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ORIGINAL CONTRIBUTION

Predictive/fitting capabilities of differential constitutive models for polymer melts—reduction of nonlinear parameters in the eXtended Pom-Pom model

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Abstract A phenomenological modification of the eXtended Pom-Pom (XPP) model is proposed with the aim to reduce the number of free nonlinear parameters. The modified XPP model includes three parameters per mode in total (two linear viscoelastic parameters—linear relaxation time λ and shear modulus G, and one nonlinear parameter). The original XPP model contains five parameters (two linear viscoelastic parameters and three nonlinear ones, one nonlinear parameter participates in the second normal stress difference prediction). The predictive/fitting capabilities of the modified model are compared with the Giesekus, eXtended Pom-Pom, and modified Leonov models using various low-density PE materials in steady and transient shear and uniaxial elongational flows. It has been found that the modified model is capable of predicting/fitting the rheological properties, with the exception of the second normal stress difference, for studied LDPE materials with sufficient accuracy, including strain hardening in uniaxial elongational flow.

Keywords Constitutive model · XPP model · LDPE materials · Strain hardening · Elongational flow · Shear flow

Introduction

Understanding the rheological properties of polymeric materials plays a key role for modelling of their processing. The rheological properties are subject to the molecular structure of the material and to the character of the flow. Based on the molecular structure, the materials can be divided into linear, branched, and cross-linked. In principle, the character of the flow can be differentiated as shear or elongational (according to the type of deformation) and steady or transient (dependence on time). The rheological properties simultaneously generated by the material used and by the flow character are approximated by means of the constitutive models. The constitutive models represent, of course, only an idealized and simplified form of polymer melt flow description, as it is not possible to achieve a more complete description due to the complexity of the materials and the difficulty of solving numerically the corresponding balance equations. Unlike a constitutive equation (CE), two remaining ones—the continuity equation and equation of motion—are of standard (unchangeable) forms. A CE completing this set of equations can be proposed in various forms.

In the following, an overview of six frequently used differential constitutive models will be given with an emphasis on the number of parameters used for the description of individual rheological characteristics. For clarity, the mathematical description of all six models including the number of parameters per mode is summarized in Table 1. The introduced numbers of parameters involve not only so-called free parameters but also two linear viscoelastic parameters (linear relaxation time λ and relaxation modulus G) of the Maxwell model determined by the oscillatory characterization. It implies that the total numbers of free parameters per mode in the discrete relaxation spectrum are reduced by two for each model introduced in Table 1.

The frame invariant-based Maxwell model proposed by Lodge [1] is in its differential version known as the upper-convected Maxwell model (UCM). This model has two parameters (relaxation time $\lambda=\eta/G$ and relaxation modulus G, where η represents shear viscosity). The UCM model predicts constant steady shear viscosity η and first normal stress coefficient ψ_1 and zero second normal stress coefficient ψ_2. The extensional viscosity η_e attains the values from a triple of zero

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Table 1 The dissipative term $\boldsymbol{H}(\boldsymbol{c})$ for the individual differential constitutive models (supposing ξ=0)

Model	Dissipative term $\boldsymbol{H}(\boldsymbol{c})$	Number of parameters (incl. linear λ, G)	Nonlinear parameters
UCM [1]	$\mathbf{c}-\mathbf{I}$	2	–
PTT linear [3]	$[1+\varepsilon(\mathrm{tr}\boldsymbol{c}-3)](\boldsymbol{c}-\boldsymbol{I})$	3	ε
PTT exp. [3]	$\exp[\varepsilon(\mathrm{tr}\boldsymbol{c}-3)](\boldsymbol{c}-\boldsymbol{I})$	3	ε
Giesekus [2]	$a(\boldsymbol{c}-\boldsymbol{I})^2+\boldsymbol{c}-\boldsymbol{I}$	3	α
XPP [6]	$a(\boldsymbol{c}-\boldsymbol{I})^2+F_{XPP}\boldsymbol{c}-\boldsymbol{I}$	5	λ_s, q, α
PTT-XPP [9]	$F_{PTT-XPP}(\boldsymbol{c}-\boldsymbol{I})$	4	λ_s, q
Leonov [11]	$\frac{b}{2}\left(\boldsymbol{c}^2-\frac{\mathrm{tr}\,\boldsymbol{c}-\mathrm{tr}\,\boldsymbol{c}^{-1}}{3}\boldsymbol{c}-I\right)$	4	ζ, v
Present	$F\boldsymbol{c}-I$	3	β

$$F_{XPP}=2\frac{\lambda}{\lambda_s}\exp\left[\frac{2}{q}(\Lambda-1)\right]\left(1-\frac{1}{\Lambda}\right)+\frac{1}{\Lambda^2}\left[1-\alpha-\frac{\alpha}{3}tr\left(\boldsymbol{c}^2-2\boldsymbol{c}\right)\right]$$

$$F_{PTT-XPP}=2\ \frac{\lambda}{\lambda_s}\exp\left[\frac{2}{q}(\Lambda-1)\right]\left(1-\frac{1}{\Lambda}\right)+\frac{1}{\Lambda^2}$$

$$F\ =\ \exp[\beta(\Lambda-1)]\left(2-\frac{1}{\sqrt{\Lambda}}\right)$$

$$\Lambda\ =\ \sqrt{\frac{\mathrm{tr}\ \boldsymbol{c}}{3}}$$

Leonov [11] $b=\exp[-\zeta(\mathrm{tr}\ \boldsymbol{c}-3)]+\frac{\sinh[v(\mathrm{tr}\ \boldsymbol{c}-3)]}{v(\mathrm{tr}\ \boldsymbol{c}-3)}-1$

Modified Leonov [8] $b=\exp[-\zeta(\mathrm{tr}\ \boldsymbol{c}-3)]+\frac{\sinh[v(\mathrm{tr}\ \boldsymbol{c}-3)]}{v(\mathrm{tr}\ \boldsymbol{c}-3)+1}$

shear viscosity η_0 (for extensional rate $\dot{\varepsilon} << 1/\lambda$) to infinity (for $\dot{\varepsilon} = 1/2\lambda$) .

