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Od Redakcji / Editorial Note

Niniejszy zeszyt „Polimerów" jest poświecony zagadnieniom związanym z reologią polimerów. Zespół Redakcyjny wyraża serdeczne podziękowanie prof. dr. hab. inż. Tomaszowi Sterzyńskiemu za inicjatywę wydania tego zeszytu oraz za cenną pomoc merytoryczną w jego przygotowaniu.

This issue of „Polimery" journal is devoted to problems related to the rheology of the polymers. The editorial team expresses its sincere gratitude to Prof. Dr. Tomasz Sterzyński for the initiative to publish this issue and his valuable and substantial assistance in editorial activities.

Recent advances in modeling of polymer melt rheology

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Abstract: To understand the link between polymerisation of a specific monomer and the product properties, it is extremely helpful to perform a rheological characterization under conditions as close as possible to those occuring in industry. A reliable rheological constitutive equation with as less free parameters as possible is also extremely necessary to reproduce accurately the experimental results obtained for a broad variety of polymer samples at different types of deformations. This allows the establishment of quantitative structure-property relations and permits simulations for specific polymer processes by numerical methods. It is the main objective of the present work to stress the role of rheology in melt processing in the framework of the rheotens experiment, and to give an overview about recent advances in modeling of polymer melt rheology. We discuss grandmastercurves obtained from the rheotens curves, as well as the rupture stress of polymer melts. In the context of rheological constitutive equations, we remind of the limitations of the rubber like-liquid and Doi-Edwards models. The introduction of the interchain tube pressure concept into the molecular stress function (MSF) model is explained. This approach permits to describe quantitatively the transient and steady-state uniaxial viscosities as well as the shear flow response of different nearly monodisperse linear polymers, without any free parameter.

Keywords: rheotens, rheology, constitutive equation, Doi-Edwards tube model, MSF model.

Postęp w modelowaniu reologii stopionych polimerów

Streszczenie: W ocenie zależności między polimeryzacją danego monomeru a właściwościami wytworzonego polimeru, korzystne jest wykorzystanie charakterystyki reologicznej w warunkach możliwie

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najbardziej zbliżonych do występujących w procesie przemysłowym. Aby szczegółowo odwzorować wyniki badań eksperymentalnych, uzyskane dla różnorodnych próbek polimerów przy różnych typach odkształceń, niezbędny jest dobór odpowiedniego konstytutywnego równania reologicznego z jak najmniejszą liczbą parametrów wolnych. Umożliwia to w konsekwencji określenie ilościowych zależności pomiędzy strukturą a właściwościami polimerów oraz symulację numeryczną specyficznych procesów w przepływach polimerów. Celem pracy jest podkreślenie znaczenia pomiarów reologicznych w badaniach procesów przetwórstwa stopionych polimerów, z wykorzystaniem eksperymentu reometrii rozciągającej typu Rheotens, a także zaprezentowanie ostatnich osiągnięć w dziedzinie modelowania reologii stopionych polimerów. Omówiono ogólne krzywe (*grandmastercurves*) wyznaczone na podstawie wyników próby typu Rheotens oraz naprężenie zrywające rozciąganych polimerów w stanie stopionym. Wyjaśniono ograniczenia dotyczące modelu cieczy kauczukopodobnej oraz modelu Doi-Edwardsa w odniesieniu do konstytutywnych równań reologicznych. Określono wprowadzenie koncepcji międzyłańcuchowego ciśnienia rurkowego (*interchain tube pressure*) do modelu funkcji naprężenia molekularnego (MSF). Umożliwiło to dokonanie ilościowego opisu lepkości w przejściowych i ustalonych stanach jednoosiowych oraz ocenę odpowiedzi w przepływie ścinającym, dla różnych polimerów liniowych, w przybliżeniu monodyspersyjnych bez parametrów wolnych.

Słowa kluczowe: Rheotens, reologia, równanie konstytutywne, model rurkowy Doi-Edwardsa, model MSF.

Rheology is the science that studies the deformation and flow of matter. The definition reflects the interdisciplinarity of this field. The present work is restricted to polymer materials which are used to produce plastic products used in daily life. A specific product with well defined properties is based on a polymer with a definite chemical structure. Starting from the monomer, the first step is the production of polymer chains, which are obtained through polymerisation. The type of polymerisation determines the topology of the macromolecules, *i.e.* whether the polymers obtained are linear or contain short or long chain branches, as well as the type of branches to be expected. The topology of the molecules influences their entanglements and consequently the rheological properties. Special interest is paid to the rheological properties in the melt state, because it is in this state that the material is processed (Fig. 1).

A rheological characterization can be performed either in the linear or nonlinear viscoelastic regime, depending on the magnitude of the deformation applied to the sample. The linear viscoelastic limit has been used typically to correlate the storage and loss dynamic modulus with the molecular weight distribution of the sample [1], to investigate the relationship between the equilibrium properties and the molecular structure [2], and to determine the relaxation spectrum of the material [3], which is required for modeling nonlinear phenomena.

