

Constitutive equations for polymer melts and rubbers: Lessons from the 20th century

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Abstract

Refinements of classical theories for entangled or crosslinked polymeric systems have led to incommensurable models for rubber networks and polymer melts, contrary to experimental evidence, which suggests a great deal of similarity. Uniaxial elongation and compression data of linear and branched polymer melts as well as of crosslinked rubbers were analyzed with respect to their nonlinear strain measure. This was found to be the result of two contributions: (1) affine orientation of network strands, and (2) isotropic strand extension. Network strand extension is caused by an increasing restriction of lateral movement of polymer chains due to deformation, and is modelled by a molecular stress function f , which in the tube concept of Doi and Edwards is the inverse of the relative tube diameter. Up to moderate strains, f^2 is found to be linear in the average stretch for melts as well as for rubbers, which corresponds to a constant tube volume. At large strains, rubbers show maximum extensibility, while melts show maximum molecular tension. This maximum value of the molecular stress function governs the ultimate magnitude of the strain-hardening effect of linear and long-chain branched polymer melts in extensional flows.

1. Introduction: Classical Theories

Modelling a flexible macromolecule as a linear array of a large number of point masses connected by freely-jointed links has been a basic feature of any kinetic theory relating stress and strain of polymeric materials. A rubber consists of a single coherent network of flexible macromolecules, which are crosslinked at certain isolated points along the molecular chains. If intermolecular interaction between network strands and intramolecular interaction along a strand are neglected, and if crosslinks are assumed to move affinely with the macroscopic deformation, kinetic theory leads to the classical stress-strain relation for a rubber:

$$\boldsymbol{\sigma}(t) = -p\mathbf{E} + G_{\infty}\mathbf{C}_T^{-1}(t_0) \quad (1)$$

$\boldsymbol{\sigma}$ is the stress tensor, p the isotropic pressure, \mathbf{E} the unit tensor, G_{∞} the small-strain equilibrium shear modulus, which is given by

$$G_{\infty} = kTN \quad (2)$$

(k is Boltzmann's constant, T the absolute temperature, and N the number of strands in unit volume). $\mathbf{C}_T^{-1}(t_0)$ is the Finger strain tensor relating the deformed state at time t to the undeformed state at time t_0 .

Classical network theory is well suited to explain elasticity of elastomers qualitatively. Quantitatively, however, mechanical behaviour of real systems of crosslinked polymer chains is influenced by intermolecular interactions: The number of possible conformations available to network strands is reduced due to topological constraints. This "entanglement" contribution to the entropic force does not only determine the time dependence of the transient part of the stress, it also affects the relationship between equilibrium stress and strain, and invalidates the simple proportionality of eq. (2) between the small strain equilibrium shear modulus, G_{∞} , and the number of network strands in unit volume, N .

Elastic recovery of polymer melts can be as high as recovery of crosslinked elastomers (Wagner and Meissner, 1980). Polymer melts are viscoelastic liquids and do not possess permanent crosslinks. Therefore all entropic elasticity has to be attributed to the action of "entanglements". Temporary junction network theories (Green and Tobolsky, 1946; Yamamoto, 1956; Lodge, 1956) were the first to explain elasticity of rubberlike liquids. They model entanglements as physical junctions defined by "two points of two molecular chains moving together for at least a certain minimum length of time greater than the fluctuation period which is needed for the molecular chains to pass through almost all of their thermodynamic states". If the further assumptions are made that creation and decay mechanisms of network strands are not affected by flow, the rubberlike-liquid constitutive equation is obtained (Lodge, 1956):

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$$\sigma(t) = -p\mathbf{E} + \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} \mathbf{C}_t^{-1}(t') dt' \quad (3)$$

$G(t)$ is the linear-viscoelastic shear relaxation modulus. Again, many aspects of viscoelasticity are explained qualitatively by the rubberlike-liquid constitutive equation, while its strain measure fails quantitatively at higher strains, indicating that the entanglement structure of the temporary junction network is strain dependent (Wagner and Meissner, 1980; Wagner, 1976).

The equivalence of the strain measure in eqs. (1) and (3) is evident, and indeed eq. (1) is comprised in eq. (3) as long-time limit with

$$\lim_{t \rightarrow \infty} G(t) = G_{\infty} \quad (4)$$

The origin of the "universality" of this particular strain measure for rubbers and polymer melts can be traced back to the freely-jointed chain with neglect of molecular interactions except at isolated (permanent or temporary) junctions. Later refinements of molecular theory have resulted in mutually exclusive models for rubber networks and polymer melts, and we will consider just a few examples which are of relevance here.

2. Theories from Continuum Mechanics and Their Microscopic Equivalents

Eq. (3) can be generalized by continuum mechanics arguments to

$$\sigma(t) = -p\mathbf{E} + \int_{-\infty}^t \dot{m}(t-t') \mathbf{S}_t(t') dt' \quad (5)$$

which preserves the experimentally well documented separability of time and deformation (Wagner, 1976; Laun, 1978; Wagner and Laun, 1978), and is sometimes called a separable Rivlin-Sawyers equation (Larson, 1988). In terms of continuum mechanics, the nonlinear strain measure \mathbf{S} can be expressed by

$$\mathbf{S} = h_1(I_1, I_2) \mathbf{C}^{-1} + h_2(I_1, I_2) \mathbf{C} \quad (6)$$

as a linear combination of the Finger strain tensor \mathbf{C}^{-1} and the Cauchy strain tensor \mathbf{C} , where the dependence on the observation time t and the past time t' is taken for granted. The strain functions h_1 and h_2 depend on deformation via the first and second invariant I_1 and I_2 of the Finger strain tensor. In the limit of $h_1 = 1$, $h_2 = 0$, eq.(5) reduces to the rubberlike-liquid constitutive equation of Lodge, eq. (3). If the strain functions h_1 and h_2 can be derived from a strain energy function, eq. (5) is referred to as being of the K-BKZ type (Kay, 1962; Bernstein and co-workers, 1963). If h_1 and h_2 are assumed to be constants, eq. (5) in the long-time limit is equivalent to the well-known Mooney-Rivlin equation:

$$\sigma(t) = -p\mathbf{E} + 2C_1 \mathbf{C}_t^{-1}(t_0) - 2C_2 \mathbf{C}_t(t_0) \quad (7)$$