The constitutive model proposed by Giesekus [2] is based on anisotropic drag which is expressed by the coefficient α, attaining values between 0 (corresponding to minimum anisotropy) and 1 (maximum anisotropy). For α=0, the UCM model is recovered. The Giesekus model predicts nonzero second normal stress coefficient ψ_2. Description of the shear thinning behaviour is governed by the only free parameter α. The elongational viscosity η_{E} shows monotonic increase up to a constant maximum for α>0.

Phan-Thien and Tanner [3] developed a model (so called PTT model) in which the nonaffine motion is enabled with the help of the Gordon-Schowalter derivative. The model assumes two forms—linear and exponential. Each form uses four parameters, among which two free parameters ξ and ε participate in controlling the nonaffine motion (for ξ=0 affine motion is recovered) and governing shear thinning, respectively. The model predicts zero second normal stress coefficient ψ_2 when the affine motion is assumed. Its exponential version exhibits a maximum in steady elongational viscosity. For the nonaffine motion (i.e. $\xi \neq 0$), the unphysical oscillations in η, ψ_1 and ψ_2 occur during a start-up of steady shear at higher rates.

The derivation of the Pom-Pom model proposed by McLeish and Larson [4] is based on the idealized theory for branched molecules. It assumes generalized molecules of H structure having an arbitrary number of branches q at the end of the backbone, creating a branching point. For the prediction of the rheological behaviour of commercial materials with more complex structure by the Pom-Pom model, the multi-mode version was introduced by Inkson et al. [5]. Verbeeten et al. [6] introduced the eXtended Pom-Pom (XPP) model, which eliminated the following shortcomings of the Pom-Pom model:

1. Solutions in steady state elongation exhibiting discontinuities,
2. For high strain rates, unboundedness of the equation for orientation,
3. Impossibility to predict a second normal stress difference in shear.

Both models (Pom-Pom and XPP) include four parameters representing the same quantity (linear relaxation time λ and relaxation modulus G, and two free parameters: stretch relaxation time λ_s and number of arms q). Unlike the Pom-Pom model, the XPP model has one additional free Giesekus parameter α linearly involved in the term participating in predicting the second normal stress coefficient. The predictive/fitting capabilities of the XPP model were verified on steady and transient shear and elongational flows, e.g. in [7, 8]. It was shown that the XPP model is capable of fitting all the rheological properties characterizing these flows. The XPP model can be slightly modified by replacing the upper-convected derivative by the Gordon-Schowalter one (see Tanner and Nasseri [9]) to fit/predict steady shear viscosity with the help of the additional free parameter ξ included in the term of the Gordon-Schowalter derivative. Use of the Gordon-

Schowalter derivative results in the unphysical oscillations in the transient shear characteristics.

Tanner and Nasseri [9] demonstrated that both the original PTT [3] and XPP [6] models can be considered as special cases of the general network model (PTT-XPP) if the upper-convected derivative is replaced by the Gordon-Schowalter one, the Giesekus term containing α is neglected, and the dissipative term $\boldsymbol{H}(\boldsymbol{c})=F\boldsymbol{c}\text{-}\boldsymbol{I}$ is replaced by $\boldsymbol{H}(\boldsymbol{c})=F(\boldsymbol{c}\text{-}\boldsymbol{I})$ resulting in the simplified form of dissipative term expressed in stress tensor $\boldsymbol{H}(\boldsymbol{\tau})$. For the XPP and PTT-XPP models this term is $\boldsymbol{H}(\boldsymbol{\tau})=F_{\mathrm{XPP}}\boldsymbol{\tau}/G+(F\text{-}1)\boldsymbol{I}$ and $\boldsymbol{H}(\boldsymbol{\tau})=F_{\mathrm{PTT\text{-}XPP}}\boldsymbol{\tau}/G$, respectively. The PTT-XPP model uses the identical four parameters as the Pom-Pom and XPP models and one additional free parameter ξ given by replacing the upper-convected derivative by the Gordon-Schowalter one. The model was also tested in steady and transient shear and elongational flows [7]. It implied an ability to describe the steady shear and elongational properties, as well as the transient elongational properties of the commercial materials. However, the unphysical oscillations caused by application of the Gordon-Schowalter derivative occur in the transient shear characteristics. Tanner [10] suggested the reduction of the parameters in the PTT-XPP model by replacing the term $2\lambda/\lambda_s$ by $12q$ in the extra function.

The modified Leonov model predicts both strain hardening and nonzero second normal stress coefficient. Apart from two linear parameters (linear relaxation time λ and relaxation modulus G) there are two nonlinear adjustable parameters depending on the relaxation time. Leonov model [11] is derived from heuristic thermodynamics arguments, resulting from the theory of rubber elasticity. A modification of the dissipation function employed in this work was proposed by Zatloukal [8].

As the commercial polymeric materials include a large number of polymer molecules of different lengths, they are characterized by the distribution of relaxation times λ_i and moduli G_i. Consequently, the stress tensor $\boldsymbol{\tau}$ is given by a sum of the contributions from each relaxation elements spectrum

$$\boldsymbol{\tau} = \sum_{i=0}^{N} \boldsymbol{\tau}_i \tag{1}$$

where N is the number of relaxation elements.

As is apparent from the above overview, a number of entry free parameters seems to be one of the crucial points in presentation of the individual models. However, a reduction of the free parameters can be reflected in the range of rheological characteristics that are predicted by the models—more often it concerns the (im)possibility of predicting strain hardening (concerning elongation characteristics) and the second normal stress coefficient.

Simultaneously with the above presented molecular-based or thermodynamically based models, the phenomenological models can be relatively efficient for a description of rheological characteristics of studied materials. Their structure quite often emanates from the classical models such as Cross (Liang and Zhong [12]), Carreau (Zatloukal [13]), Carreau-Yasuda (Phan-Thien et al. [14]), or is based on other algebraic formulae (Fuchs and Ballauf [15]). Liang and Zhong [12] proposed the 5-parameter phenomenological Cross-type model describing a steady uniaxial elongational flow including strain hardening.

