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RHEOLOGICAL CHARACTERISATION OF LDPE MATERIALS BY MEANS OF DIFFERENTIAL CONSTITUTIVE EQUATIONS

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Summary: *For rheological description of branched LDPE melts (Escorene LD165BW1 a Bralen RB0323) the following differential constitutive equations were used: eXtended Pom-Pom, Phan Thien-Tanner-XPP, and modified Leonov models. There was carried out quantitative and qualitative comparison of efficiency of the predictions determined by these models with the experimental data measured at 200°C. For both materials there were measured linear viscoelastic properties, shear and uniaxial extensional viscosities.*

1. Introduction

Application of differential constitutive equations allows direct investigation of usually unknown relationships between molecular structures of the polymers and their rheological responses during the modern processes which can be both steady and transient. With the aim to understand more thoroughly the behaviour and possible differences of the differential constitutive equations, we decided to concentrate on three models, two molecular ones i.e. the eXtended Pom-Pom model (Verbeeten et al. (2001)) and PTT-XPP one (Tanner & Nasseri (2003)), and the modified Leonov model (Zatloukal (2003)). In more detail, the attention will be paid to their predictive/fitting capabilities in the particular types of the steady and transient flow situations typically occurring during polymer processing. Two common LDPE materials (Escorene LD165BW1, Exxon, USA and RB0323, Slovnaft, Slovakia) were used.

2. The eXtended Pom-Pom (XPP) model

The original Pom-Pom model (McLeish & Larson (1998)) was later extended by Verbeeten et al. (2001). A single equation for viscoelastic stress is given by

$$\overset{\nabla}{\boldsymbol{\tau}} + \lambda\left(\boldsymbol{\tau}\right)^{-1}\boldsymbol{\tau} = 2G\boldsymbol{D} \tag{1}$$

where $\boldsymbol{\tau}$ represents a stress tensor, G is a relaxation modulus, $\boldsymbol{D}$ is a rate-of-deformation tensor

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$$\boldsymbol{D} = \frac{1}{2}\left(\boldsymbol{L} + \boldsymbol{L}^{\mathrm{T}}\right) \quad , \quad \boldsymbol{L} = (\nabla \boldsymbol{v})^{\mathrm{T}} \tag{2}$$

$\boldsymbol{v}$ represents the velocity field, T denotes the transpose of a tensor, ∇ is the gradient operator. The upper-convected derivation of the stress tensor $\overset{\nabla}{\boldsymbol{\tau}}$ is defined as

$$\overset{\nabla}{\boldsymbol{\tau}} = \frac{\partial \boldsymbol{\tau}}{\partial t} + (\boldsymbol{v} \cdot \nabla)\boldsymbol{\tau} - \boldsymbol{\tau}\boldsymbol{L}^{T} - \boldsymbol{L}\,\boldsymbol{\tau} \tag{3}$$

and the relaxation time tensor is given by

$$\lambda(\boldsymbol{\tau})^{-1} = \frac{1}{\lambda_{0b}}\left\{\frac{\alpha}{G}\boldsymbol{\tau} + f(\boldsymbol{\tau})^{-1}\boldsymbol{I} + G\left[f(\boldsymbol{\tau})^{-1} - 1\right]\boldsymbol{\tau}^{-1}\right\} \tag{4}$$

where α is a Giesekus parameter, λ_{0b} is a linear relaxation time.

The extra function in Eq.4 is of the form

$$\frac{1}{\lambda_{0b}} f(\boldsymbol{\tau})^{-1} = \frac{2}{\lambda_{\mathrm{S}}}\left(1 - \frac{1}{\Lambda}\right) + \frac{1}{\lambda_{0b}\Lambda^{2}}\left(1 - \frac{\alpha.\mathrm{tr}(\boldsymbol{\tau}.\boldsymbol{\tau})}{3G^{2}}\right) \tag{5}$$

where Λ represents a backbone tube stretch, λ_{S} denotes a stretch relaxation time

$$\Lambda = \sqrt{1 + \frac{\mathrm{tr}(\boldsymbol{\tau})}{3G}} \quad , \quad \lambda_{\mathrm{S}} = \lambda_{0\mathrm{S}}\, e^{-\nu(\Lambda - 1)} \quad , \quad \nu = \frac{2}{q} \tag{6}$$

λ_{0S} and q (amount of the arms at the end of a backbone) are the adjustable parameters.