In microscopic terms, stress in polymeric systems originates from extension of entropic springs, which can be thought of e.g. representing molecular strands between entanglements. An isotropic distribution of molecular strands normalized with respect to their equilibrium length can be described by an isotropic distribution of unit vectors \mathbf{u} . Assuming affine deformation, the inverse deformation gradient \mathbf{F}^{-1} transforms a unit vector \mathbf{u} into a deformed vector \mathbf{u}' ,

$$\mathbf{u}' = \mathbf{F}^{-1} \cdot \mathbf{u} \quad (8)$$

The Finger strain tensor can then be expressed as

$$\mathbf{C}^{-1} = 3 \langle \mathbf{u}' \mathbf{u}' \rangle \quad (9)$$

$\langle \dots \rangle$ denotes an integral over an isotropic distribution of unit vectors before deformation,

$$\langle \dots \rangle = \frac{1}{4\pi} \int \dots d\Omega \quad (10)$$

where $d\Omega$ is an infinitesimal solid angle, and the integration is over the surface of a unit sphere.

A similar scheme can be used to find a microscopic representation of the Cauchy strain tensor \mathbf{C} . If \mathbf{n} represents an isotropic distribution of unit surfaces, and if these are assumed to be deformed affinely, the deformation gradient \mathbf{F} transforms a unit surface vector \mathbf{n} into the deformed surface vector \mathbf{n}' ,

$$\mathbf{n}' = \mathbf{n} \cdot \mathbf{F} \quad (11)$$

The Cauchy strain tensor \mathbf{C} can then be expressed as

$$\mathbf{C} = 3 \langle \mathbf{n}' \mathbf{n}' \rangle \quad (12)$$

Considering further that the invariants I_1 and I_2 are equivalent to

$$I_1 = 3 \langle u'^2 \rangle \quad (13)$$

$$I_2 = 3 \langle n'^2 \rangle \quad (14)$$

where u' and n' are the length of the vector \mathbf{u}' and \mathbf{n}' respectively,

$$u' = \sqrt{\mathbf{u}' \cdot \mathbf{u}'} \quad (15)$$

and

$$n' = \sqrt{\mathbf{n}' \cdot \mathbf{n}'} \quad (16)$$

the strain measure \mathbf{S} of eq.(6) can be expressed in

microscopic terms as

$$\mathbf{S} = H_1(\langle u'^2 \rangle, \langle n'^2 \rangle) \langle \mathbf{u}'\mathbf{u}' \rangle + H_2(\langle u'^2 \rangle, \langle n'^2 \rangle) \langle \mathbf{n}'\mathbf{n}' \rangle \quad (17)$$

where the strain functions H_1 and H_2 converge to $H_1+H_2=3$ in the linear-viscoelastic limit (Wagner and co-workers, 1998).

3. Modelling Topological Constraints

While eq. (17) expresses the strain measure \mathbf{S} of eq. (6) in terms of the primitive quantities \mathbf{u} and \mathbf{n} , it is by no means guaranteed that this is the most appropriate representation of the strain measure when taking into account topological constraints of the macromolecular chains.

The kinetic theory of Doi and Edwards (1978) models intermolecular interaction for concentrated systems of monodisperse linear polymer chains by the tube concept: The mesh of constraints caused by surrounding chains confines the molecular chain laterally to a tubelike region. Relaxation occurs by two mechanisms: "chain retraction" by equilibration along the tube contour, and "chain diffusion" by reptation out of the tube. As chain retraction is fast compared to chain diffusion, this model explains naturally the experimentally observed time-deformation separability of the nonlinear relaxation modulus for times greater than the equilibration time.

Assuming that the diameter of the tube is not changed by deformation, or equivalently that the tension in the deformed polymer chain is equal to its equilibrium value, Doi and Edwards derived (by use of the independent alignment assumption IAA) a single integral constitutive equation of the form

$$\boldsymbol{\sigma}(t) = -p\mathbf{E} + 5 \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} \langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \rangle dt' \quad (18)$$

As shown by Doi and Edwards, the strain measure in eq. (18) can be expressed in terms of eq. (6); however, the resulting strain functions h_1 and h_2 are not analytic functions of the strain invariants. The Doi-Edwards (IAA) strain measure is equivalent to the second rank orientation tensor.

For monodisperse polymer solutions, the Doi-Edwards strain measure seems to give an acceptable description of material behaviour in step-shear experiments. For polydisperse linear and branched polymer melts, on the other hand, although time-deformation separability often works over most or even the entire (experimentally attainable) time range, the measured stresses in shear and extensional flows are often much higher than predicted by the Doi-Edwards strain measure (Wagner, 1980; Leblans and Scholtens, 1987; Larson, 1988; Wagner, 1990).

Marrucci (1979) and Graessley (1982) extended the tube idea of Doi and Edwards to crosslinked systems. By

assuming equilibration of tension in the network strands between crosslinks, they derived the following stress-strain relation for rubbers:

$$\boldsymbol{\sigma} = -p\mathbf{E} + \frac{15}{4}G_{\infty} \langle \frac{\mathbf{u}'\mathbf{u}'}{u'} \rangle \quad (19)$$

However, the difference between eqs. (1) and (19) is much too small to account for the observed experimental deviations from classical stress-strain behaviour. It is obvious that the strain measures of eqs. (18) and (19), although based on the same physical principle, predict different strain dependences and are mutually exclusive for either polymer melts or rubbers, respectively.