The aim of this contribution is to present a 3N-parameter (three parameters per mode) phenomenological modification of the XPP constitutive model (only one free parameter) capable of predicting all rheological characteristics except for the second normal stress coefficient but including strain hardening. It means that both shear thinning and strain hardening behaviour is modelled with help of one free parameter only (per one mode in the discrete relaxation spectrum). For an evaluation of polymer melt behaviour any reduction of free parameters simplifies numerical procedures and substantially reduces computational time, especially in the presence of one free parameter only as no attention has to be paid to appearance of possible ambiguity. In addition to it, this facilitation of the whole approach is linearly proportional to the number of modes taken into account. The applicability of the proposed model is demonstrated on a series of various LDPE materials enabling evaluation of the predictive/fitting capabilities using IUPAC [16], Dow 150R [8], and Escorene LD165BW1 [7]. The similar results were also obtained for Lupolen 1840 [7], Bralen RB0323 [8], and LDPE1 [17]. These materials differ among other things in polydispersity and molecular weight. This indicates that the applicability of the model is not restricted to a relatively narrow class of LDPE materials. The comparison under steady and transient shear and uniaxial elongational flow situations with the Giesekus model [2] (not providing simultaneous modelling of strain hardening and consequent thinning behaviour), eXtended Pom-Pom model [6], and Leonov model [11] gives favourable results with respect to the number of free parameters.

Proposed modification of the XPP model

A phenomenological modification of the XPP model is proposed for the rheological characterization of the polymer melts with the aim of minimizing a number of additional (nonlinear) parameters—it contains two linear parameters (relaxation time λ and elastic shear modulus G), and only one free nonlinear parameter β which affects the level of strain hardening in elongational flows as well as shear thinning in shear flows.

A nonnegligible number of CEs (UCM, PTT, Giesekus, XPP, Leonov—see Table 1) suppose the following relation between extra stress tensor $\boldsymbol{\tau}$ and symmetrical conformation tensor $\boldsymbol{c}$

$$\boldsymbol{\tau} = G(\boldsymbol{c} - \boldsymbol{I}), \tag{2}$$

where G represents the elastic shear modulus and $\boldsymbol{I}$ denotes the unit tensor.

In general, the evolution equation of the models can be written in the form

$$\frac{dc}{dt} - \nabla \boldsymbol{\nu} \cdot \boldsymbol{c} - \boldsymbol{c} \cdot \nabla \boldsymbol{v}^T + \frac{\xi}{2}\left(\dot{\gamma} \cdot\ \boldsymbol{c} + \boldsymbol{c}\ \cdot \dot{\gamma}\right) + \frac{1}{\lambda}\boldsymbol{H}(\boldsymbol{c}) = 0 \tag{3}$$

where v is the velocity, $\dot{\gamma}$ is the rate of deformation tensor $\nabla \boldsymbol{v} + \nabla \boldsymbol{v}^T$, λ is the relaxation time, and $\boldsymbol{H}(\boldsymbol{c})$ is the dissipative term depending on conformation tensor $\boldsymbol{c}$. The parameter ξ is the nonaffine motion parameter ($0 \leq \xi \leq 2$). If the parameter ξ attains the limiting values 0 and 2, the conformation tensor represents contravariant (upper convected derivative) and covariant (lower convected derivative) form, respectively. For many polymer systems the parameter ξ takes the zero value.

A constitutive equation proposed in this work supposes $\xi = 0$. Generally, the parameter ξ can attain nonzero value ($0 \leq \xi \leq 2$). However, there are two reasons why to choose $\xi = 0$. First, the principal aim of the proposed modified model is to reduce a number of nonlinear parameters as much as possible. Second, the presence of nonzero value of the parameter ξ evokes unphysical oscillations in transient shear characteristics at high shear rates (see Figs. 8 and 9 in [7]). On the other hand, a nonzero value of ξ significantly contributes to a more pronounced shear thinning (see Fig. 3 in [7]).

The dissipative term $\boldsymbol{H}(\boldsymbol{c})$ is of a simple form

$$\boldsymbol{H}(\boldsymbol{c}) = F\boldsymbol{c} - \boldsymbol{I} \tag{4}$$

where the extra function F and stretch characteristic Λ are defined as

$$F = exp[\beta(\Lambda - 1)]\left(2 - \frac{1}{\sqrt{\Lambda}}\right) \tag{5}$$

$$\Lambda = \sqrt{\frac{\mathrm{tr}\,\boldsymbol{c}}{3}} \tag{6}$$

From here, the evolution equation can be rewritten as follows:

$$\lambda \check{\boldsymbol{c}} + F\boldsymbol{c} - \boldsymbol{I} = 0 \tag{7}$$

where $\check{\boldsymbol{c}}$ denotes the upper-convected derivative.

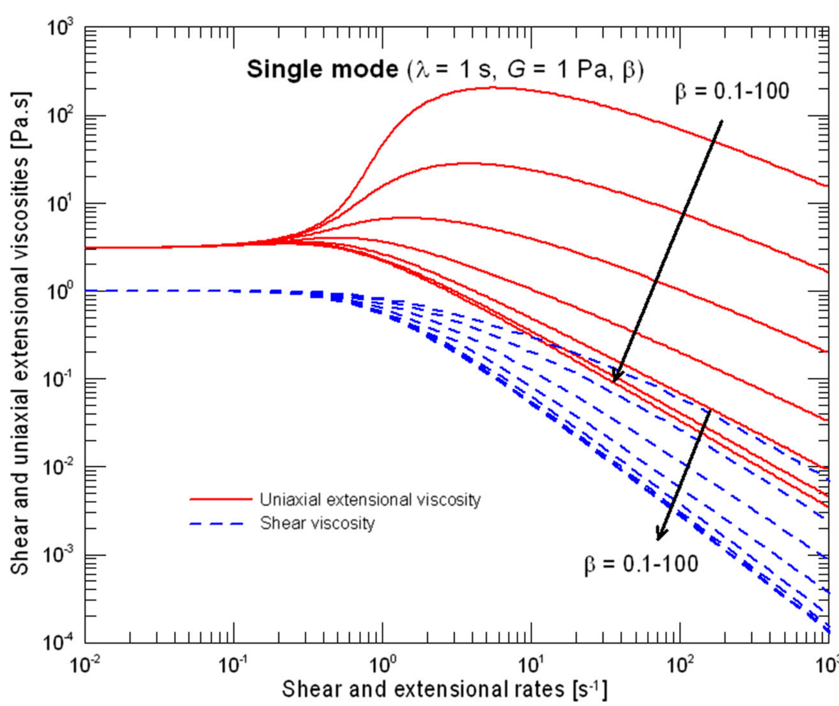


Fig. 1 Predictions of shear and uniaxial extensional viscosities of the modified XPP model in single mode (λ=1 s, G=1 Pa, β={0.1, 0.316, 1, 3.16, 10, 31.6, 100})