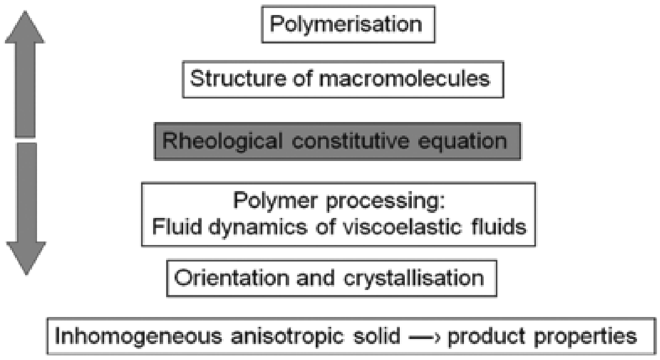

Fig. 1. Schematic describing the link between polymerisation and product properties as well as the role of rheology in understanding structure-property relations

Measurements in the nonlinear viscoelastic regime are intended to understand the influence of the structure, either physical or chemical, on the rheological response. Furthermore, nonlinear viscoelastic phenomena like strain hardening in uniaxial deformation are important effects in polymer processing, like in thermoforming [4, 5], extrusion [6], film casting [7, 8] or film blowing [5]. Thus, experiments performed in the nonlinear regime at different types of deformation are essential to optimize processing techniques [5].

While elongational flow at constant strain rate and constant stress conditions determine well-defined material functions such as tensile stress growth coefficient and tensile creep compliance, constant force elongation represents an important test condition in its own right for polymer melt characterization in relation to processing behavior [9, 10]. Constant force elongation is of great industrial relevance, since it is the correct analogue of steady fiber spinning, as *e.g.* exemplified by the so-called Rheotens test [11—14]. In fiber spinning at constant draw-down force, a material element experiences the same deformation condition in a spatial (Eulerian) reference frame as a material element in constant force elongational flow, *i.e.* fiber spinning is the Eulerian equivalent of Lagrangian constant force elongational flow [15].

Numerical simulations allow understanding more complex processes like induced orientation and crystallization which lead to an inhomogeneous anisotropic material in the solid state, corresponding to the final product properties. For simulating a specific polymer process by numerical methods, *i.e.* fluid dynamics of viscoelastic fluids, it is necessary to have a reliable constitutive equation, with as less free parameters as possible. This equation should reproduce quantitatively experimental results obtained at different types of deformations, for a broad variety of polymers. Therefore, measurements in the nonlinear viscoelastic limit are used also to contrast the data with the performance of different constitutive equations [16].

Figure 1 is a simplification of the reality, but it emphasizes not only the crucial path of a polymer material from the monomer to the product, but also *vice versa*, since this is also a great aim, *i.e.* to have the answer to the question: how to synthesize a specific monomer that should cover specific mechanical properties in a specific final product.

It is the main objective of the present work to stress the role of rheology in melt processing in the framework of the rheotens experiment, and to present an overview about the recent advances in modeling of polymer melt rheology, using the molecular stress function (MSF) model for nearly monodisperse linear samples, which allows obtaining predictions in shear and uniaxial elongation without any free nonlinear parameter.

INFLUENCE OF POLYMER PROPERTIES ON POLYMER PROCESSING: THE RHEOTENS EXPERIMENT

The rheotens experiment is a prototype industrial flow developed by Meissner [11] as a tensile test which, by slowly increasing the drawdown, allows probing a whole set of melt spinning conditions in one test run [17, 18]. The experimental setup for rheotens measurements consists of an extruder (serving as a melt feeder) operated in pressure controlled mode (Fig. 2a). Several dies can be used. The pressure regulating the feedback loop is measured in front of the entry [19]. The polymer strand is extruded continuously and it is taken up by the wheels of the rheotens after a spinline length *L*. The velocity of the wheels increases, drawing down the polymer strand. The resistance of the material against this drawdown is measured by a force balance in the arm onto which the wheels are fixed, leading to an extension diagram, *i.e.* the force as a function of drawdown velocity (Fig. 2b).

The velocity v_s corresponds to the actual die exit velocity of the strand. At higher draw ratios, the experimental curves starts to oscillate, an effect called draw resonance, which is a hydrodynamic instability [12]. The maximum force at rupture is referred to as melt strength, and the maximum velocity, as drawability [19].

As seen from Fig. 3a for low density polyethylene (PE-LD), the measured tensile force F at the take-up is a complicated function of the properties of the polymer melt, the geometry of die entrance, die land and spinline, as well as the processing conditions like the extrusion pressure p, die exit velocity v_0, melt temperature T, and drawdown velocity v.

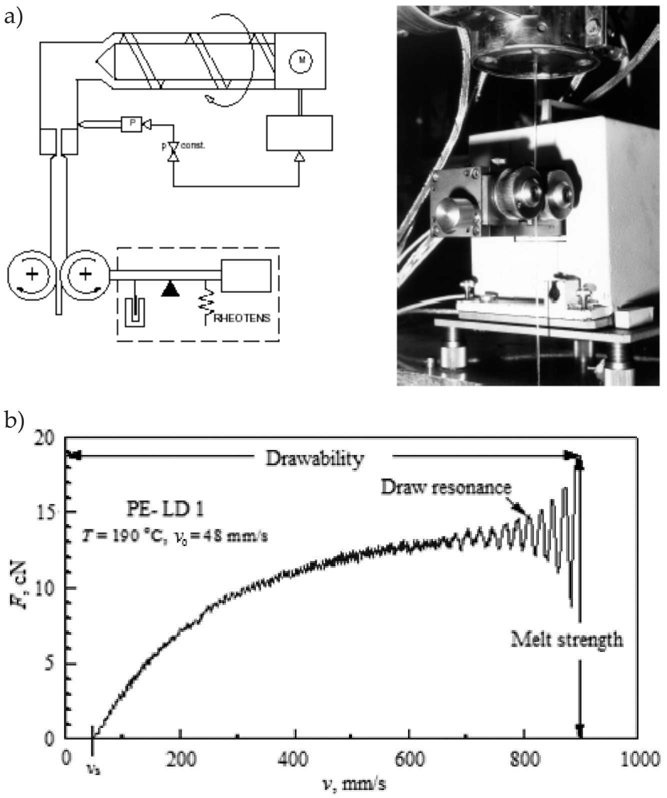

Fig. 2. a) Experimental set-up for rheotens measurements, b) characteristic rheotens curve: melt strength as a function of drawdown velocity (according to [19])