3. The PTT-XPP model

It was recently shown by Tanner & Nasseri (2003), Tanner (2005) that the well known PTT and XPP models can be viewed as the special cases of the general network model i.e. that the XPP model can be described as a general network model plus a Giesekus term. Based on this finding, a new combined model denoted as the PTT-XPP one has been suggested (Tanner & Nasseri (2003)). In more detail, the PTT-XPP model introduces an additional term $f_{gs}(\boldsymbol{\tau},\boldsymbol{D})$ in the equation for viscoelastic stress (Eq.(7)) in comparison with the XPP model and simultaneosly neglects both a Giesekus parameter α and $(f(\boldsymbol{\tau})^{-1} - 1).\boldsymbol{I}$ term. The description of the PTT-XPP model is given by the following set of the equations:

Viscoelastic stress is related to the rate-of-deformation tensor by the equation

$$\overset{\nabla}{\boldsymbol{\tau}} + f_{\mathrm{gs}}(\boldsymbol{\tau}, \boldsymbol{D}) + \boldsymbol{\lambda}(\boldsymbol{\tau})^{-1}\boldsymbol{\tau} = 2G\boldsymbol{D} \tag{7}$$

where f_{gs} is a non-affine deformation defined by

$$\boldsymbol{f}_{\mathrm{gs}} = \xi\left(\boldsymbol{D}\,\boldsymbol{\tau} + \boldsymbol{\tau}\boldsymbol{D}\right) \tag{8}$$

A simplified relaxation time tensor is of the form

$$\boldsymbol{\lambda}(\boldsymbol{\tau})^{-1} = \frac{1}{\lambda_{0b}} f(\boldsymbol{\tau})^{-1} \boldsymbol{I} \tag{9}$$

and an extra function

$$\frac{1}{\lambda_{0b}} f(\boldsymbol{\tau})^{-1} = \frac{2}{\lambda_{\mathrm{S}}}\left(1 - \frac{1}{\Lambda}\right) + \frac{1}{\lambda_{0b}\Lambda^2} \quad . \tag{10}$$

A backbone tube stretch and a stretch relaxation time are the same as in the XPP model, rel.(6).

4. The modified Leonov (mLeonov) model

The constitutive equation is based on the original Leonov model (Leonov & Prokunin (1994)) with the modified dissipation term *b* proposed by Zatloukal (2003).

The relation between stress $\boldsymbol{\tau}$ and elastic Cauchy strain $\boldsymbol{c}$ is given by

$$\boldsymbol{\tau} = 2\left(\boldsymbol{c}\frac{\partial \boldsymbol{W}}{\partial I_1} - \boldsymbol{c}^{-1}\frac{\partial \boldsymbol{W}}{\partial I_2} \right) \tag{11}$$

where $\boldsymbol{W}$ denotes elastic potential depending on the invariants I_1 and I_2 of the recoverable Finger tensor $\boldsymbol{c}^{-1}$. Elastic potential is defined by

$$\boldsymbol{W} = \frac{3G}{2(n+1)}\left\{(1-\beta)\left[\left(\frac{I_1}{3}\right)^{n+1} - 1\right] + \beta\left[\left(\frac{I_2}{3}\right)^{n+1} - 1\right]\right\} \tag{12}$$

where G denotes a linear elastic modulus, β and n are the nonlinear parameters.
The dissipation term b is included in the relation for the irreversible rate of strain $\boldsymbol{e}_p$

$$\boldsymbol{e}_p = b\left[\boldsymbol{c} - \left(\frac{I_1}{3}\right)\boldsymbol{I}\right] - b\left[\boldsymbol{c}^{-1} - \left(\frac{I_2}{3}\right)\boldsymbol{I}\right] \quad . \tag{13}$$

The elastic strain $\boldsymbol{c}$ and the rate-of-deformation tensor $\boldsymbol{D}$ are related as follows

$$\overset{0}{\boldsymbol{c}} - \boldsymbol{c}\cdot\boldsymbol{D} - \boldsymbol{D}\cdot\boldsymbol{c} + 2\boldsymbol{c}\cdot\boldsymbol{e}_p = 0 \tag{14}$$

The modified parameter b is defined by

$$b(I_1) = \frac{1}{4\lambda}\left\{\exp\left[-\xi(\lambda)\sqrt{I_1 - 3}\right] + \frac{\sinh\left[\nu(\lambda)(I_1 - 3)\right]}{\nu(\lambda)(I_1 - 3) + 1}\right\} \tag{15}$$

where $\xi(\lambda)$ and $\nu(\lambda)$ are the adjustable parameters subjected to the relaxation time λ.

As the real polymeric fluids are characterized by a distribution of relaxation times $\lambda_{\mathrm{b,i}}$ and moduli G_i the stress tensor $\boldsymbol{\tau}$ is given as a sum of the contributions from each element of relaxation spectra ($\lambda_{\mathrm{b,i}}$, G_i)

$$\tau = \sum_{i=1}^{N} \tau_i \tag{16}$$

where N is the number of relaxation times. The relaxation spectrum ($\lambda_{b,i}$, G_i) is determined from the oscillatory measurements by the help of generalized Maxwell model.