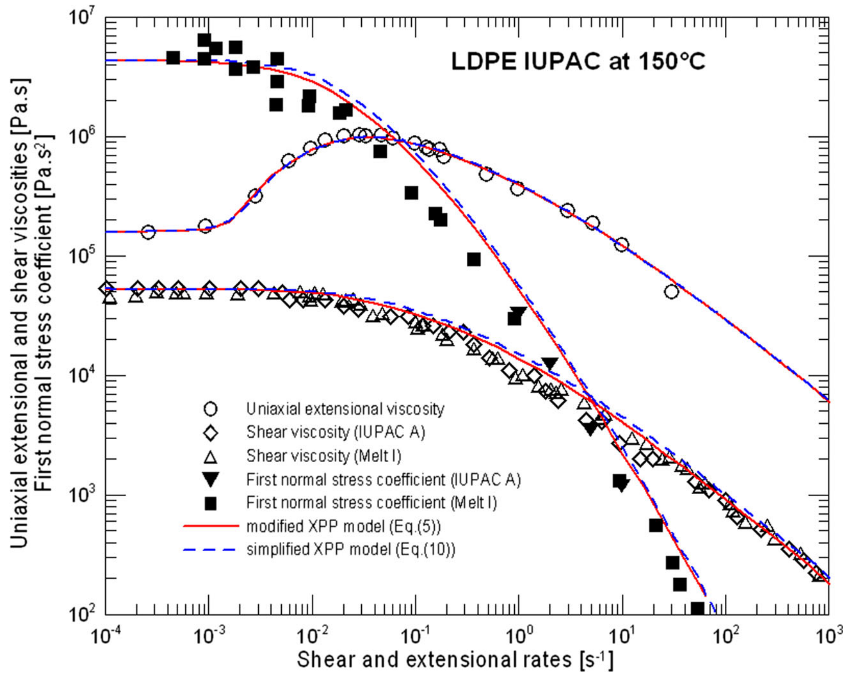


Fig. 2 Comparison between measured steady shear and uniaxial extensional viscosity data and fits/predictions of the modified XPP (Eq. (5)) and simplified XPP (Eq. (10)) models for LDPE IUPAC at 150 °C

The proposed form (5) is the modification of the originally proposed extra function F_{XPP} in Verbeeten [6]

$$F_{\mathrm{XPP}} = 2\frac{\lambda}{\lambda_s}\exp\left[\frac{2}{q}(\Lambda-1)\right]\left(1-\frac{1}{\Lambda}\right)+\frac{1}{\Lambda^2}\left[1-\alpha-\frac{\alpha}{3}\mathrm{tr}\left(\boldsymbol{c}^2-2\boldsymbol{c}\right)\right] \tag{8}$$

After formal setting

$$\alpha = 0, \lambda = \lambda_s, \beta = 2/q \tag{9}$$

Eq.(8) is simplified to

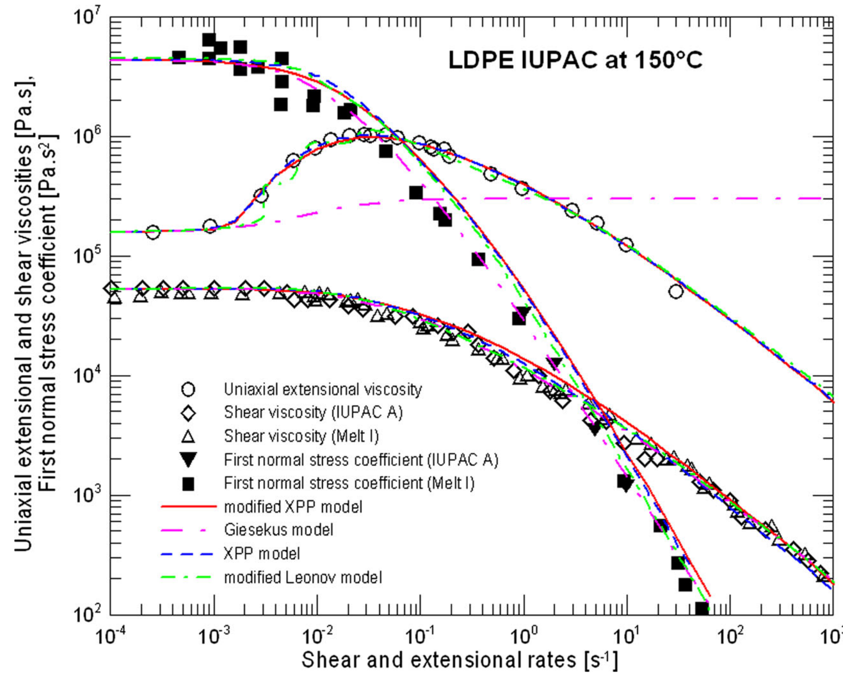
$$F_{\mathrm{simplifiedXPP}} = 2\exp[\beta(\Lambda-1)]\left(1-\frac{1}{\Lambda}\right)+\frac{1}{\Lambda^2} \tag{10}$$

Unlike the parameter q representing a number of arms, β is now supposed to attain any positive number. Both versions of the extra function F (Eqs. (5) and (10)) exhibit formally similar but not equal characteristics (extra function F as a function of stretch characteristic Λ). Nevertheless, a value of β in Eq. (5) is also influenced by stretch

Table 2 Relaxation spectrum and estimated values of the parameters of the the modified XPP, Giesekus, XPP, and modified Leonov models for LDPE IUPAC at 150 °C