Flory and Erman (1977; 1978) assume that junction fluctuations are restricted by neighboring chains, which confine junctions initially to spherical domains. Upon deformation, these domains are transformed into ellipsoids, and junction fluctuations become anisotropic. By use of a parameter k , which is a measure of the severity of entanglement constraints on junctions, deviations of real rubber networks from the stress-strain relation of eq. (1) can be fitted successfully. It is obvious that this theory which restricts itself to permanent networks with fixed cycle rank and does not consider time dependence, cannot be generalized in any simple way to comprise both rubbers and polymer melts.

In the model of Ball, Doi, Edwards, and Warner (1981) for rubber elasticity, slip links provide a sliding contact between polymer chains. By use of a parameter h , which is a relative measure of freedom of a slip link to slide, stress-strain relations of real networks can be fitted successfully (Thirion and Weil, 1984; Edwards and Vilgis, 1986; Brereton and Klein, 1988). Again, this model is restricted exclusively to crosslinked rubbers.

Thus, refinements of the classical theory have led to incommensurable models for rubber networks and polymer melts. On the other hand, experimental evidence suggests a great deal of similarity between material behaviour of rubbers and polymer melts. The most dramatic single point of similarity is large elastic recoil as already mentioned; others are:

(1) time-deformation separability, which is observed by rubbers (Smith, 1962; Tsuge *et al.*, 1978; Scholtens and Leblans, 1986) and polymer melts (Laun, 1978; Wagner and Laun, 1978; Wagner, 1978; Raible *et al.*, 1982), and which allows the experimental determination of strain measures (Smith, 1962; Wagner, 1978; Wagner and Demarmels, 1990);

(2) irreversible strain effects in polymer melts (Wagner and Stephenson, 1979; Wagner *et al.*, 1998) and in rubbers (Roland, 1989);

(3) similar strain measures for polymer melts and rubber networks: in uniaxial elongation for both melts and rubbers the classical strain measure of eq. (1) represents the upper

limit, and the Doi-Edwards strain measure of eq. (18) the lower limit (Wagner, 1980; Leblans and Scholtens, 1987).

In the following, we will first concentrate on the similarities of strain measures for polymer melts and rubbers. We restrict attention to increasing uniaxial elongation and compression (which is equivalent to equibiaxial extension) starting from the isotropic, stress-free state, and compare the experimentally determined strain measures of polymer melts and crosslinked rubbers. We will then present a generalized strain measure for melts and rubbers, and discuss shortly its dependence on crosslink density, before we consider some more recent developments.

4. Mooney Stress and Damping Function for Rubbers and Melts

For uniaxial elongation (extension ratio $\lambda > 1$) and compression ($\lambda < 1$) at constant volume, classical rubber elasticity theory, eq. (1), predicts a true stress $\sigma_t = \sigma_{11} - \sigma_{33}$,

$$\sigma_t = G_\infty \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (20)$$

To emphasize deviations of material behaviour from eq. (20), it is customary to define a Mooney stress (or reduced stress) σ_M

$$\sigma_M = \sigma_t / \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (21)$$

and to present elongation and compression data as Mooney-Rivlin plots (Mooney stress σ_M versus $1/\lambda$).

Similarly, in polymer melt rheology, damping functions are used to assess deviations from the rubberlike-liquid strain measure C_t^{-1} (Wagner, 1976). For relaxation experiments in elongation/compression, the damping function h is defined as

$$h = \frac{\sigma_{11} - \sigma_{33}}{G(t) \left(\lambda^2 - \frac{1}{\lambda} \right)} = \frac{\sigma_M}{G(t)} \quad (22)$$

Note that due to time-deformation separability, h can also be calculated from constant strain-rate start-up flows (Wagner, 1978; Wagner, 1979).

From the definition of the damping function for uniaxial elongation/compression, eq. (22), it is obvious that h can be considered as Mooney stress normalized by the linear-viscoelastic shear relaxation modulus. The damping function approach can be applied to both polymer melts and rubbers. If the equilibrium stress is measured for a rubber, the corresponding modulus is G_∞ .

Forty years of research into the elongation/compression behaviour of rubbers are summarized in Fig. 1, where the damping function h , i.e. the Mooney stress σ_M normalized by the small-strain equilibrium shear modulus G_∞ ,

$$h = \frac{\sigma_M}{G_\infty} \quad (23)$$

is presented for several rubber networks crosslinked in bulk (Wagner and Schaeffer, 1993). Contrary to customary Mooney-Rivlin plots, a logarithmic scale is used to ensure equal representation of elongation and compression data. Data (symbols) are for a randomly crosslinked natural rubber (Rivlin and Saunders, 1951), two randomly crosslinked PDMS networks (Pak and Flory, 1979), and three endlinked PDMS networks (Xu and Mark, 1990). It is obvious from Fig. 1 that within experimental scatter, the strain data of these six different rubber networks superimpose. For elongation, the data can be approximated by a (normalized) Mooney-Rivlin equation,

$$h = \left(2C_1 + \frac{2C_2}{\lambda} \right) / G_\infty \quad (24)$$

with $2C_1 = 0.55 G_\infty$ and $2C_2 = 0.45 G_\infty$ (broken line in Fig. 1). As is well known this approximation fails in

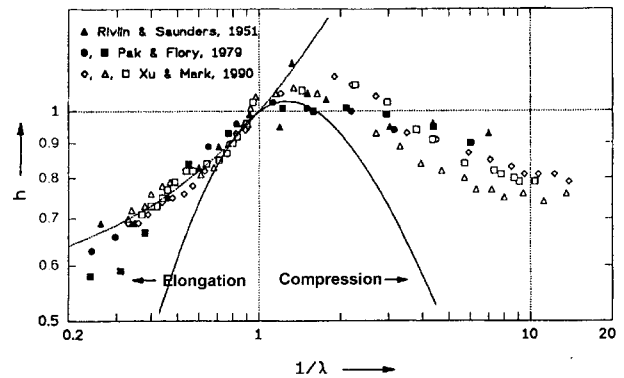


Fig. 1. Normalized Mooney stress $h = \sigma_M / G_\infty$ of several cross-linked rubbers (symbols) as a function of inverse extension ratio $1/\lambda$. Broken line is given by normalized Mooney-Rivlin equation (24). Solid line represents Doi-Edwards damping function from eq. (18) in elongation and compression.