5. Experimental

Two highly branched LDPE materials widely used in the film blowing process (LDPE Escorene LD 165BW1, Exxon, USA and LDPE Bralen RB0323, Slovnaft, Slovakia) were chosen for the experiments carried out at the temperature of 200°C.

For both materials the linear viscoleastic properties (storage modulus G', loss modulus G''), transient shear viscosity and first normal stress coefficient were measured with use of the Advanced Rheometric Expansion System (ARES 2000) Rheometrics rheometer. Uniaxial extensional viscosity was measured using the ARES 2000 rheometer equipped with the SER Universal Testing Platform (SER-HV-A01 model) from Xpansion Instruments. Steady shear data was obtained from the capillary rheometer RH7-2 (Rosand Precision Ltd.) and from the oscillatory measurements (with the help of the Cox-Merz rule) using the ARES 2000 rheometer. First ψ_1 and second ψ_2 normal stress coeficients were obtained with the help of Han's method (Han (1976)), for an application for which a slit die was appended to a barrel of the capillary rheometer RH7-2.

6. Results and discussion

The application of the individual models to the experimental data for both materials is depicted in Figs.1-8. As can be seen there exist some differences between the models behaviour which are presented below.

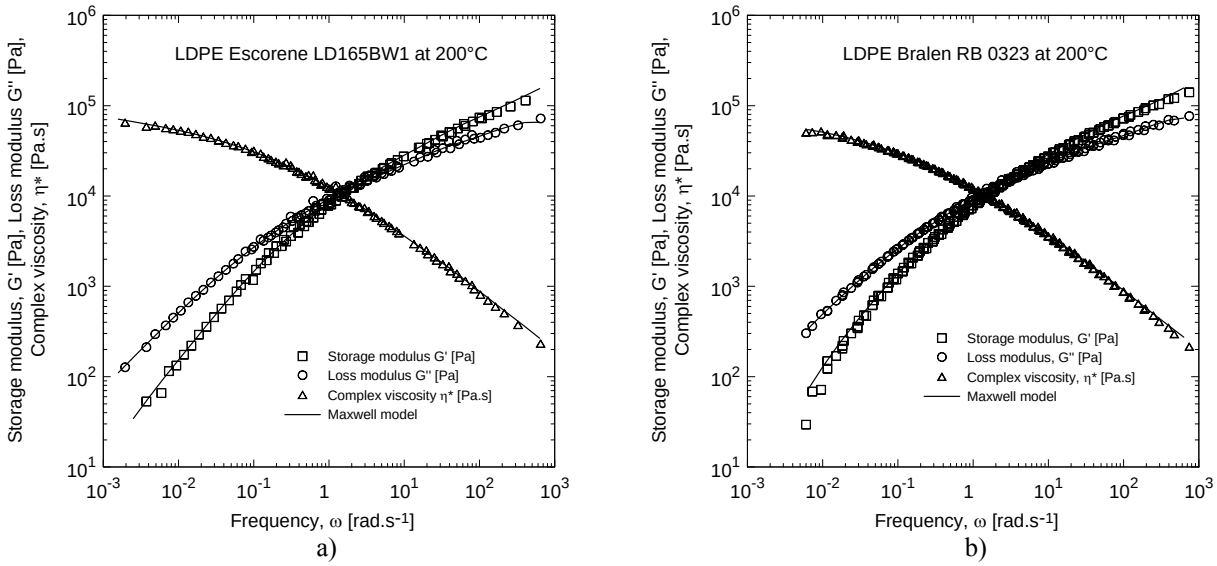

Fig.1 Comparison between the Maxwell model fits and measured complex viscosity η^*; storage G' and loss G'' moduli for a) LDPE Escorene LD165BW1, b) LDPE Bralen RB 0323 at 200°C.