	Maxwell parameters		modified XPP	Giesekus	XPP			modified Leonov	
i	λ [s]	G [Pa]	β [−]	α [−]	λ/λ_s [−]	q [−]	α [−]	ζ [−]	ν [−]
1	0.001	152,000	2.5	0.5	5.0	1	0.1	0	0.08
2	0.005	40,050	2.2	0.5	5.0	1	0.1	0	0.08
3	0.028	33,260	2.0	0.5	5.0	1	0.1	0	0.08
4	0.14	16,590	1.7	0.5	4.0	1	0.1	0	0.08
5	0.7	8,690	1.4	0.7	4.0	2	0.05	0	0.08
6	3.8	3,151	1.0	0.7	2.5	3	0.0333	0	0.08
7	20	859.6	0.67	0.4	2.0	4	0.025	0.6	0.005
8	100	128.3	0.26	0.2	1.1	8	0.0125	0.46	0.0015
9	500	1.8495	0.065	0.1	1.1	37	0.027	0.27	6.0

Fig. 3 Comparison between measured steady shear viscosity, uniaxial extensional viscosity, and first normal stress coefficient data and fits/predictions of the modified XPP, Giesekus, XPP, and modified Leonov models for LDPE IUPAC at 150 °C



characteristic Λ due to functional restructuralization of the extra function. Although, the proposed modification (Eq. (5)) and simplified version (Eq.(10)) show the same steady uniaxial extensional viscosity characteristics, the proposed modification exhibits lower steady shear viscosity in nonlinear region, which better corresponds to the measured data (see Fig. 2).

The form of the evolution equation Eq. (7) used in the modified version of the XPP model is the same as in the case of the XPP model (see Table 1), if the Giesekus parameter α is equal to zero (Eq. (9)). Physically, it implies the impossibility to predict the second normal stress difference. The evolution equation (Eq. (7)) together with the stress equation (Eq. (2)) and extra function (Eqs. (5) and (6)) define a complete set of equations of viscoelastic constitutive model. Substituting Eq. (2) into Eq. (7), the CE can be expressed in the term of extra stress tensor

$$\lambda \breve{\boldsymbol{\tau}} + F\boldsymbol{\tau} + G(F-1)\boldsymbol{I} = \lambda G\dot{\gamma} \tag{11}$$

Basic properties of the modified XPP model

The proposed modification involves three parameters per mode (two linear parameters: relaxation time λ and elastic shear modulus G, and one nonlinear parameter β). The relaxation time λ and elastic shear modulus G are usually obtained from oscillatory shear under linear viscoelastic limit (typically $\gamma\approx10^{-2}-10^{-1}$ for polymer melts and solutions). The nonlinear adjustable parameter β affects both shear thinning and

Table 3 Original relaxation spectrum and estimated values of the parameters of the modified XPP, XPP, and modified Leonov models for LDPE Dow LD 150R at 200 °C

	Maxwell parameters		modified XPP	XPP			modified Leonov	
i	λ [s]	G [Pa]	β [−]	λ/λ_s [−]	q [−]	α [−]	ζ [−]	v [−]
1	0.0001	202,935.5	1.5	9.0	1	0.1	0	0.2
2	0.001	110,089.3	2.0	9.0	1	0.1	0	0.2
3	0.01	50,474.2	2.2	9.0	1	0.1	0	0.2
4	0.1	25,026.4	2.5	6.0	1	0.1	0	0.2
5	1	10,621.6	2.8	6.0	1	0.1	0	0.5
6	10	2,779.5	0.9	6.0	1	0.1	1	0.6
7	100	346.3	0.3	1.7	9	0.0111	0.22	0.001
8	1,000	23.3	1.3	9.0	9	0.0111	0	0.001
9	10,000	1.3	3	6.0	10	0.01	0	0.001

Table 4 Recalculated relaxation spectrum and estimated values of the parameters of the modified XPP model for LDPE Dow LD 150R at 200 °C

	Maxwell parameters		modified XPP
i	λ [s]	G [Pa]	β [−]
1	0.0001	244,120	2.5
2	0.00139	111,580	2.8
3	0.01931	47,177.6	2.9
4	0.26827	20,515.2	3.0
5	3.72759	6,018.61	3.0
6	51.7947	759.665	0.33
7	719.686	40.098	0.95
8	10,000	1.46318	3.0

extensional strain hardening. The values of the parameter β are expected to be nonnegative in which case the extra function F can attain its minimum value equal to 1. In the limiting case $F\rightarrow 1_+$, the model is reduced to the upper-convected Maxwell model. If $F\rightarrow 1_+$ and $\lambda\rightarrow 0_+$, the proposed model reduces to the Newtonian one. Steady shear and uniaxial extensional viscosity characteristics of the model in a single mode (λ=1 s, G=1 Pa, β=0.1, 0.316, 1, 3.16, 10, 31.6, 100) are shown in Fig. 1. As can be seen, the parameter β strongly influences both characteristics (shear viscosity—dashed lines, uniaxial extensional viscosity—full lines). Strain hardening is more manifested with decreasing values of the β parameter. On the other hand, an increase in values of the parameter β results in more pronounced shear thinning.

The behaviour of the model under steady state shear and uniaxial elongation flows has been analysed. Simple shear and uniaxial extensional flows are described by the velocity vector $\boldsymbol{v}=(\dot\gamma_0 y,0,0)$ and $\boldsymbol{v}=\left(\dot\varepsilon_0 x,-\frac{1}{2}\dot\varepsilon_0 y,-\frac{1}{2}\dot\varepsilon_0 z\right)$, respectively. For analyzing the steady state behaviour in the shear flow, shear viscosity η $\left(\eta=\tau_{xy}/\dot\gamma_0\right)$, the first ψ_1 and second ψ_2 normal stress coefficients $\left(\psi_1=\left(\tau_{xx}-\tau_{yy}\right)/\dot\gamma_0^{\,2},\psi_2=\left(\tau_{yy}-\tau_{zz}\right)/\dot\gamma_0^{\,2}\right)$ were used. In the case of steady state of the uniaxial extensional flow, extensional viscosity $\eta_E\left(\eta_E=\left(\tau_{xx}-\tau_{yy}\right)/\dot\varepsilon_0\right)$ was used for analysis of the model.