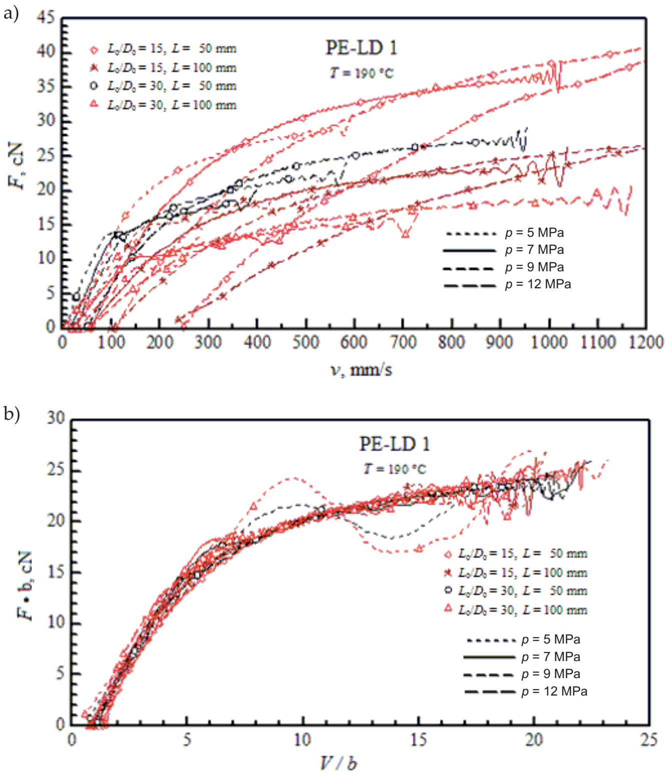

Fig. 3. a) Drawdown force $F(v)$ for melt PE-LD 1, varying the flow rate, die and spinline geometry, b) rheotens grandmastercurve for melt PE-LD 1 (according to [19])

A considerable simplification in the analysis of constant force extension resulted from the discovery of rheotens mastercurves for thermorheologically simple polymer melts: Wagner *et al.* [20, 21] showed that the rheotens test is invariant with respect to changes of melt temperature, and changes of the average molar mass, depending only on the extrusion pressure (or the wall shear stress in the extrusion die) and the relative molar mass distribution of the polymer melt. Rheotens mastercurves provide the rheologically correct basis for a direct and quantitative comparison of the extensibility of polymer melts under processing conditions. Surprisingly, even for rheotens experiments performed at different extrusion pressures, rheotens mastercurves could be found, if force and draw ratio was scaled appropriately [21]. These mastercurves, which represent mastercurves of mastercurves, were termed „rheotens supermastercurves". Considering the draw ratio V, and the draw ratio V_m given as [12]:

$$V = \frac{v}{v_0}, \quad V_m = \frac{v_m}{v_0} \qquad (1)$$

with v_m is the strand velocity at the end of the spinline, it was proposed to shift the measured curves $\sigma(V)$ onto a chosen reference curve characterized by a specific reference draw ratio V_b. This led to the definition of a shift factor b as:

$$b = \frac{V_m}{V_b} \qquad (2)$$

and the so-called rheotens grandmastercurve [12]:

$$bF(V) = \frac{\sigma\left(\frac{V}{b}\right)A_0}{\frac{V}{b}} \qquad (3)$$

with A_0 the cross section of the die. They contain as special cases the rheotens supermastercurves (invariance with respect to changes in mass flow rate or extrusion pressure at constant geometry of die and spinline) and rheotens mastercurves (invariance with respect to changes of temperature and average molar mass of the polymer melt at constant extrusion pressure and constant geometry of die and spinline) as obtained by Wagner *et al.* [20, 21] by use of a more restricted argument, and demonstrated experimentally for several polyethylene melts. Scaling drawdown force F and draw ratio V according to Eq. (3), all 16 rheotens curves coincide on the same force-extension diagram (Fig. 3b) the rheotens grandmastercurve. The different extent of the draw-resonance effect has to be neglected in this comparison, because the magnitude of the draw resonance depends not only on the draw ratio, but also on the absolute velocity. The concept of grandmastercurves in the rheotens experiments is advantageous because material and processing dependence can be separated. Fig. 3a describes the material behavior of constant force extension under quasi-isothermal conditions, meanwhile a graph of b vs. v_0 contains all information on the process dependence of the rheotens test [12].

The rheotens experiment provides a suitable means to evaluate rupture mechanisms and rupture stress, which limit the performance of polymer processes like melt spinning, film blowing, calandering and milling, thermoforming, foam extrusion, blow molding, film casting and extrusion coating, as reviewed by Ghijsels *et al.* [22]. The critical stress is reached at the smallest diameter of the fibre, where the material fails by brittle fracture [22].