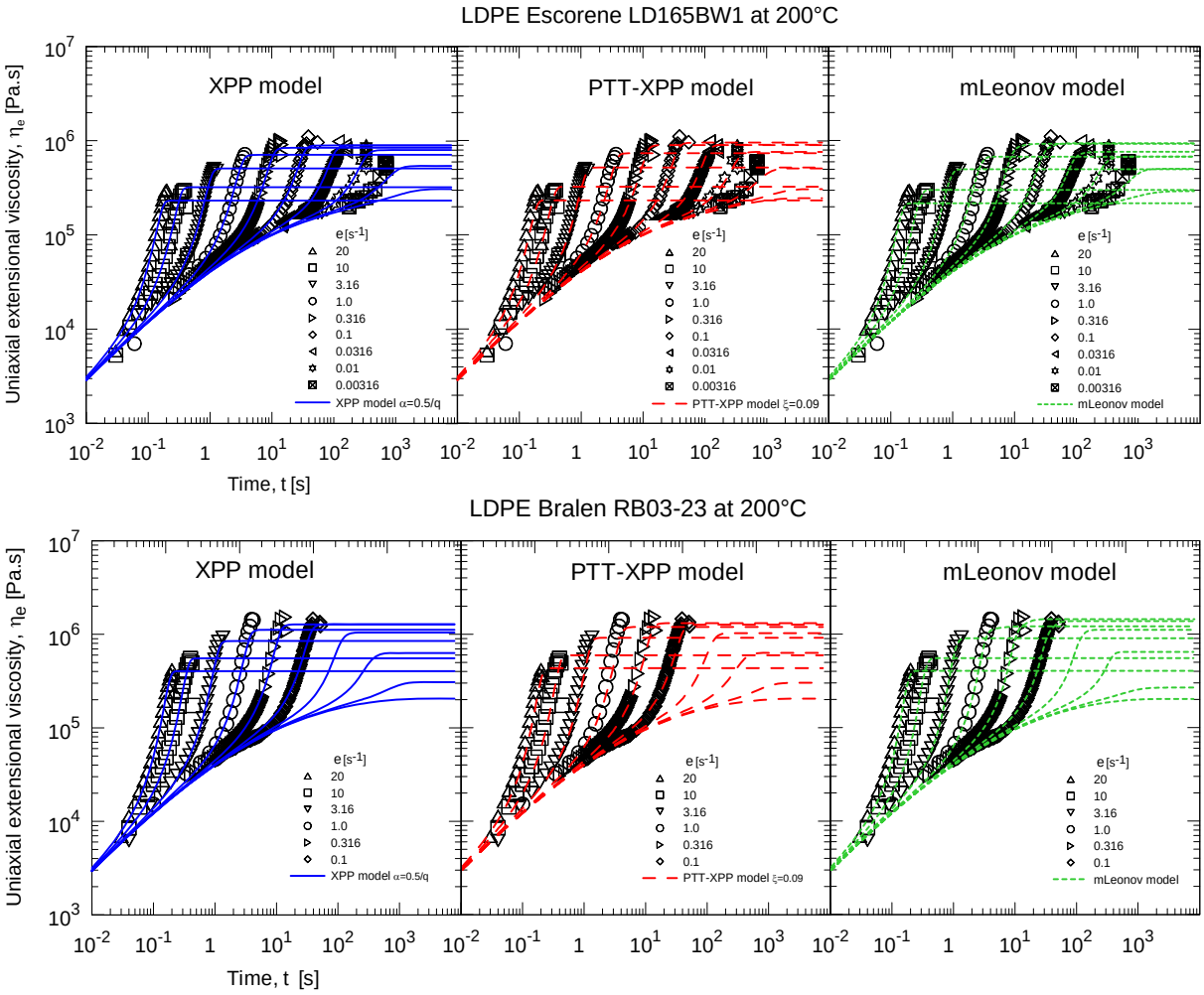

Fig.2 Comparison of the measured transient uniaxial extensional viscosity and the predictions of the XPP, PTT-XPP and mLeonov model for LDPE Escorene LD165BW1 and LDPE Bralen RB0323 at 200°C (theoretical transient elongational viscosity curves correspond to $\dot{\varepsilon}$ =20, 10, 3.16, 1, 0.316, 0.1, 0.0316, 0.001, 0.000316s^{-1} – from left to right).