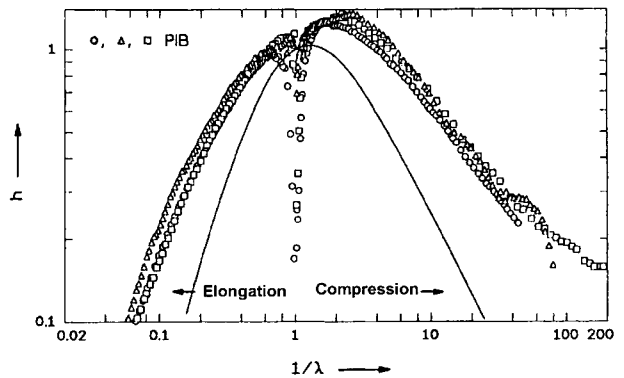


Fig. 2. Damping function of PIB melt (symbols) as a function of inverse extension ratio $1/\lambda$. Solid line represents Doi-Edwards damping function from eq. (18) in elongation and compression.

compression, where the data show a maximum in the damping function at $\lambda \approx 0.5$. Also shown in Fig. 1 is the Doi-Edwards strain measure (line) from eq. (18). Note that although the Doi-Edwards damping function fails quantitatively, its general shape is in qualitative agreement with the data.

The strain dependence of a well characterized polyisobutene (PIB) melt as measured by Demarmels and Meissner (1985; 1986) was analyzed by Wagner and Demarmels (1990), and Wagner and Schaeffer (1992). In Fig. 2, the damping function h for uniaxial elongation and compression of this PIB is plotted as a function of $1/\lambda$ (symbols). The data were converted from Hencky strain ϵ to extension ratio λ by the relations $\lambda = \exp(\epsilon)$ (elongational strain ϵ) and $\lambda = \exp(-2\epsilon)$ (equibiaxial strain ϵ) respectively. Also shown in Fig. 2 is the Doi-Edwards damping function, which again fails quantitatively to describe the data (Wagner, 1990).

5. A Generalized Strain Measure for Extension of Melts and Rubbers

It is obvious from Fig. 2 that Doi-Edwards' assumption of constant tube diameter or constant molecular tension is not supported by the data, not even in first order in strain. The tension of the average polymer chain increases with increasing deformation. We defined a "molecular stress function" $f(\langle u' \rangle)$, which is a representation of the mean stress field of the surrounding polymer chains and its effect on the macromolecule considered. The molecular stress function f describes the tension in the chain relative to its equilibrium value, and depends on the average stretch $\langle u' \rangle$. This is in contrast to a similar approach taken by Marrucci *et al.* (Marrucci and de Cindio, 1980; Marrucci and Hermans, 1980), where f is assumed to depend on the stretch of individual segments, u' , of the tube.

The molecular stress function constitutive equation is given by (Wagner and Schaeffer, 1992)

$$\sigma(t) = -pE + 5 \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} f^2 \left\langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \right\rangle dt' \quad (25)$$

The strain measure of eq. (25) is seen as being the result of two contributions:

- (1) affine orientation of network strands, i.e. a network strand characterized by a unit vector \mathbf{u} is orientated in the new direction \mathbf{u}'/u' ;
- (2) isotropic strand extension, i.e. a network strand of unit length is extended to length $f(\langle u' \rangle)$.

Note that strand extension is independent of strand orientation, i.e. all strands in all directions are subject to the same extension, which is represented by the molecular stress function f . In the tube concept, extension of a network strand can only be achieved by reduction of the tube diameter (there are no "Maxwellian demons" pulling

at the ends of the chain, while there is an increasing restriction of lateral motion of the chain caused by the surrounding chains), and indeed it can be shown that f is the inverse of the relative tube diameter (Wagner and Schaeffer, 1992). At small strains, f^2 is found to be linear in $\langle u' \rangle$. This can be rationalized in terms of the tube concept by the assumption of a constant volume $V = V_0$ of the tube: with tube diameter a_0 and a , and contour length L_0 and $L = L_0 \cdot \langle u' \rangle$ in the undeformed and deformed state respectively, and

$$\frac{V}{V_0} = \frac{a^2 L}{a_0^2 L_0} = 1 \quad (26)$$

follows immediately (Wagner and Schaeffer, 1992)

$$f^2 = \frac{a_0^2}{a^2} = \frac{L}{L_0} = \langle u' \rangle \quad (27)$$

Alternatively, eq. (27) can be considered as resulting from an affine deformation of the tube diameter a , which represents the mean field of the topological constraints. At higher average stretches, a maximum molecular stress function, f_{\max} , corresponding to a minimum tube diameter, a_{\min} , is reached for polymer melts, the level of which is clearly depending on the degree of long-chain branching (Wagner and Schaeffer, 1992).