The rupture stress σ_B was found to be largely independent of extrusion velocity as well as die and spinline geometry [19]. Figure 4a shows for the case of high density polyethylene PE-HD 1 that σ_B is not temperature dependent. The values of σ_B in Fig. 4a and Fig. 4b were corrected with $\rho \cdot T$ according to Wang and Drda [23], with T_0 being the reference temperature of 190 °C (463 K) and ρ the melt density. The same result was found for linear low density polyethylene PE-LLD 2 (Fig. 4b), except for the

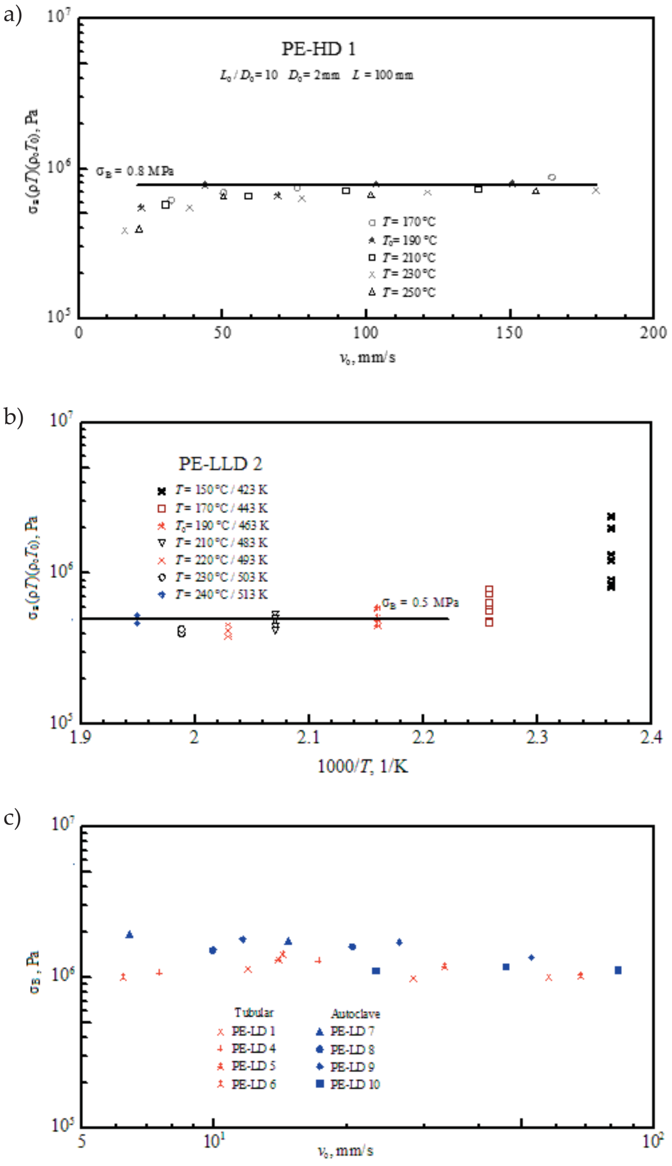

Fig. 4. Rupture stress σ_B as a function of temperature: a) for melt PE-LD 1, b) for melt PE-LLD 2 (crystallization observed at low temperatures), c) for PE-LD melts (comparison of tubular vs. autoclave reactor technology) (according to [19])

crystallization effect which is discernable at low temperatures [19].

Comparing the rupture stress of PE-LD samples produced by tubular and autoclave technologies (Fig. 4c), the autoclave melts show a tendency for a higher rupture stress than the tubular melts, which was interpreted by a higher degree of long chain branching in samples produced by autoclave reactors [19]. A true rupture stress in the range between 1 and 2 MPa was found for all PE-LD melts, meanwhile a considerably lower rupture stress, in the range between 0.5 and 0.6 MPa, was measured for PE-LLD.

FROM QUALITATIVE TO QUANTITATIVE DESCRIPTION OF EXPERIMENTAL DATA: THE RHEOLOGICAL CONSTITUTIVE EQUATION

The constitutive equations considered in this work obey the principle of time-deformation separability, *i.e.* are K-BKZ separable [24, 25], and have the general form:

$$\underline{\underline{\sigma}}(t) = \int_{-\infty}^{t} m(t-t')\underline{\underline{S}}_m(t,t')dt' \tag{4}$$

The are assumed to be factorizable in a time-dependent memory function $m(t-t')$, and in a deformation-dependent general strain measure denoted as $\underline{\underline{S}}_m(t,t')$. The memory function is related to the linear relaxation modulus $G(t-t')$ by:

$$m(t-t') \equiv \frac{dG(t-t')}{dt'} \tag{5}$$

The expression for $G(t)$ depends on the type of material considered. For entangled polymer materials is widely used the generalized Maxwell model [26]:

$$G(t) = \sum_{i=1}^{N} g_i e^{\frac{-t}{\tau_i}} \tag{6}$$

where partial relaxation moduli g_i and relaxation times τ_i form the so-called discrete relaxation spectrum. The general strain measure $\underline{\underline{S}}_m(t,t')$ contains the type of deformation applied to the material. This is the part of the constitutive equation (Eq. 4), where the physical assumptions of a model are reflected to reproduce nonlinear effects, keeping linear viscoelasticity as a limit case. The Rubber-like liquid (RLL) constitutive equation, also known as Lodge equation [24] is recovered if:

$$\underline{\underline{S}}_m(t) = \underline{\underline{C}}_t^{-1}(t') \tag{7}$$

where: $\underline{\underline{C}}_t^{-1}(t')$ — the so-called relative Finger strain tensor.

The Lodge equation is based on the assumption that temporary network strands are deformed affinely with the macroscopic deformation. A severe limitation of this theory is the constant steady-state shear viscosity predicted, leading to an over-prediction of the experimental data with increasing shear rate [27]. Also, the first normal stress coefficient is predicted to be independent of shear rate, the second normal stress function is zero at all shear rates [28, 29], and the strain hardening prediction lies above experimental data as shown in Fig. 5 for the nearly monodisperse polystyrene (PS) data from Bach *et al.* [30].

