   submitted for publication to International Polymer Processing

IV “Transient Viscoelastic Stress Calculation in Multi-Layer Coextrusion Dies: Die Design and Extensional Viscosity Effects on the Onset of ‘Wave’ Interfacial Instabilities”
   M. Zatloukal, J. Vlček, C. Tzoganakis, P. Sáha
   submitted for publication to International Polymer Processing

This short version of PhD thesis only gives overview of the particular problems, solution methods and conclusions. For more details, the reader is referred to the full version of the thesis [1].
THEORETICAL BACKGROUND AND RESEARCH RESULTS

1 EQUATIONS OF FLUID DYNAMICS

For all materials, the density, $\rho$, depends on the local thermodynamic state variables, such as pressure, temperature, and composition. However, for liquids it is often a very good assumption to take the density to be constant. Such an idealized fluid is often called an ‘incompressible fluid’. Polymer melts are considered to be incompressible and their motion in general is described by the equations of conservation of mass, momentum, and energy [2]:

Continuity: $$(\nabla \cdot \mathbf{v}) = 0 \quad \text{or} \quad \frac{D}{Dt}\rho = 0 \quad (1.1)$$

Motion: $$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \mathbf{\sigma} + \rho g \quad (1.2)$$

Energy: $$\rho C_p \frac{DT}{Dt} = k \nabla^2 T + \mathbf{\sigma} : \nabla \mathbf{v} \quad (1.3)$$

The equation of continuity (in the second form given here) states that as one follows along with the fluid, the density does not change with time.

The equation of motion expresses the fact that the mass-times-acceleration of a fluid element equals the sum of the pressure, stress, and gravitational forces acting on the element. Paper III [3] and Paper IV [4] show how the knowledge of the stresses in the fluid can be used to potentially detect the onset of flow instabilities and their suppression.

The energy equation states that the temperature of a fluid element changes as it moves along with the fluid because of heat conduction (the $k$-term) and heat production by friction generation. The importance of heat dissipation for polymer melts flow in a complicated 3D die geometry is discussed in Paper II [5].
2 CONSTITUTIVE EQUATIONS

Constitutive equations (CEs) are mathematical relationships that allow to calculate the stress, $\mathbf{\sigma}$, in a liquid with a given flow history. They are derived from different assumptions and idealizations about mechanisms that produce stress. In general, CEs can be sorted into two groups according to their form - differential or integral.

2.1 Integral CEs – Kaye-BKZ Class of Equations

Integral CEs give the stress tensor as the integral of all stress contributions from the remote past, $t'=-\infty$, to the present time, $t$. In this group the Kaye-BKZ class of equations is most popular. This class is motivated by the ideas of rubber elasticity theory. In the Kaye-BKZ equation for viscoelastic fluids, elastic potential, $W$, and stress, $\mathbf{\tau}$, are allowed to relax. $W$ therefore depends on the history of the first and second invariants ($I_1$ and $I_2$) of the Finger tensor, $C$. Under an empirical assumption that $W$ is a history integral over a function of $I_1$, $I_2$, and $t - t'$, it can be expressed as

$$W = \int_{-\infty}^{t} u(I_1, I_2, t - t') dt' \quad (2.1.1)$$

The corresponding stress tensor is

$$\mathbf{\tau} = \int_{-\infty}^{t} \left[ 2 \frac{\partial u}{\partial I_1} C^{-1}(t, t') - 2 \frac{\partial u}{\partial I_2} C^{-1}(t, t') \right] dt' \quad (2.1.2)$$

The above given Kaye-BKZ constitutive equation must be taken as a class of equations because it describes a great variety of behaviors, depending on the choice of the kernel, $u(I_1, I_2, t - t')$. A specific CE of the Kaye-BKZ class can be obtained by choosing a specific form for $u(I_1, I_2, t - t')$ with several nonlinear parameters. If sets of nonlinear stress data are available, they allow determining of $\frac{\partial u}{\partial I_1}$ and $\frac{\partial u}{\partial I_2}$, from which one must calculate $u(I_1, I_2, t - t')$. After this procedure, Eq. (2.1.2) can be used for stress calculation. Further details about Kaye-BKZ CEs can be found in the literature [2, 6].