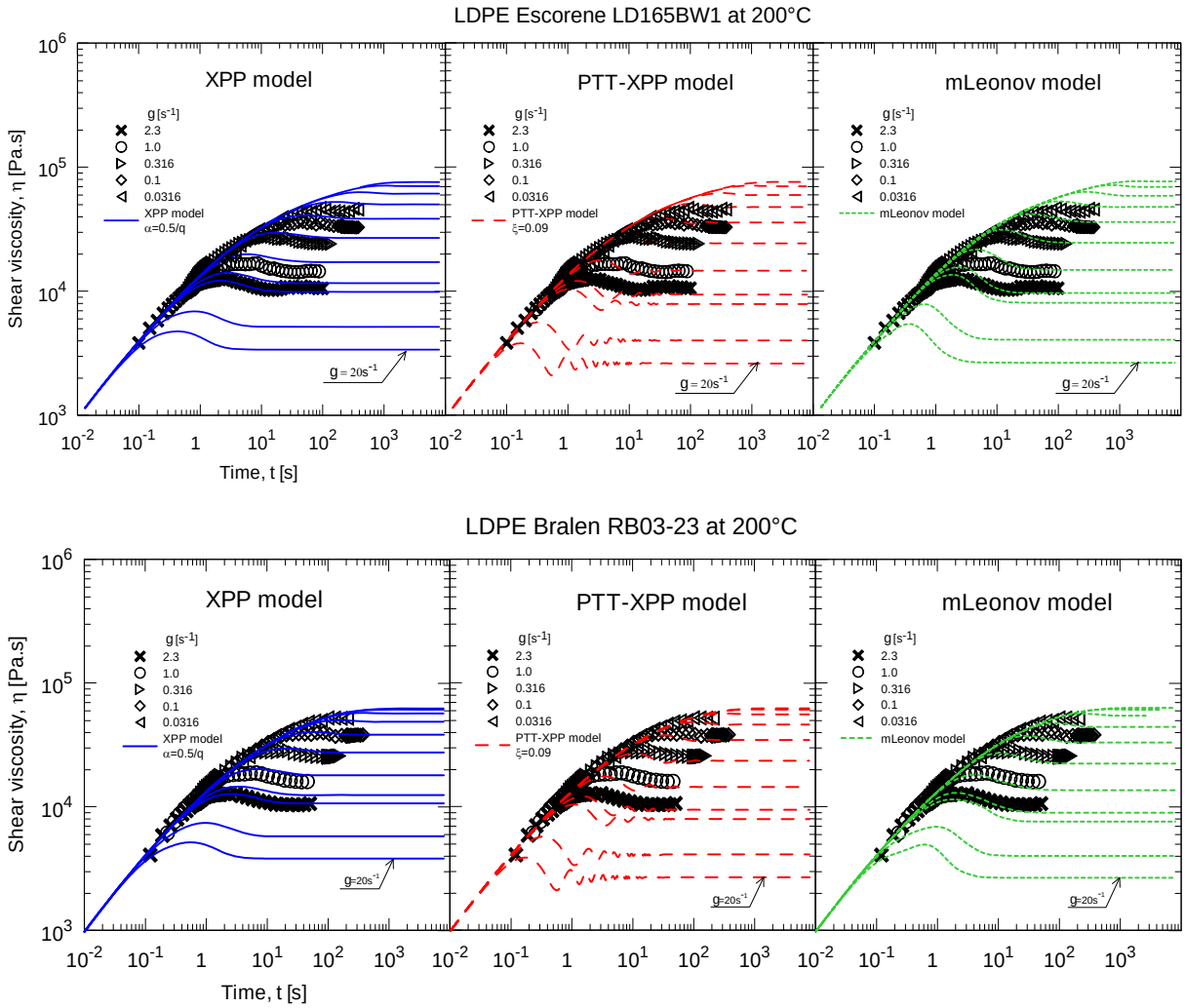

Fig.3 Comparison between experimentally determined transient shear viscosity data and predictions of the XPP, PTT-XPP and mLeonov models for LDPE Escorene LD165BW1 and LDPE Bralen RB0323 at 200°C (theoretical transient shear viscosity curves correspond to e =20, 10, 3.16, 2.3, 1, 0.316, 0.1, 0.0316, 0.001s^{-1} – taken upwards).