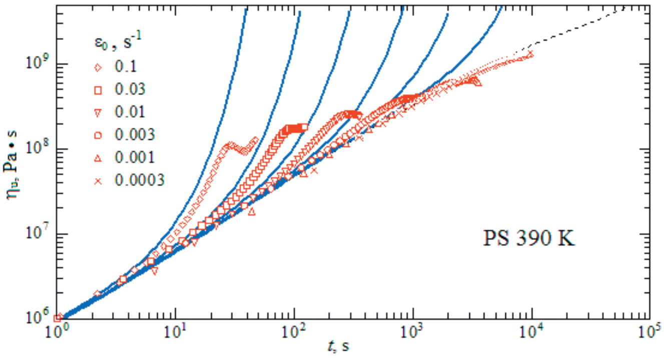

Fig. 5. Comparison of measured elongational viscosity data (symbols) of nearly monodisperse PS melt to predictions of the RLL model (lines). Dotted line indicates η_0*(t)*

It was realized that the lack of quantitative predictions of the RLL model lays in the assumption that the flow has no effect on the rate of disentanglement of network strands. Therefore, the so-called damping function was introduced into the RLL constitutive equation with the objective to account for the change in the structure of the temporary polymer network due to deformation [28]. For a review about this widely used approach, see Rolón-Garrido and Wagner [31].

Another relevant approach is the so-called Doi-Edwards (DE) model [32], which proposes that the molecules in a concentrated system, as in a polymer melt, cannot move freely since the chains cannot pass through each other. A single polymer chain is assumed to be restricted to a tube-like region with a diameter at equilibrium a_0. The central line of such tube is called the primitive path or primitive chain and it is assumed to be in the equilibrium state as a freely jointed chain with step length of the order of the radius of the tube *a*. Although a real polymer is wriggling around the primitive chain, the movement of a chain is basically restricted to occur along the primitive chain causing the constant renewal of the tube. It was further assumed that, the tangent vectors associated to the tube segments deform independently of other parts of the chain. This last hypothesis corresponds to the so-called DE model with the independent alignment (IA) approximation (DE-IA) [32]. The strain measure $\underline{\underline{S}}_{DE}^{IA}$ of this model is given by:

$$\underline{\underline{S}}_m = 5\left\langle \frac{\underline{u}'\underline{u}'}{u'^2} \right\rangle_o = 5\underline{\underline{S}} \equiv \underline{\underline{S}}_{DE}^{IA}(t,t') \tag{8}$$

where: $\underline{u}'\underline{u}'$ — the dyad of a deformed unit vector $\underline{u}' = \underline{u}'(t,t')$,

$$\underline{u}' = \underline{\underline{F}}_t^{-1} \cdot \underline{u} \tag{9}$$

where: $\underline{\underline{F}}_t^{-1} = \underline{\underline{F}}_t^{-1}(t,t')$ — the relative deformation gradient tensor, u' — the length of $\underline{u}'$.

The orientation average is indicated by $\langle ... \rangle_0$:

$$\langle ... \rangle_0 \equiv \frac{1}{4\pi} \oint\int [...] \sin\theta_0 d\theta_0 d\varphi_0 \tag{10}$$

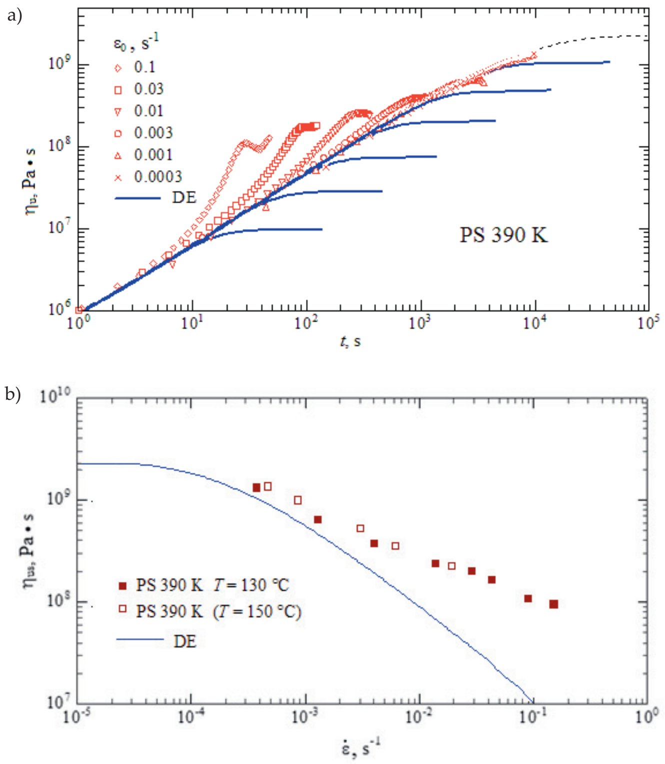

Fig. 6. Comparison of measured (symbols): a) transient elongational viscosity data, b) the corresponding steady state values of nearly monodisperse PS melt to predictions of the DE-IA model (lines). Dotted line indicates $\mu_0(t)$. (Reprinted from [46]. Copyright © 2005, with kind permission from the Society of Rheology)

i.e. an average over an isotropic distribution of unit vectors $\underline{u}$. This model presents as disadvantages an exaggerated shear thinning, no overshoot in the growth of the first normal stress difference after start-up of steady shearing and poor predictions in reversing double-step strains [24]. It has been shown that this model is also unable to predict nonlinear behaviour in general extensional flow of polyisobutylene melt [33]. The transient elongational viscosities, and consequently their steady state values are underpredicted as shown for nearly monodisperse PS melt in Fig. 6a, and Fig. 6b, respectively. Therefore its general performance has been rated as more qualitative than quantitative [24].