Inserting eq. (27) into eq. (25) results in the constitutive equation of the linear molecular stress function theory:

$$\sigma(t) = -pE + 5 \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} \langle u' \rangle \left\langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \right\rangle dt' \quad (28)$$

The corresponding damping function can be solved by closed integration for uniaxial elongation and compression, and the result is for elongation ($\lambda \geq 1$):

$$h = \frac{1}{4} \frac{\lambda^2}{\lambda^3 - 1} \left(1 + \frac{\sinh^{-1} \sqrt{\lambda^3 - 1}}{\sqrt{\lambda^3} \sqrt{\lambda^3 - 1}} \right) \left[\frac{3\lambda^3}{\lambda^3 - 1} \left(1 - \frac{\tanh^{-1} \sqrt{\lambda^3 - 1}}{\sqrt{\lambda^3 - 1}} \right) - 1 \right] \quad (29)$$

for compression ($\lambda \leq 1$):

$$h = \frac{1}{4} \frac{\lambda^2}{\lambda^3 - 1} \left(1 + \frac{\sin^{-1} \sqrt{1 - \lambda^3}}{\sqrt{\lambda^3} \sqrt{1 - \lambda^3}} \right) \left[\frac{3\lambda^3}{1 - \lambda^3} \left(1 - \frac{\tanh^{-1} \sqrt{1 - \lambda^3}}{\sqrt{1 - \lambda^3}} \right) - 1 \right] \quad (30)$$

Predictions (line) of eqs. (29) and (30) are compared with experimental data for PIB melt (symbols) in Fig. 3. Deviations of data and theory at small strains $\lambda \approx 1$ can be attributed to measurement errors, while deviations at large strains ($\lambda \ll 1$ and $\lambda \gg 1$) are related to the plateau value of f^2 .

Fig. 4 shows a comparison of rubber data (symbols from Fig. 1) with predictions of the linear molecular stress function theory (line). For all six rubber networks at small and medium strains agreement of data and theory is

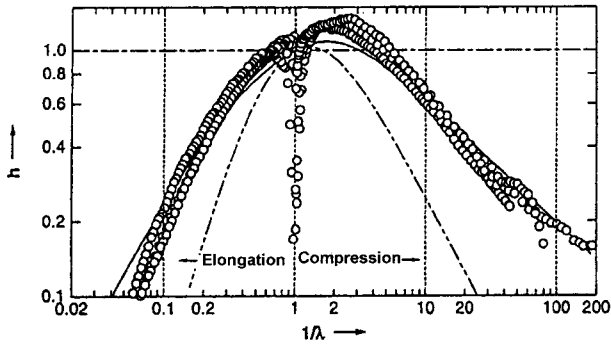


Fig. 3. Damping function for PIB melt (symbols) as a function of inverse extension ratio $1/\lambda$. Solid line is prediction by the linear molecular stress theory, in elongation, eq. (29), and compression, eq. (30). Broken line represents Doi-Edwards damping function from eq. (18).

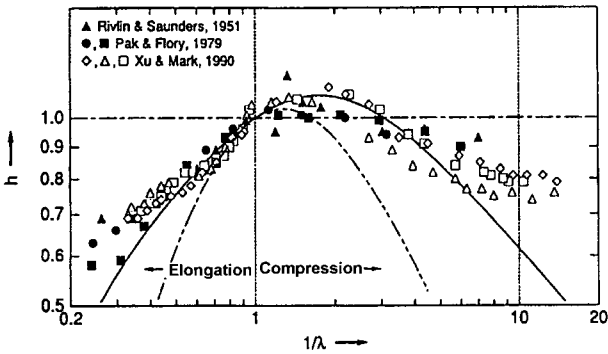


Fig. 4. Normalized Mooney stress $h = \sigma_M/G_\infty$ of several rubbers (symbols) as a function of inverse extension ratio $1/\lambda$. Solid line is prediction by the linear molecular stress theory, in elongation, eq. (29), and compression, eq. (30). Broken line represents Doi-Edwards damping function from eq. (18).

remarkable. Note that this agreement is obtained by use of a single scaling parameter, G_∞ . Deviations at large strains are due to finite extensibility of crosslinked networks (Wagner and Schaeffer, 1993).

6. Influence of Crosslink Density

The success of the molecular stress function theory, eq. (25), for rubbers was further substantiated by Wagner (1994). To assess the influence of crosslink density on the strain dependence of rubber networks, the extensive data set of Mullins (1959) on uniaxial elongation of peroxid cured natural rubber was considered. An analysis of these data shows that eq. (25) or equivalently its long-time limit,

$$\sigma = -pE + 5G_\infty f^2 \left\langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \right\rangle \quad (31)$$

describes the strain dependence of elongational stress at

small and moderate crosslink densities. When G_∞ reaches a critical niveau G_e^* , which corresponds to the plateau modulus G_N of the un-crosslinked parent melt, chemical crosslinks have effectively replaced all entanglements of the melt state, and the average distance between crosslinks is equal to the tube diameter a_0 of the melt. For $G_\infty \leq G_e^*$, the strain measure of the rubber is indistinguishable from the strain measure of the corresponding melt for small and moderate strains, and the stress calculator is given by eq. (31) with G_∞ being a measure of the tube diameter a_{0r} of the rubber.

Note that in contrast to other theories employing the tube model in rubber elasticity, eq. (31) does not distinguish between the contribution of covalent bonds (chemical junctions) and the effect of entanglements: for $G_\infty \leq G_e^*$, the strain measure of physical entanglements is the same as the strain measure of chemical junctions. However, higher crosslink densities result in a classical contribution to the strain measure which reflects phantom chain behaviour. This can be rationalized by considering that short network strands with length scale below the entanglement spacing (or tube diameter a_0) are not restricted by neighboring chains. The stress calculator is then given by

$$\sigma = -pE + 5G_e^* \langle \mathbf{u}' \rangle \left\langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \right\rangle + 3G_c \langle \mathbf{u}'\mathbf{u}' \rangle \quad (32)$$

with

$$G_\infty = G_e^* + G_c \quad (33)$$

We call G_e^* the critical "entanglement" contribution, which is a measure of the tube diameter a_0 of the un-crosslinked parent melt and therefore represents the maximum entanglement effect of neighboring chains, and G_c the "classical", phantom-chain contribution to the equilibrium modulus G_∞ .