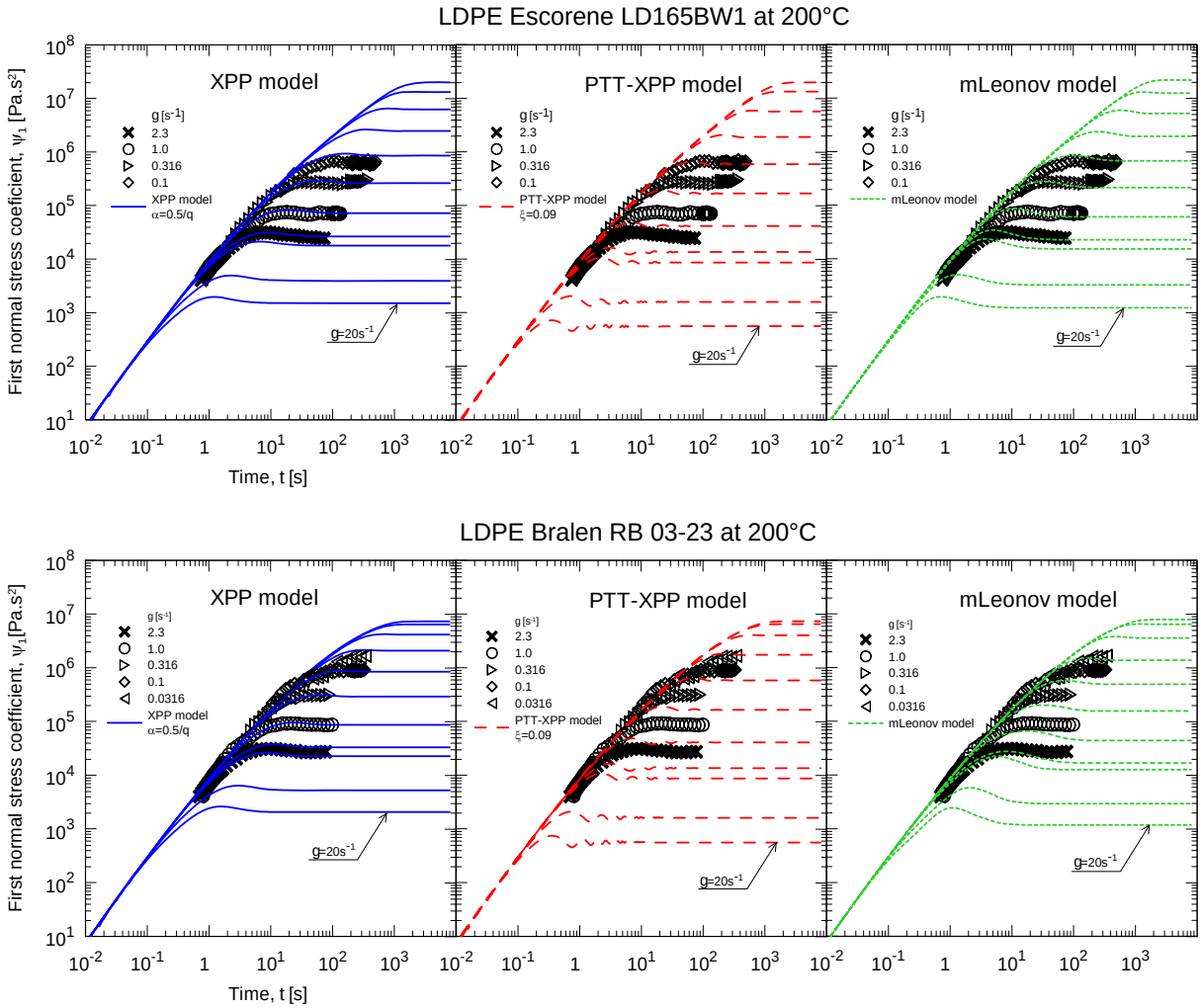

Fig.4 Comparison between experimentally determined transient first normal stress coefficient and predictions of the XPP, PTT-XPP and mLeonov models for LDPE Escorene LD165BW1 and LDPE Bralen RB0323 at 200°C (notation of the theoretical curves as in Fig.3 – taken upwards)

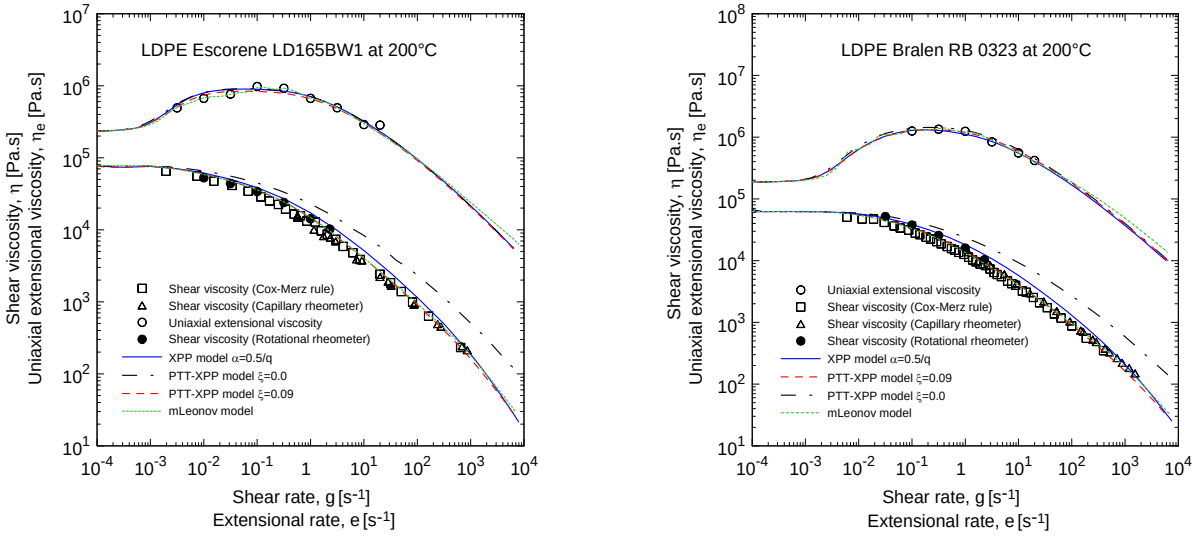

Fig.5 Comparison between measured steady shear and uniaxial extensional viscosity data and fits/predictions of the XPP, PTT-XPP and mLeonov models for LDPE Escorene LD165BW1 and LDPE Bralen RB0323 at 200°C.