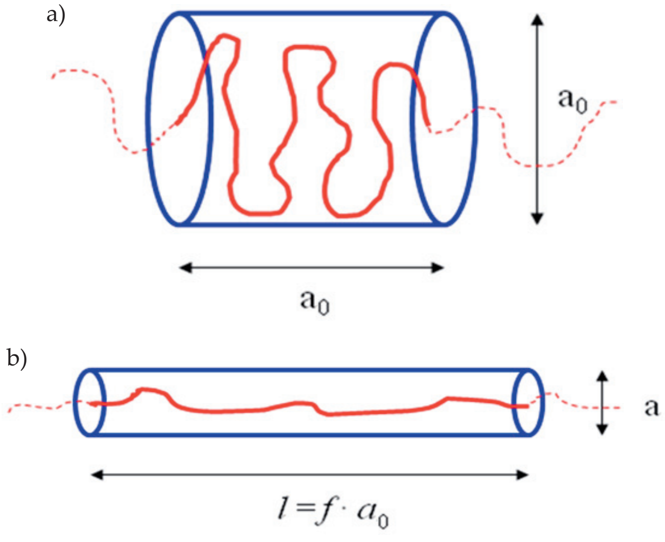

Fig. 7. Tube segment with: a) constant tube diameter as in the DE model, b) decreasing tube diameter as in the MSF model

Due to the lack of reliable quantitative results through the original tube model, it was necessary to reconsider its basic assumptions. The molecular stress function (MSF) model [34—36] is a single tube approach that generalizes the DE model. Meanwhile the DE model considers only orientation of the chain segments and keeps the tube diameter constant at its equilibrium value a_0 (Fig. 7a), the MSF model allows also the chain stretch. Chain stretch is considered as a consequence that the tube diameter decreases from its equilibrium value a_0 to a value a with increasing deformation.

The previous assumptions are originated in the relation between the contour length l of a tube segment with diameter a, in a chain consisting of n links, and b being the effective bond length [32]:

$$nb^2 = la \tag{11}$$

In the case of the DE model $l = a_0$ and the tube diameter remains always the same, *i.e.*, a_0, leading to:

$$nb^2 = a_0^2 \tag{12}$$

as represented in Fig. 7a, but in the MSF model due to the possibility of change in the diameter, Eq. (11) and Eq. (12) lead to:

$$l = \frac{a_0}{a} a_0 = f a_0 \tag{13}$$

where: f — the molecular stress function, defined as:

$$f = \frac{a_0}{a} \tag{14}$$

which is associated indeed with the stretch of the tube segment as illustrated in Fig. 7b.

A further assumption of the MSF model is that the tube diameter is independent of the orientation of tube segments. Under the previously mentioned assumptions, the nonlinear strain measure of the MSF model is given by [34—36]:

$$\underline{\underline{S}}_m = f^2 \underline{\underline{S}}_{DE}^{IA} \tag{15}$$

f^2 is obtained through a material dependent evolution equation. This section is restricted to the quantitative description of nearly monodisperse linear polymers. Nevertheless, the MSF model has been applied to quantify experimental data of a wide variety of materials under different types of deformations and also in numerical simulations. For a review about the MSF model, see [37].

To analyze polymer melts with a linear structure, it could be attractive to use conventional arguments [38, 39], and to assume that the affine deformation of the chain is balanced by a linear spring force, leading to an evolution equation for f, which takes the form [40]:

$$\frac{\partial f}{\partial t} = f(\underline{\underline{\kappa}}:\underline{\underline{S}}) - \frac{1}{\tau_R}(f-1) \tag{16}$$

with the velocity gradient $\underline{\underline{\kappa}}$ and the Rouse relaxation time τ_R of the chain. The Rouse time governs the time scales for the basic chain motions that are involved in all relaxation processes [16] and depends on the molecular characteristics of the polymer like the molar mass M, critical molar mass $\overline{M}_c$, density ρ, and the zero shear viscosity η_0, at a given temperature T through [41—44]:

$$\tau_R = \frac{12M\eta_0}{\pi^2 \rho RT}\left(\frac{M_c}{M}\right)^{2.4} \tag{17}$$

The prediction of the steady state viscosity values is reasonable only at low values of elongational rate, before a catastrophic increase in the predicted values occurs (Fig. 8).

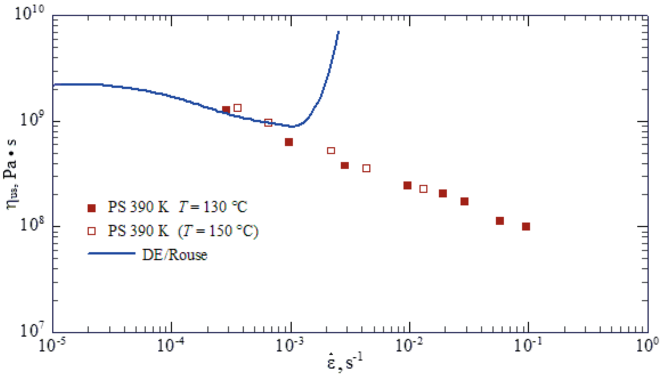

Fig. 8. Comparison of measured (symbols) steady state values of nearly monodisperse PS melt to predictions of the Rouse model, considering the evolution equation (13) (line)

To explain this disagreement, Marrucci and Ianniruberto [45] considered that the thermal pressure exerted by a polymer chain on a box, which has smaller dimensions than the chain, can be calculated to be normal in the x-direction as [32], leading to an evolution equation for the tube diameter that counts for the interchain tube pressure effect given by Marrucci and Ianniruberto [45]:

$$\frac{\partial a}{\partial t} = -\dot{\varepsilon} a + \frac{a_0}{\tau_a}\left(\frac{a_0^3}{a^3} - 1\right) \tag{18}$$

where τ_a has been called the tube-diameter relaxation time, representing the relaxation of the topological constraints caused by the many surrounding chains [46].