The final set of the model equations in steady simple shear regime is given by

$$\tau_{xy}=\frac{\lambda\dot\gamma_0}{F}\left(\tau_{yy}+G\right), \tag{12}$$

$$\tau_{xx}=\frac{2\lambda\dot\gamma_0}{F}\tau_{xy}-G\left(1-\frac{1}{F}\right),$$

$$\tau_{\rm yy}=\tau_{zz}=-G\left(1-\frac{1}{F}\right)$$

The final form of the material functions is as follows ($\eta_0=\lambda G$):

$$\eta=\frac{\eta_0}{F^2},\psi_1=\frac{2\lambda\eta_0}{F^3},\psi_2=0 \tag{13}$$

As the extra function F (defined by Eqs.(5) and (6)) attains its minimum at one, the maximum of the steady shear viscosity is η_0, and the maximum of the first normal stress coefficient is $2\lambda\eta_0$.

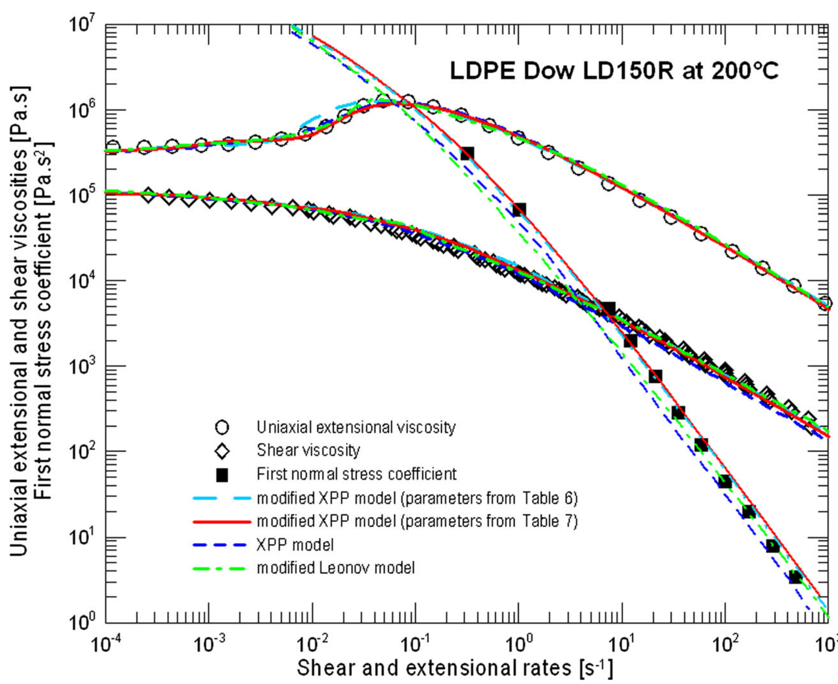


Fig. 4 Comparison between measured steady shear viscosity, uniaxial extensional viscosity, and first normal stress coefficient data and fits/predictions of the modified XPP, XPP, and modified Leonov models for LDPE Dow LD150R at 200 °C

Table 5 Relaxation spectrum and estimated values of the parameters of the modified XPP, XPP, and modified Leonov models for LDPE Escorene LD165BW1 at 200 °C

	Maxwell parameters		modified XPP	XPP			modified Leonov	
i	λ [s]	G [Pa]	β [−]	λ/λ_s [−]	q [−]	α [−]	ζ [−]	ν [−]
1	0.00154	109,430	0.8	2.4	1	0.1	0	0.01
2	0.00633	37,352.6	0.7	2.2	2	0.05	0	0.01
3	0.02602	32,409.3	0.7	2.2	3	0.0333	0	0.01
4	0.10686	15,251.2	0.65	1.8	3	0.0333	0.2	0.008
5	0.43891	11,081.2	0.6	1.8	4	0.025	0.53	0.006
6	1.80281	4,835.09	0.39	1.3	5	0.02	0.6	0.006
7	7.40488	1,986.65	0.38	1.2	6	0.0167	0.5	0.005
8	30.4149	494.69	0.38	1.2	6	0.0167	0.38	0.005
9	124.927	110.156	0.38	1.2	6	0.0167	0.37	0.005
10	513.127	33.3765	0.38	1.1	6	0.0167	0.33	0.005

The final set of the model equations in steady uniaxial extensional flow is expressed by the following:

$$\tau_{xx} = -\frac{G\left(F-2\lambda\dot{\epsilon}_0-1\right)}{F-2\lambda\dot{\epsilon}_0}, \tag{14}$$

$$\tau_{yy} = \tau_{zz} = -\frac{G\left(F+\lambda\dot{\epsilon}_0-1\right)}{F+\lambda\dot{\epsilon}_0}$$

Then, the steady uniaxial extensional viscosity is of the form

$$\eta_E = \frac{3\eta_0}{\left(F-2\lambda\dot{\epsilon}\right)\left(F+\lambda\dot{\epsilon}_0\right)} \tag{15}$$

A value of the steady uniaxial extensional viscosity at low rates $\left(F\rightarrow 1 \text{ and } \dot{\varepsilon}_0\rightarrow 0\right)$ attains $3\eta_0$ thus respecting the Trouton's ratio.

Predictive/fitting capabilities of the modified XPP model

The testing and comparison of the present modification of the XPP constitutive model with the Giesekus, XPP, and modified Leonov models in the steady and transient shear and uniaxial elongational flows is motivated by the following arguments. The Giesekus model uses the same number of parameters (three) per mode as the modified model. The XPP model represents a basis from which the modification was proposed.