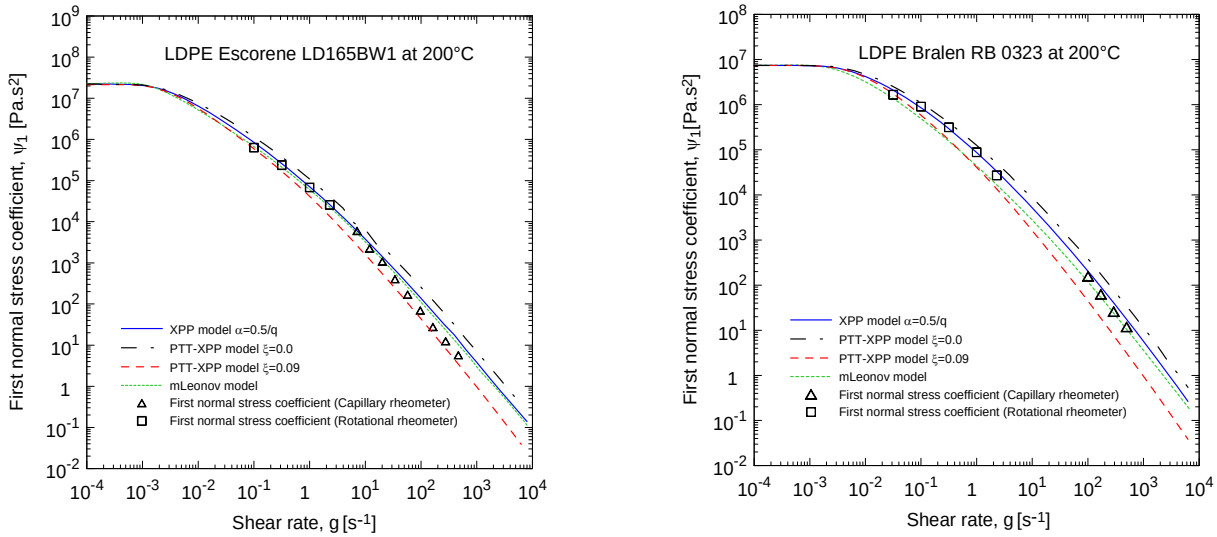

Fig.6 Comparison between measured first normal stress coefficient and fits/predictions of the XPP, PTT-XPP and mLeonov models for LDPE Escorene LD165BW1 and LDPE Bralen RB0323 at 200°C.

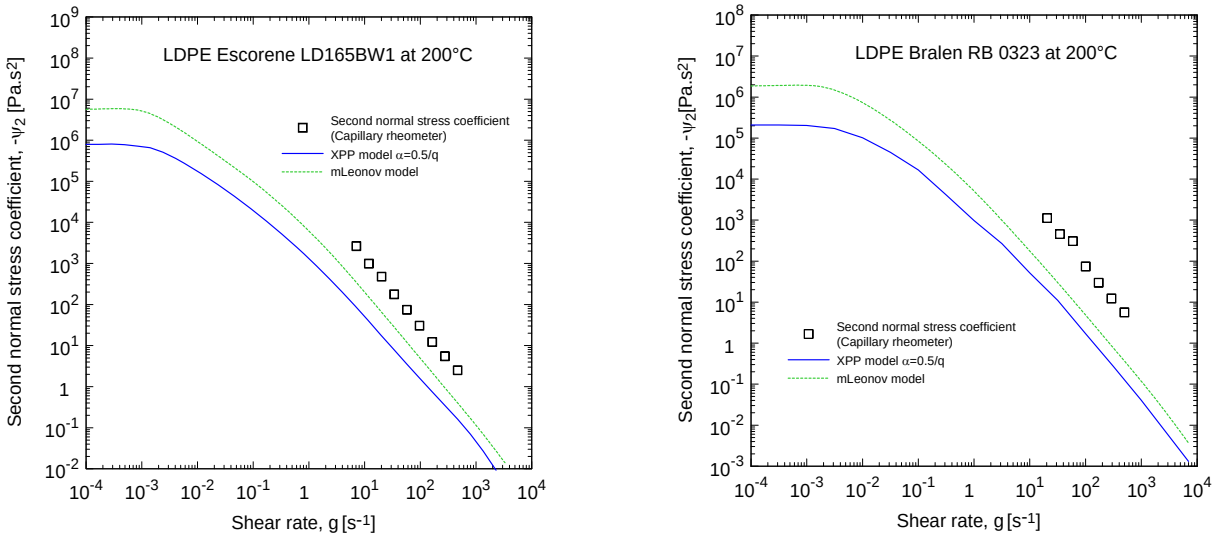

Fig.7 Comparison between measured second normal stress coefficient and fits/predictions of the XPP and mLeonov models for LDPE Escorene LD165BW1 and LDPE Bralen RB 0323 at 200°C.