Although it has been found that the particular Kaye-BKZ CEs are very good for the description of the rheological behavior of the fluid, these models have big disadvantages for their application in numerical simulations: it is necessary to calculate stresses in every node of the flow domain. Since the integral models require integrating over the history of the particle, one has to find a trajectory of the particle flowing through the node, and perform the integration. Such a trajectory must be determined for every node. This makes the requirement on the computer time very high. From this point of view, our attention is more focused on differential CEs, which can be used in numerical simulation in an easier way. The reason is that in every node of the flow domain where the stress is to be calculated, only a set of differential equations for this node is solved. This does not load the computation so heavily and these models can be reasonably used for simulations.
2.2 Differential CEs – Leonov Model

Differential CEs give the present stress as the solution of a particular set of differential equations. Although in the literature a number of CEs can be found, for our purposes we have chosen a modified Leonov model. There are two main reasons for choosing this model: firstly, it properly describes the viscoelastic behavior, as was shown by fitting experimental data [7], and secondly, the model exhibits mathematical stability [8].

The Leonov model employs both relaxation spectrum and adjustable parameters. In principle, the relaxation spectrum may be determined from a number of experimentally measurable linear viscoelastic properties [9], however, most often employed are storage ($G'$) and loss ($G''$) moduli obtained from oscillatory shear experiments. The adjustable parameters controlling highly non-linear behavior, on the other hand, may only be determined from measurable non-linear viscoelastic properties in extensional and shear flows. In Paper I [10] we show that the knowledge of these non-linear properties can be used not only for calculation of the adjustable model parameters but also for extracting the linear viscoelastic relaxation spectrum.

The Leonov constitutive equation is derived from a thermodynamic rather than molecular approach [7, 11-14]. Leonov’s approach is to relate the stress tensor to the elastic strain stored in the material. Mathematically it means relating the stress and elastic strain defined as

$$\tau = 2 \sum_{i=1}^{N} \left( \frac{C_i \partial W_i}{\partial I_{1,i}} - C_i^{-1} \frac{\partial W_i}{\partial I_{2,i}} \right)$$  \hspace{1cm} (2.2.1)

where $W_i$, the elastic potential, depends on the invariants of the Finger strain tensor, $C_i$, here $I_{1,i}$ and $I_{2,i}$. The elastic potential $W_i$ is defined as

$$W_i = \frac{3}{2} G_i \left(1 - \beta \right) \left[ \left(\frac{I_{1,i}}{3}\right)^{n+1} - 1 \right] + \beta \left[ \left(\frac{I_{2,i}}{3}\right)^{n+1} - 1 \right]$$  \hspace{1cm} (2.2.2)

where $G_i$ is the linear Hookean elastic modulus, and $\beta$ and $n$ are numerical parameters. Equation (2.2.2) yields the Mooney potential for $n=0$, and the neo-Hookean potential for $n=\beta=0$.

Leonov assumed that dissipative processes act to produce an internal or irreversible rate of strain, $e_{pi}$, which spontaneously reduces the rate of accumulation of elastic strain.

$$\varepsilon_{pi,j} = \frac{1}{4 \cdot \theta} \left[ b_{1,i} \left[ C_i - \left( \frac{I_{1,i}}{3} \right) \delta_i \right] - b_{2,i} \left[ C_i^{-1} - \left( \frac{I_{2,i}}{3} \right) \delta_i \right] \right]$$  \hspace{1cm} (2.2.3)