7. The Molecular Stress Function of Melts and Rubbers

By the early nineties it became clear that the strain behaviour of linear as well as long-chain branched polymer melts and rubber networks below a critical equilibrium modulus G_e^* (which corresponds to the plateau modulus G_N of the uncrosslinked parent system) is universal for small and moderate increasing strains starting from the isotropic, stress-free state. This result is summarized in Fig. 5: for polymer melts as well as crosslinked homopolymers, the square of the molecular stress function, f^2 , is linear in the average stretch $\langle u \rangle$ up to moderate strains. f was calculated from data of Demarmels and Meissner (Demarmels and Meissner, 1986; Wagner and Schaeffer, 1992) for PIB melt and from data of Laun (1980) for several linear (PS, HDPE) and branched (LDPE III, LDPE IUPAC A) polymer melts (Wagner and

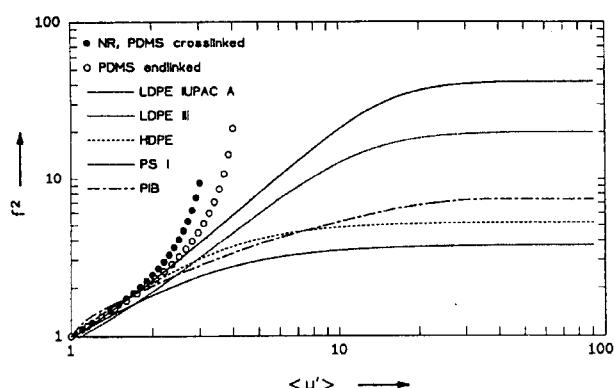


Fig. 5. Square of molecular stress function, f^2 , as a function of average stretch $\langle u' \rangle$ for several linear and branched polymer melts, and for several crosslinked rubbers.

Schaeffer, 1992).

At large deformations, polymer melts show a maximum molecular tension f_{\max} (corresponding to a minimum tube diameter). The plateau value increases with the degree of long-chain branching. Molecular tension increase due to tube deformation is limited by "chain slip" or "constraint release".

Crosslinked polymer networks show finite extensibility, i.e. f diverges at finite deformation. Maximum deformation is much less than would be expected from phantom chain theory. This is due to topological constraints ("trapped entanglements") which are permanent in crosslinked networks, because there is no chain slip. At higher deformations these permanent constraints (both chemical and physical) cause deviation from Gaussian chain behaviour.

8. Recent Developments

A special version of the molecular stress function theory can be derived by generalizing the strain energy function of the Doi-Edwards model (Wagner *et al.*, 1998). The strain energy function is a scalar integral of the strain measure; it thus reduces a tensorial quantity (the stress tensor) to a scalar one. The strain energy function W_{DE} of the Doi-Edwards (IAA) theory is (Larson, 1988; Currie, 1982; Marrucci and Grizzuti, 1983)

$$W_{DE} = 5 \int_0^{\infty} \dot{m}(s) \langle \ln(u') \rangle ds \quad (34)$$

Upon deformation, the entropy of a tube segment represented by its unit vector, is reduced by $3k\langle \ln(u') \rangle$, and the free energy is increased by $3kT\langle \ln(u') \rangle$. The quantity $\langle \ln(u') \rangle$ in eq. (34) is thus seen to represent the relative orientational free energy of the average tube segment, normalized with respect to $3kT$. It is important to note that the (scalar) stretch field L/L_0 experienced by the average tube segment can be expressed as

$$\ln(L/L_0) = \langle \ln(u') \rangle \quad (35)$$

or

$$L = L_0 e^{\langle \ln(u') \rangle} \quad (36)$$

Generalizing eq. (34) to

$$W = 5 \int_0^{\infty} \dot{m}(s) w(\langle \ln(u') \rangle) ds \quad (37)$$

with $w(\langle \ln(u') \rangle)$ being a dimensionless strain energy function of the average logarithmic stretch, leads to a strain measure

$$\mathbf{S} = 5 \frac{\partial w}{\partial \langle \ln(u') \rangle} \left\langle \frac{\mathbf{u}' \mathbf{u}'}{u'^2} \right\rangle \quad (38)$$

This is clearly of the molecular stress function-type of eq. (25), with

$$f^2 = \frac{a_0^2}{a^2} = \frac{\partial w}{\partial \langle \ln(u') \rangle} \quad (39)$$

The molecular stress function f and the tube diameter a are thus seen to depend now on the orientational free energy $\langle \ln(u') \rangle$.

To find specific expressions for the molecular stress function f , we need again additional assumptions. For linear polymers, the most natural assumption on the basis of the tube concept seems to be again the constant tube volume assumption, which leads to

$$f^2 = \frac{a_0^2}{a^2} = L/L_0 = e^{\langle \ln(u') \rangle} \quad (40)$$

As f^2 is linear in the scalar stretch field L/L_0 , we call eq. (40) again the "Linear Molecular Stress Function theory", and abbreviate it by LMSF.

To derive an expression for the molecular stress function of longchain-branched polymer melts, we treat branch points simplistically as junctions of a crosslinked system and resort to the theory of rubber elasticity. Following Flory (Flory, 1977), we allow for junction fluctuations, which leads to a molecular stress function of the form (Wagner *et al.*, 1999)

$$f^2 = \frac{1}{2} e^{2\langle \ln(u') \rangle} + \frac{1}{2} \quad (41)$$

Eq. (41) reduces to eq. (40) in first order of $\langle \ln(u') \rangle$. We will therefore use eq.(41) in the following to describe the strain-hardening behaviour of long-chain branched polymer melts. As f^2 is quadratic in the stretch, we call it the "Quadratic Molecular Stress Function (QMSF) theory".