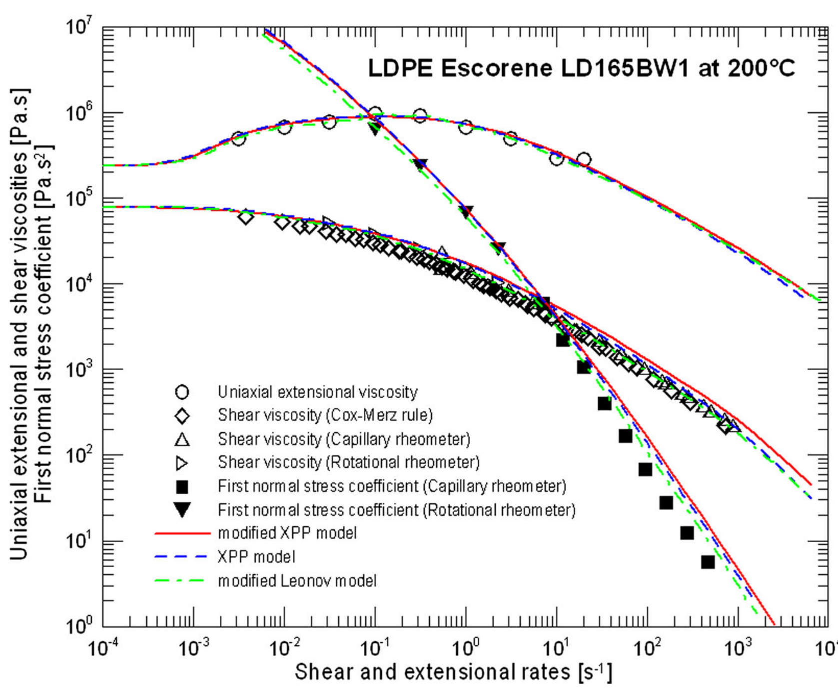


Fig. 5 Comparison between measured steady shear viscosity, uniaxial extensional viscosity, and first normal stress coefficient data and fits/predictions of the modified XPP, XPP, and modified Leonov models for LDPE Escorene LD165BW1 at 200 °C

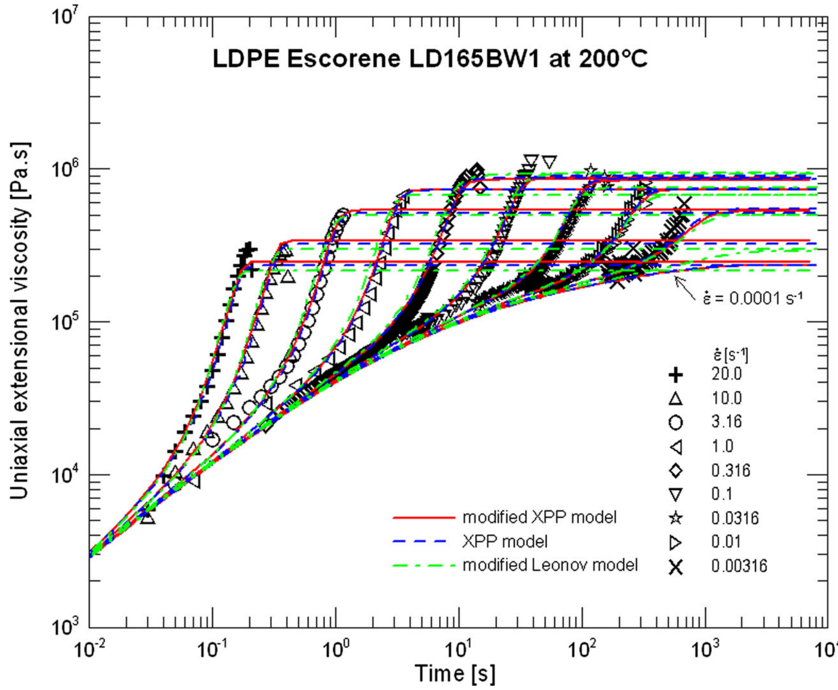


Fig. 6 Comparison between measured transient uniaxial extensional viscosity data and fits/predictions of the modified XPP, XPP, and modified Leonov models for LDPE Escorene LD165BW1 at 200 °C

The modified Leonov model has been chosen for its predictive/fitting capabilities to fit the LDPE materials. For all three LDPE materials, the Giesekus parameter α in the XPP model has been taken as the ratio of $0.1/q$, i.e. the nominal number of five parameters in the XPP model was reduced by this choice to four only (more details on reasons for choosing this value for α are introduced in Verbeeten et al. [6]). This corresponds to a number of parameters (four per mode) used in the modified Leonov model.

For numerical evaluation, the ode15s variable order multistep solver based on the numerical differentiation formulas (NDFs) was applied using the MATLAB software [18]. This solver is based on the backward differentiation formulas (BDFs, also known as Gear's method). For introductory basic orientation, the ode23s one-step solver (based on a modified Rosenbrock formula of order 2) was used.

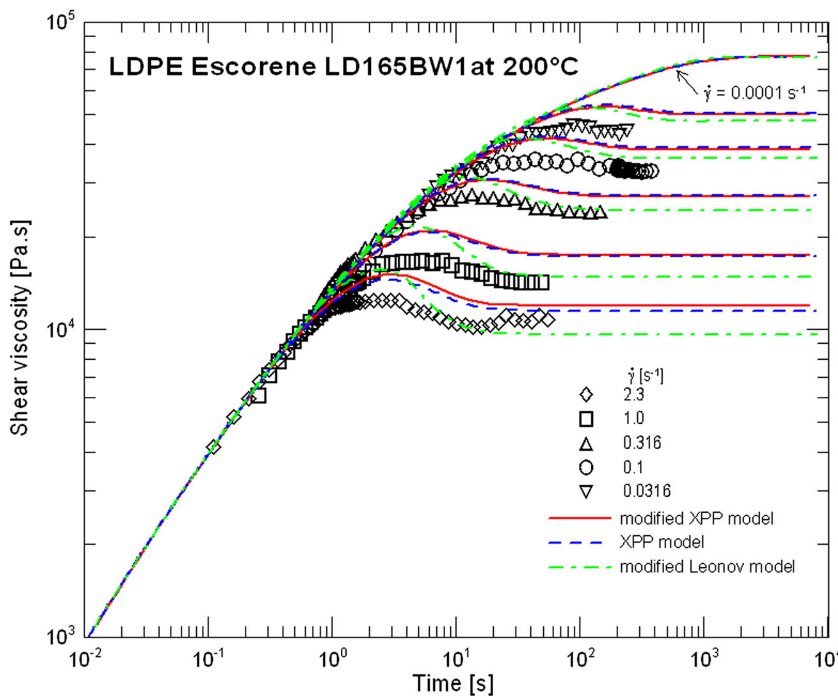


Fig. 7 Comparison between measured transient shear viscosity data and fits/predictions of the modified XPP, XPP, and modified Leonov models for LDPE Escorene LD165BW1 at 200 °C