Relating the elastic strain and the deformation history gives the equation

$$\frac{\partial}{\partial t} C_i + 2 \cdot C_i \cdot \varepsilon_{pi,j} = 0$$  \hspace{1cm} (2.2.4)

where $\frac{\partial}{\partial t} C_i$ is the upper convected time derivative of the Finger tensor. The simplest choice is to let $b_{1,i}=b_{2,i}=1$. This is known as the standard ‘Leonov model’. Henceforth, we shall refer to the CE with $b_{1,i}=b_{2,i}=1$ and the neo-Hookean potential as a ‘simple’ model. While this simple choice assures the proper linear viscoelastic limit, and can also be expected to describe weak nonlinearities, it may not suffice for the description of highly nonlinear phenomena. These phenomena can be described if other formulas for $b_{1,i}$ and $b_{2,i}$ are chosen. Some of them are as follows:

$$b = b_{1,i} = b_{2,i}$$  \hspace{1cm} (2.2.5)

$$b = \left( \frac{I_{2,i}}{I_{1,i}} \right)^m$$  \hspace{1cm} (2.2.6)

$$b = \exp \left[ -m \left( I_{1,i} + I_{2,i} - 6 \right) \right]$$  \hspace{1cm} (2.2.7)

$$b = (1-n) \left( \frac{I_{2,i}}{I_{1,i}} \right)^m + n \cdot \exp \left[ m \left( \frac{I_{1,i}}{I_{2,i}} - 1 \right) \right]$$  \hspace{1cm} (2.2.8)
In these equations \( m \) and \( n \) are adjustable parameters. Applications of these equations for \( b \) in the Leonov model are discussed by Simhambhatla and Leonov \cite{Simhambhatla1995} in \cite{Leonov1991}. Larson \cite{Larson1997}, on the other hand, has proposed the following relationship

\[
b = \left[ 1 + \frac{2 \cdot \vartheta}{\pi} \cdot \arctan \left( \frac{W_{si}}{10 \cdot G_i} \right) \right]^{-1} \tag{2.2.9}
\]

where \( \vartheta \) is an adjustable parameter, and \( W_{si} \) is a symmetrized form of the neo-Hookean potential defined as

\[
W_{si} = \frac{1}{2} \left[ W_i(I_{1i}, I_{2i}) + W_i(I_{2i}, I_{1i}) \right] \tag{2.2.10}
\]

When \( \vartheta \) parameter is zero, this model reduces to the ‘simple’ Leonov model. The effect of \( \vartheta \) on the properties of the model is also discussed by Tanner \cite{Tanner1998}.

If the modified Leonov model employs the general form of elastic potential, \( W \), defined by Eq. (2.2.2) and irreversible rate of strain, \( \dot{\varepsilon}_{pi} \), (Eq. 2.2.3) with functions \( b_{1i} \), \( b_{2i} \) obeying Eqs. (2.2.5-2.2.6), three adjustable parameters (\( \beta \), \( n \) and \( m \)) arise.

In the pure shear flow, only \( n \) controls the shape of \( \eta \) and \( N_1 \) while \( N_2 \) is controlled by parameters \( n \) and \( \beta \). A wide modification of the extensional viscosity can be easily done through \( \beta \), \( m \) and \( n \) (Fig. 1). If \( n \) is kept as a constant obtained from the shear behavior, the prediction of extensional viscosity does not influence the shear viscosity and \( N_1 \).
Fig. 1  The 8-mode modified Leonov model predictions of the steady uniaxial extensional viscosity for various parameters $\beta$, $n$ and $m$. 
3 RELAXATION SPECTRUM (Paper I)

The relaxation time spectrum of a polymer contains significant information about its molecular structure and it has been used extensively for polymer characterization and in applications of linear or nonlinear viscoelastic constitutive equations in modeling of polymer processing operations. Therefore, determination of the relaxation spectrum is very important and it is not surprising that considerable progress has been made in recent years towards the computation of the relaxation spectrum from experimental rheological data [17-30]. In principle, the relaxation spectrum may be determined from a number of experimentally measurable linear viscoelastic properties. However, the experimental measurements usually employed are those of the storage (\(G'\)) and loss (\(G''\)) moduli obtained from oscillatory shear experiments. Once the relaxation spectrum has been determined other linear viscoelastic material properties may be calculated from it [31].