9. Strain Hardening of Linear and Long-chain Branched Polymer Melts in Extensional Deformations

Fig. 6 shows the uniaxial (μ_u), equibiaxial (μ_e), and

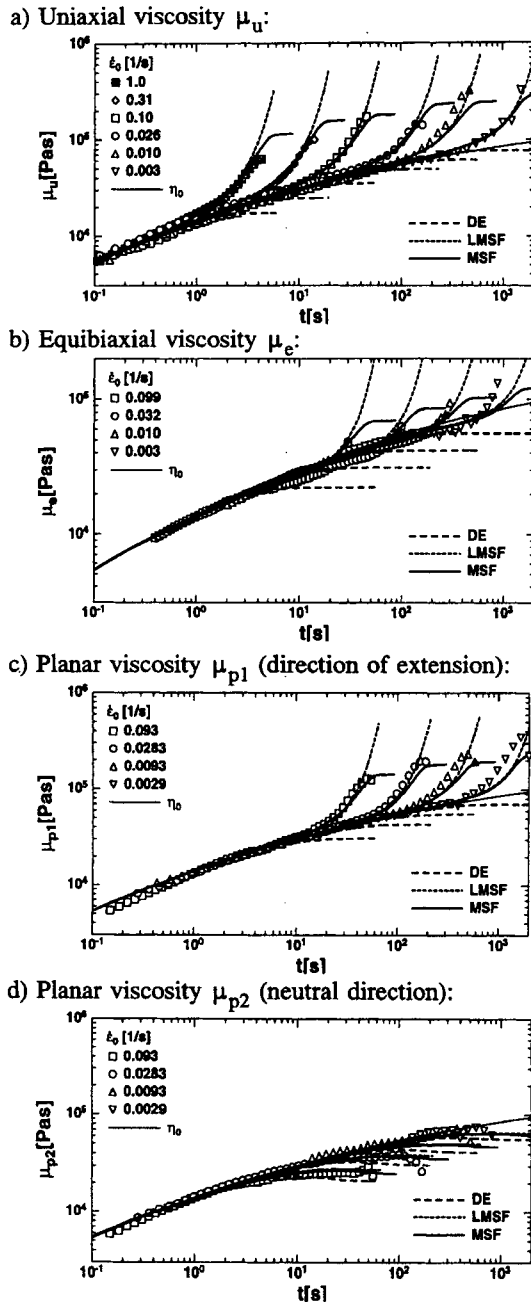


Fig. 6. Time-dependent extensional viscosities (symbols) of HDPE. Lines are predictions using the Doi-Edwards (DE) model, eq. (18), the Linear Molecular Stress Function (LMSF) theory, eq. (40), and the one-parameter Molecular Stress Function (MSF) theory, eq. (42).

planar (μ_{p1} and μ_{p2}) viscosities of HDPE measured at 150°C and at constant strain rates (Wagner *et al.*, 1999). The definition of extensional viscosities μ as used here includes normalisation constants, which rescale all viscosities in the linear-viscoelastic limit to the time-dependent zero-shear viscosity $\eta_0(t)$, which is also shown in Fig. 6.

Fig. 6 also presents the extensional viscosities calculated

by use of eq. (18) for the Doi-Edwards (DE) model, as well as the LMSF model according to eq. (40). It is obvious from Fig.6 that the Doi-Edwards model does not predict any strain-hardening in extensional flow, while the molecular stress function theory with the simple exponential dependence on the average logarithmic stretch gives an accurate description of the strain-hardening behaviour up to large deformations. Note that this is a zero-parameter theory! It is also seen that within experimental accuracy, time-strain separability is a valid assumption, i.e. the calculated viscosities do not exhibit any systematic deviation from the upturn of the measured viscosities as a function of strain rate.

At large deformations, the Linear Molecular Stress Function theory predicts an unbounded growth of the uniaxial (μ_u), equibiaxial (μ_e), and planar (μ_{p1}) viscosities, while the experimental data indicate the existence of steady-state viscosities. To model this saturation effect, we allow for increasing slip between the stretching of a test chain and the stretch field, which can be modelled e.g. by

$$f^2 = 1 + f_{\max}^2 - 1 \left[1 - \exp \left(- \frac{e^{\langle \ln(u) \rangle} - 1}{f_{\max}^2 - 1} \right) \right] \quad (42)$$

f_{\max} , the maximum value of the molecular stress function, is the only free nonlinear material parameter of the theory. For small deformations, eq. (42) reduces to eq. (40). From the data in Fig. 6, a value of $f_{\max}^2 = 30$ can be estimated, which corresponds to a maximum stretch ratio of the macromolecular chains of $f_{\max} = 5.5$.

As seen from Fig. 6, the HDPE melt investigated shows a considerable "strain-hardening" effect in the extensional viscosities. Usually, strain-hardening is considered to be mainly an effect of long-chain branching, and it might be argued that the strain-hardening of these HDPE melts is caused by a small amount of long-chain branching. However, investigations by Linster and Meissner on HDPE indicated that also a small amount of very long, linear molecules in the molecular weight distribution of the polymer with no or almost no long-chain branching leads to the same phenomenon.