Generalizing the first term of Eq. 18 and using the property (Wagner et al. 2005b):

$$\frac{\partial a}{\partial t} = -a_0 \frac{1}{f^2}\frac{\partial f}{\partial t} \tag{19}$$

an evolution equation for the MSF model was proposed with the form [46]:

$$\frac{\partial f}{\partial t} = f\left(\left(\underline{\underline{\kappa}}:\underline{\underline{S}}\right) - \frac{1}{\tau_a} f\left(f^3 - 1\right)\right) \tag{20}$$

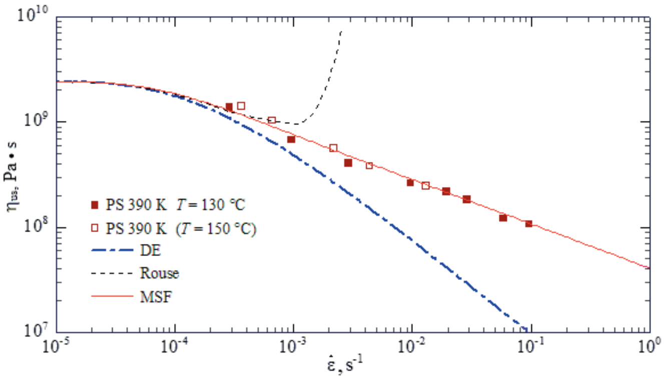

Fig. 9. Comparison of measured (symbols) steady state values of nearly monodisperse PS melt to predictions of the Rouse (dotted line), DE (dashed dotted line), and MSF (continuous line) models

The first term on the right hand side of Eq. (20) describes affine chain stretch and the second term represents the interchain tube pressure contribution. As shown in Fig. 9, the steady state elongational viscosity is in excellent agreement with the data, considering the value of the tube diameter relaxation time fitted to τ_α = 1462 s [46].

Even with the success of describing transient and steady-state elongational viscosities [46], or birefringence experiments [47], the question of the molecular origin of the tube diameter relaxation time was still an issue. Equation 20 was later rewritten as [47]:

$$\frac{\partial f}{\partial t} = f\left(\underline{\underline{\kappa}}:\underline{\underline{S}}\right) - \frac{f-1}{\tau_a}\left[3 + 9(f-1) + 10(f-1)^2 + 5(f-1)^3 + (f-1)^4\right] \tag{21}$$

It is obvious that in the first order of the stretch, *i.e.* for $f - 1 < 1$, Eq.(21) reduces to the classical relation (16) with:

$$\frac{\partial f}{\partial t} = f\left(\underline{\underline{\kappa}}:\underline{\underline{S}}\right) - \frac{f-1}{\tau_a / 3} \tag{22}$$

i.e. in the limit of small stretch, the tube diameter relaxation time τ_a of the melt was identified to be:

$$\tau_a = 3\tau_R \tag{23}$$

This is an important result. However, in view of the fact that in the case of small chain stretch, tube segment length and tube diameter are nearly equal, and therefore the effect of the chain pressure on the tube wall corresponds to the tension along the chain, this result is not as surprising as it may seem at first. It was further argued that chain stretch is balanced simultaneously and additively by two restoring tensions with weights of 1/3 in the longitudinal direction, and 2/3 in the lateral direction, leading to [40]:

$$\frac{\partial f}{\partial t} = f\left(\underline{\underline{\kappa}}:\underline{\underline{S}}\right) - \frac{f-1}{3\tau_R}\left[1 + \frac{2}{3} f^2\left(f^2 + f - 1\right)\right] \tag{24}$$

To demonstrate the validity of the stretch evolution equation based simultaneously on interchain pressure and Rouse relaxation (Eq. 24), the data of Bach *et al.* [30] were analyzed. Figures 10a and 10b present comparisons