Determination of relaxation time spectra from oscillatory shear data is usually based on the generalized Maxwell model. Using the continuous representation of the Maxwell model, the relaxation spectrum \(H(\lambda)\) is related to \(G'\) and \(G''\) through the Fredholm integral equations of the first kind [31]:

\[
G'(\omega) = \int_{-\infty}^{\infty} \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} H(\lambda) d(\ln \lambda) \\
G''(\omega) = \int_{-\infty}^{\infty} \frac{\omega \lambda}{1 + \omega^2 \lambda^2} H(\lambda) d(\ln \lambda)
\]

where \(\omega\) and \(\lambda\) are the frequency and relaxation time respectively. It is well known that solving for \(H(\lambda)\) is an ill-posed problem [32-33] and during the last decade several improved numerical methods have been proposed for its solution. These methods employ either regression techniques [17-18] (linear or nonlinear) or regularization techniques [19-26] and their merits and shortcomings have been extensively discussed in the literature [30].

The first particular objective of our research is to demonstrate the estimation of the relaxation time spectrum from capillary steady shear and extensional data by using a modification of the Leonov constitutive equation and to discuss the validity and potential limitations of the proposed methodology. The motivation for this work stems from the fact that capillary measurements are easy to perform and equipment designers generally have access only to this type of rheological data. In addition, estimation of the relaxation spectrum is an integral part of the work on numerical simulations of polymer flows using nonlinear constitutive equations.

The technique we have developed for the extraction of the relaxation spectra from capillary data is described in detail in Paper I [10]. In general, a modified Leonov model is employed and the spectra and model parameters are estimated through non-linear regression using measured steady shear viscosity data and extensional viscosity data calculated by Cogswell’s method. Using the proposed methodology, the spectra of several resins were estimated and they were used in the Maxwell model to predict the linear viscoelastic properties of these resins. The predicted properties (storage and loss moduli and complex viscosity) were found to be in very good agreement with the data from oscillatory shear measurements, thus supporting the validity of the estimated relaxation spectra.
4 COEXTRUSION PROCESS

Coextrusion is a process in which two or more layers of polymers are extruded through a single die. The coextrusion process can be used to produce multi-layer sheet, blown film, cast film, tubing, wire coating, profile and others. It has been used since the early 1950’s to improve product quality and process efficiency. However, under certain conditions, the coextrusion process exhibits some flow instability phenomena, which are not fully understood yet. In some cases the flow of viscoelastic polymeric materials gives rise to unstable interfaces and undesirable layer distribution, which can significantly affect the product properties. With aim to understand these flow phenomena, we investigated both, the distribution of polymer melt stream from an extruder into an annular flow channel within a flat spiral distribution system, and merging area at which coextruded materials combine first time.

4.1 A Flat Spiral Die Distribution System (Paper II)

Spiral mandrel dies are standard type dies widely used in the blown film industry for the last 30 years. Their main function is to distribute a polymer melt stream from an extruder into an annular flow channel. A number of simplified mathematical models have been proposed to predict their performance in terms of flow distribution and pressure consumption [34-42]. In one of the more accurate simplified models [42], the flow distribution is obtained by solving the two-dimensional momentum balances using the lubrication approximation and a control volume algorithm. Because of its simplicity, this model was recently employed to determine the optimum geometry of a spiral mandrel distribution system through the Taguchi approach [43]. In addition, control volume method (CVM) based models have been recently improved by taking entrance pressure drop effects into account for extensional deformation in leakage flows from the spiral channel into the overflow gap [36-37]. Although the computations by CVM are relatively simple, they need to be tested by a more realistic three-dimensional finite element method (FEM) because of the simplified assumptions in CVM. Such comparisons for a typical spiral mandrel die have been carried out and they have demonstrated the validity of CVM algorithms [36-37, 44].

Although virtually all blown film dies employ a spiral distribution system, it is only recently that a new flat spiral distribution system used mainly in “stacked” type of annular coextrusion dies has been developed. In a flat spiral distribution system, the pressure requirements and the residence time of the material in the die are significantly reduced compared to a traditional spiral system. This is especially significant for adhesives and barrier resins, which are more prone to thermal degradation.

It should be pointed out that the idea of “stacking” the layers in coextrusion flows is not completely new. In fact, this “stacked” configuration has been previously used with blow molding dies [45-46] despite initial design drawbacks. The improved new flat spiral distribution system used in blown film dies is much more efficient at conveying the polymer melt while maintaining the distribution benefits of a traditional system. A typical flat distribution system is shown in Fig. 2.