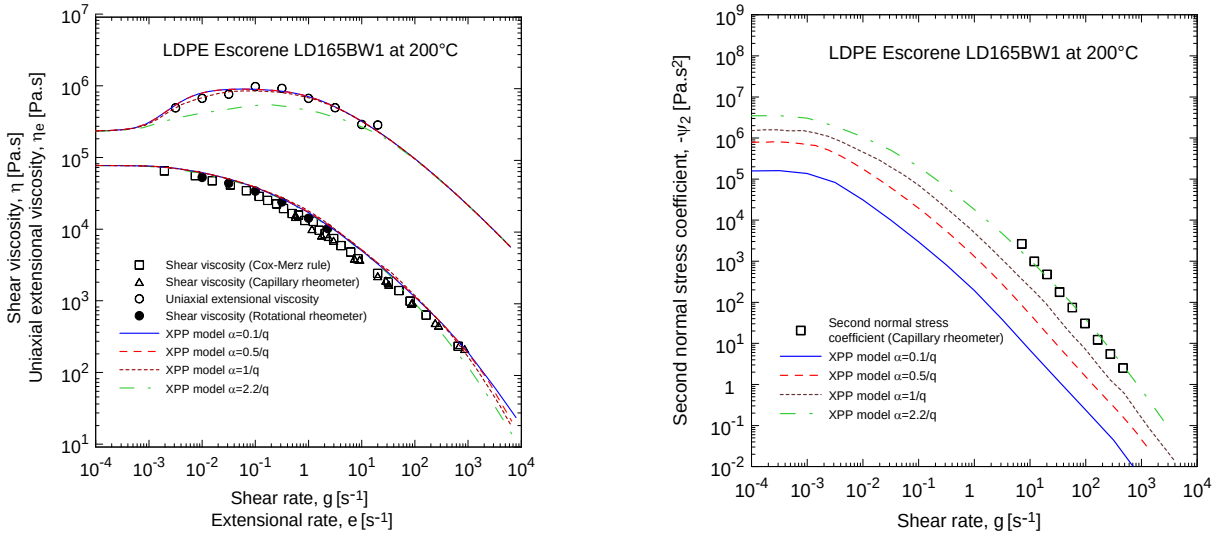

Fig.8 Comparison between measured second normal stress coefficient and fits/predictions of the XPP model for three different value of the Giesekus parameter (α = 0.1/q, 0.33/q, 0.5/q, 1/q and 2.2/q) for LDPE Escorene LD165BW1 at 200°C.

For the XPP and PTT-XPP models it was revealed (putting ξ=0 and the same parameter q for both models) that the steady uniaxial viscosity is predicted almost identically by both models and with a very good correspondence to the experimental data. However, the PTT-XPP model deviates in the prediction of steady shear viscosity. With the aim to improve this unwanted behaviour of the PTT-XPP model, a non-zero slip parameter ξ has to be used and determined through the fitting of a shear viscosity curve. Unfortunately, its non-zero value influences the extensional viscosity, and therefore it is necessary to change the parameter q to obtain desirable course of an extensional viscosity curve. This indicates that for a description of shear and extensional rheology of the LDPEs by the PTT-XPP model, one has to use more parameters as well as more complicated fitting procedure in contrary to the original XPP model.

Furthermore, it was found that neither the XPP model nor the mLeonov one fit accurately the measured second normal stress coefficient data (the PTT-XPP model has no possibility to predict this data) in spite of the fact that the prediction of the mLeonov model is more closely to the measured data than the XPP model. The Giesekus parameter α in the XPP model serves for fitting the second normal stress differences. However, the change of the Giesekus parameter reflects in the shear and elongational characteristics. When the Giesekus parameter is too large strain hardening disappears in extensional viscosity. In our case, the Giesekus parameter was adjusted to $0.33/q$ because larger modification of this parameter leads to an unacceptable change in the shear and extensional behaviour. Thus, nor the XPP model is able to fit the second normal stress coefficient in a satisfactory manner.

7. Acknowledgement

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