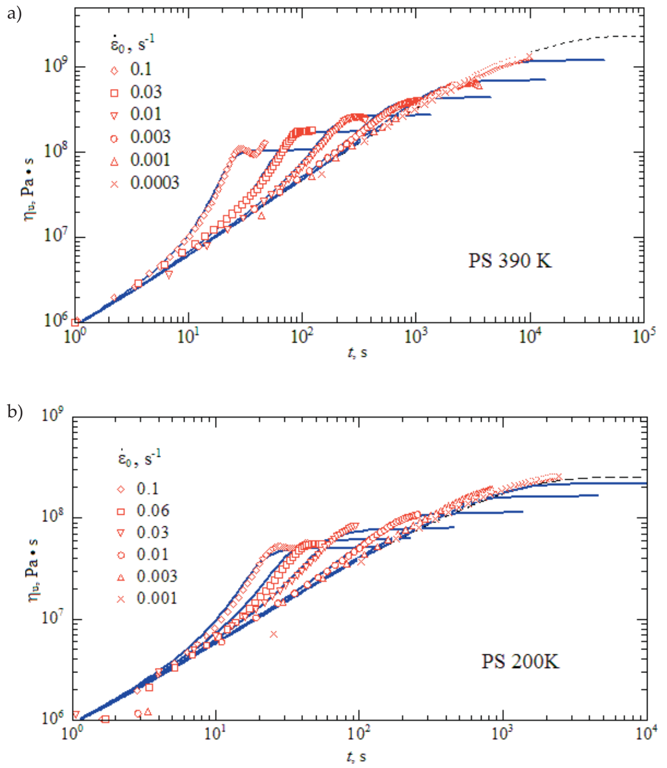

Fig. 10. Comparison of measured transient elongational viscosity data (symbols) to predictions (full lines) by MSF model with stretch evolution equation (23) for: a) PS 390K, b) PS 200K. Dotted line indicates $\mu_0(t)$. (Reprinted from [46]. Copyright © 2005, with kind permission from the Society of Rheology)

of the transient elongational viscosity data for PS 390K and PS 200K. The Rouse times τ_R being calculated with Eq. (17), giving τ_R = 329 s for PS 390K and τ_R = 91.5 s for PS 200K. The time-dependent increase as well as the plateau value of the elongational viscosities is seen to be in excellent agreement for both PS samples with the predictions of the stretch evolution equation (25). It should be noted that this agreement is achieved by use of a single material parameter, the Rouse stretch relaxation time τ_R, which is determined by the molecular characteristics of the polymer and is obtained from linear viscoelasticity.

Equation 24 has also been applied with the same success to describe shear flow experiments (Fig. 11) of two polybutadiene solutions (PBD), four SBR melts, four polyisoprene (PI) melts as well as not only the transient shear viscosity, but also the first and second transient normal stress differences of a PS melt [40, 48].

As expected, the shear stress data (Fig. 11a) confirm a negative deviation from the linear-viscoelastic start-up prediction, which is the stronger the higher the shear rate applied, *i.e.* the melts show strong shear thinning. A maximum in the shear viscosity data is also revealed, before the shear thinning itself occurs (Fig. 11b). These features are described remarkably well by the MSF model, and general agreement between experimental data and predictions of the MSF model was observed for the samples considered, and for a wide range of shear rates.

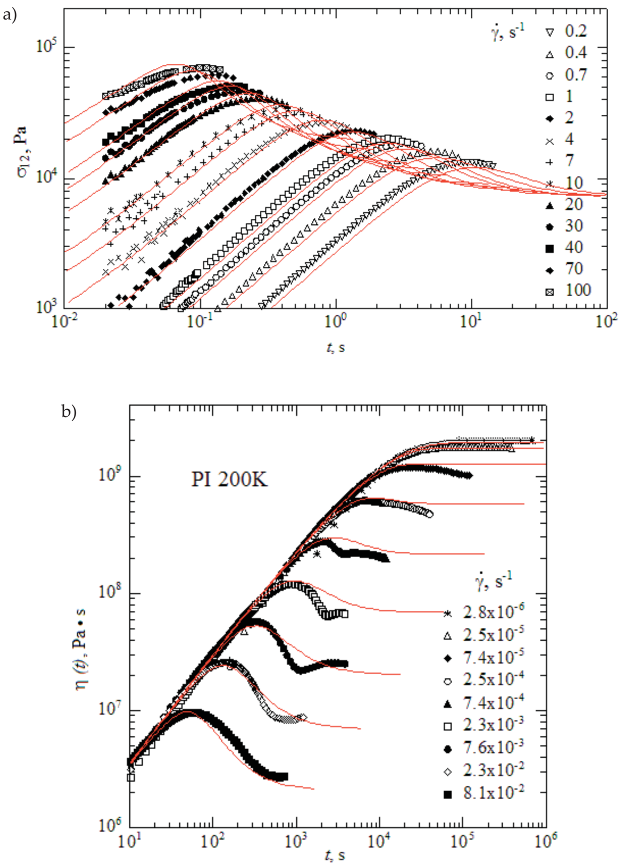

Fig. 11. Comparison of measured transient shear viscosity data (symbols) of: a) PBD — 15 K solution 1 M (15 %) with a τ_R = 1.25 s, b) PI 200K with a τ_R = 173 s at T = 23 °C to predictions (full lines) by MSF model with stretch evolution equation (21). Dotted line indicates $\eta_0(t)$

CONCLUSIONS

The role of rheology in melt processing has been demonstrated by considering the rheotens experiment. The rheotens experiment has been shown to be appropriate to assess the elongational behaviour of polymer melts under conditions which are relevant for typical industrial processing applications. The existence of rheotens grandmastercurves simplifies the description of material behaviour in the spinline. Furthermore, it is possible to characterize clearly the rupture behavior of polymer melts.

Substantial progress has been made in the area of constitutive equations for polymer melts rheology as exemplified by the molecular stress function (MSF) model for nearly monodisperse linear samples, which is based on the tube model. The analysis of experimental data in elongational and shear flow of monodisperse linear samples clearly demonstrated that the tube, *i.e.* the confinement of a test chain, is characterized by the orientation in the direction along the tube, and the diameter of the tube in the lateral dimension. Chain stretch is associated with a reduction of the tube diameter, which is balanced by a linear spring force in the longitudinal direction and a nonlinear interchain pressure in the lateral direction, both of which are governed by the Rouse time of the chain. Thus, the MSF model is able to quantify nonlinear extension and shear rheology of monodisperse linear polymer melts exclusively based on linear-viscoelastic characterization.

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