In order to better understand the flow field within this type of die, visualization experiments and isothermal 3D FEM simulations were performed [47]. The results showed that for a Newtonian liquid, numerical predictions agreed well with experimental data. However, the previous work [47-48] did not address issues related to either viscous dissipation or viscoelasticity, both deemed important in the new die design. Therefore, the primary objective of the PhD thesis is to investigate these issues and to elucidate the role of viscous dissipation and material viscoelasticity on the flow distribution and pressure drop through the flat spiral die.

Fig. 2 Typical flat spiral distribution system.
This investigation is done in Paper II [5]. In the article, the flow of a polymer melt through a flat spiral distribution system used in ‘stacked’ type dies was analyzed through 3D FEM simulations, and the predictions of the exit flow variation were compared to experimental measurements. Both isothermal and non-isothermal simulations were carried out, and the non-isothermal results were found to be in close agreement with the measured flow variation. It was revealed that for this particular flat spiral die, viscous dissipation is crucial and it may lead to generation of hot spots and increased flow variation. Further, the effect of material viscoelasticity on the flow field was simulated by using a CEF constitutive equation. No effects were detected mainly due to the inability of this model to describe the extensional deformation experienced by the material during the leakage flow from the spiral channel to the overflow gap.

4.2 Interfacial Instabilities (Paper III and Paper IV)

Interfacial instabilities appearing in coextrusion processes are a crucial problem that has been considerably investigated over the years [48-69]. Based on topography, these instabilities may be classified into three distinct types:

1. zig-zag
2. scattering
3. wave.

The zig-zag instability appears in the extruded sheet as a series of chevrons pointing to the flow direction. Scattering, on the other hand, is a disruption in the continuity of a microlayer. It is different from zig-zag; while scattering is only observed when many layers are present (>100), the individual layers are very thin (<10 µm), and adjacent layers are composed of different materials, zig-zag can occur when only two layers are present, the layers are quite thick (~500-1000 µm), and in some cases even when adjacent layers are of the same material [48, 58]. The third type of instabilities, wave instability, which is in the centre of our attention, appears in extruded sheet as a train of parabolas oriented in the flow direction, each parabola spanning the width of the sheet [59]. (See Fig. 3-5)

There are several theories of the source of interfacial instabilities. One possibility is that the interfacial instability is created just prior to the die exit region where the interface usually experiences maximum shear stress [62]. Another theory presumes that the interfacial instability originates at the point where the materials combine and the interface is created [48, 57-58].

![Fig. 3 Topographical view of the wave pattern instability in a 2-layer structure [48]](image)
Fig. 4  Topographical view of the wave pattern instability in a 3-layer structure [59]

Fig. 5  Spatial progression of the wave pattern instability in a 3-layer structure [59]
With the aim of understanding interfacial instability phenomena in Paper III [3] and Paper IV [4] we employ non-isothermal calculation of transient viscoelastic stresses in an annular coextrusion die using the 8-mode modified Leonov constitutive equation and the deformation rate field from FEM.

We demonstrate that the wave instabilities can be related to varying amounts of the material stretching across the coextrusion interface and that they are crucially influenced by the die design and extensional viscosity. Moreover, we show that the heuristic criterion based on the difference of the first normal stress differences across the layer interfaces may be used to potentially detect the onset of wave instabilities. In detail, if the resistance to deformation causes generation of higher normal stresses in the minor layer than in the major one (at least for a moment), the system becomes unstable; otherwise, it is stable. This indicates that such reverse stretching of the layers in the merging area may initiate disturbances which destabilize the coextrusion flow.

We have also found that each die geometry change which depresses the velocity rearrangement at the merging point leads to stabilization of the flow. More specifically, the geometry which permits high enough pre-acceleration of the minor flow prior to the merging point has the stabilization influence; otherwise, the geometry has destabilization effect. Overall, the results suggest that the difference of the first normal stress differences criterion may be a useful tool in the coextrusion die design as well as for proper selection of materials and processing conditions for coextrusion.
REFERENCES

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LIST OF PUBLICATIONS