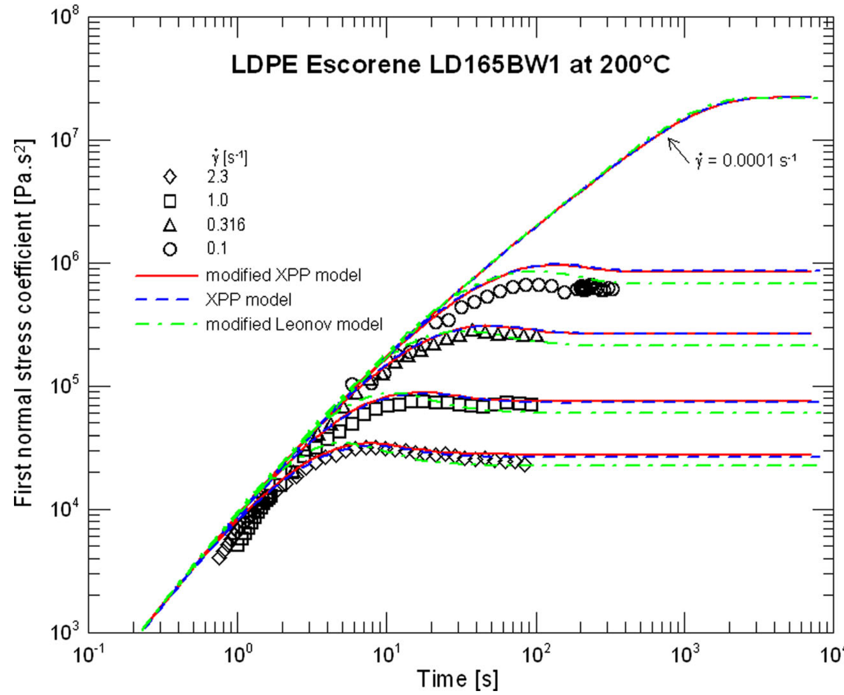


Fig. 8 Comparison between measured transient first normal stress coefficient and fits/predictions of the modified XPP, XPP, and modified Leonov models for LDPE Escorene LD165BW1 at 200 °C

The data (including the relaxation spectra) of three materials introduced below are taken as presented in the respective references. Preference of any subregions (correlated, e.g. with respect to long time and high rates tending to appearance of slip or edge fracture) is beyond the scope of this contribution.

For the materials which exhibit strain hardening behaviour in uniaxial extensional viscosity, no comparison is made with the Giesekus model (nonpredicting such behaviour).

A comparison between the modification of the XPP model and the XPP model with the simplifying relations (Eq.(10)) is documented in Fig. 2.

The LDPE IUPAC (data taken from Verbeeten [16]) has been fitted by the modified XPP, Giesekus, XPP, and modified Leonov models. The nonlinear parameters of the modified XPP (β), XPP ($r=\lambda/\lambda_s$ and q), and modified Leonov (ζ, v) models has been estimated based on fitting the steady uniaxial extensional viscosity. As mentioned above, the Giesekus parameter α of the XPP model is set to $0.1/q$. The estimated values of the models parameters are summarized in Table 2. Figure 3 shows the models fits for the steady uniaxial extensional and shear viscosities, and the first normal stress coefficient.

For relaxation spectra taken from Zatloukal [8] the modified XPP model shows a worse capability to fit the uniaxial extensional viscosity of LDPE Dow LD 150R (Table 3). This inadequacy can be overcome by adding the relaxation time within the interval (100, 1,000). After a recalculation, the corresponding spectrum is presented in Table 4. It can be seen that for an adequate interpretation of the measured data, eight relaxation modes (Table 4) instead of nine (Table 3) are sufficient (see Fig. 4).

Although the second normal stress difference data for LDPE Escorene LD165BW1 is available (Pivokonsky et al. [7]), the Giesekus term α in the XPP model is set to $0.1/q$. There are two reasons for it—the modified model is not able to fit the second normal stress difference data, and a higher value of the Giesekus parameter influences the steady state values of the extensional viscosity in the XPP mode. Table 5 summarizes the estimated parameters of the models. For the predictive/fitting capabilities of the individual models see Figs. 5, 6, 7 and 8.

Conclusions

The proposed phenomenological modification/parameter reduction of the XPP model has been tested in the steady and transient uniaxial extensional and shear flow situations. For testing, the three LDPE materials have been used. The predictive/fitting capabilities of the modified XPP model have been compared with the 3-parameter Giesekus and 4-parameter XPP and modified Leonov models. The number of parameters in the nominally 5-parameter XPP model was reduced to four by setting the Giesekus parameter α to $0.1/q$. The reasons for this were given in the preceding section. It has been found that the modified XPP model is capable of fitting reasonably the rheological properties of LDPE materials, including steady and transient elongational viscosities. However, the proposed 3-parameter modification of the XPP model exhibits higher steady shear viscosity at high strain rates in comparison to the 4-parameter XPP model. On average, evaluating behaviour of three LDPE materials, fitting of all four models is comparable with the exception of strain hardening prediction where the Giesekus model exhibits monotonous behaviour. Nevertheless, the modified XPP model has only one adjustable parameter. On the other hand, the present modification of the XPP model is not capable to predict nonzero second normal stress coefficient. The uniaxial extensional viscosity is predicted well by the present modification (in most cases the extensional viscosity is predicted identically with the XPP model). However, the only situation in which the lack of one parameter (compared with the discussed 4-parameter form of the XPP model and 4-parameter modified Leonov model) is spotlighted, is in the case of a sparsely defined relaxation spectrum at the onset of strain hardening. Then the present modification is not capable of fitting this part of the extensional viscosity with the same quality as the XPP and modified Leonov models. However, when the relaxation spectrum is recalculated as in the case of LDPE Dow LD 150R, the present modification fits the extensional viscosity at the same quality as both above mentioned models. This underlines an importance of analysis which should be given to a sound constitution of discrete relaxation spectrum preceding an application of the chosen differential model. On the other hand, the reduction of free parameters to one (but still permitting modelling of strain hardening) noticeably simplifies an overall approach to evaluation of rheological characteristics and among other things substantially reduces complexity of data processing. Quantitatively, the results obtained are comparable with those obtained by frequently used differential models.

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