A polymer clearly free of any long-chain branching is radically polymerized polystyrene (PS). Fig. 7 presents the uniaxial (μ_u) and equibiaxial (μ_e) viscosities of the PS considered here measured at a temperature of $T = 170^\circ\text{C}$ (Hachmann, 1996), which shows strain-hardening in uniaxial elongation, but very little strain-hardening in equibiaxial extension. The damping function h_u and h_e in uniaxial and equibiaxial extension were evaluated and are also shown in Fig.7. (For the definition of damping functions in extensional flows see e.g. Wagner (1978), and Wagner *et al.* (1998; 1998) Time-deformation separability is well observed in uniaxial extension for 2 decades of strain rate, while for equibiaxial extension (being a more difficult experiment to perform), h_e shows some scatter at small

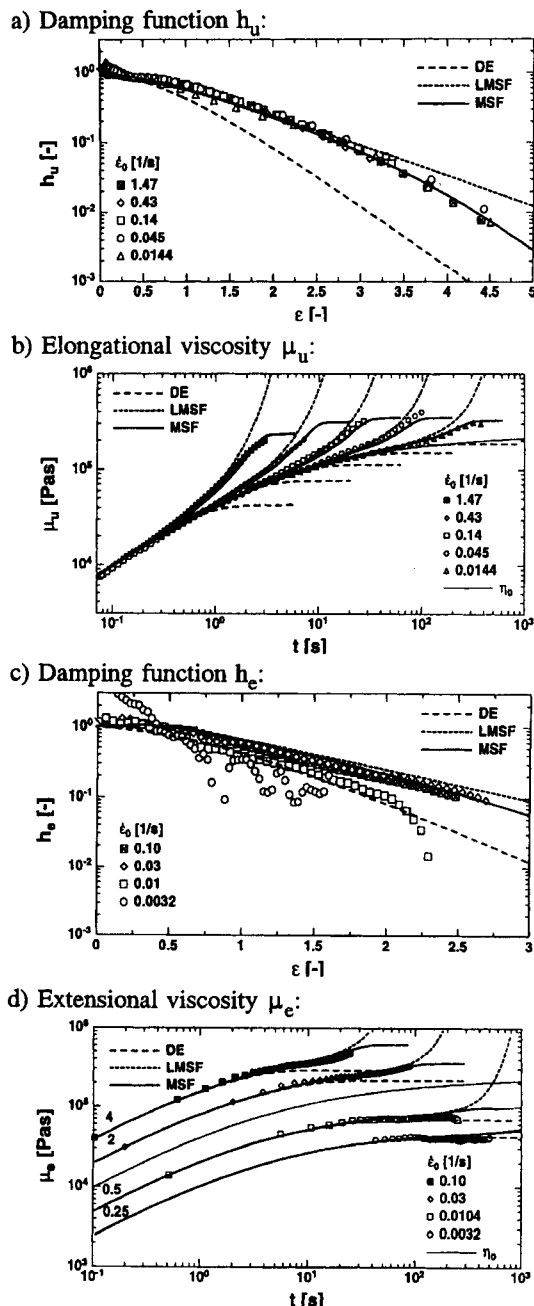


Fig. 7. Damping functions and extensional viscosities (symbols) of PS. Lines are predictions using the Doi-Edwards (DE) model, eq. (18), the Linear Molecular Stress Function (LMSF) theory, eq. (40), and the one-parameter Molecular Stress Function (MSF) theory, eq. (42).

strain rates. Included in Fig. 7 are the predictions of the Doi-Edwards model, the LMSF model of eq. (40) and the one-parameter version of eq. (42) with $f_{\max}^2 = 13$ or $f_{\max} = 3.6$. It is obvious that the molecular stress function model describes the strain measure in uniaxial and equibiaxial extension and the corresponding viscosities of this PS melt quantitatively. While the viscosity upturn and the strain-hardening behaviour is captured correctly by the Linear

Molecular Stress Function model, the value of the steady-state viscosities is fully determined by f_{\max} . If f_{\max} is small enough, as in this case, very little or no strain-hardening (in the usual sense of a viscosity above the linear-viscoelastic start-up curve) is observed in equibiaxial extension.

To summarize the results, we can state that all linear polymer melts investigated so far show strain hardening in extensional flows, whereby we define strain-hardening as an extensional viscosity upturn above the Doi-Edwards prediction. This means that all polymer melts considered show chain stretching in irrotational flows. The strain-dependence of the viscosity upturn is the same for all linear polymer melts investigated: it can consistently be described by the Linear Molecular Stress Function model with an exponential dependence of the molecular stress function on the orientational free energy, indicating an affine deformation of the average tube diameter. The ultimate magnitude of the strain-hardening effect is limited by the maximum value of the molecular stress function, f_{\max} . This material property governs the maximum stretch of the macromolecular chain, and the minimum tube diameter $a_{\min} \cdot f_{\max}$ is intimately related to the strain-hardening effect of the elongational viscosity: a large value of f_{\max} indicates a large strain-hardening effect, while for polymer melts that are usually considered to be "non-strain-hardening", small values for f_{\max} are found. In the lower limit of $f_{\max} = 1$, the Doi-Edwards model is recovered. So far, no molecular arguments are known which would allow calculation of f_{\max} , or equivalently of a minimum tube diameter, from molecular properties of the polymer melt. Clearly molecular weight distribution is important, but probably not enough.

We now consider the strain-hardening behaviour of long-chain branched polymer melts. Fig. 8 shows the uniaxial (μ_u), equibiaxial (μ_e), and planar (μ_{p1} and μ_{p2}) viscosities of LDPE measured at 150°C and at constant strain rates (Hachmann, 1996). Also included in Fig. 8 are the predictions of the Doi-Edwards model and of the Linear Molecular Stress Function theory of eq. (40). It is important to note that as expected, the upturn of the extensional viscosities of the longchain-branched LDPE is more pronounced than predicted by the LMSF model and therefore more severe than for linear polymer melts. As shown in Fig. 9, we can describe this upturn quite accurately for all deformation modes with the Quadratic Molecular Stress Function theory of eq. (41), which is again a zero-parameter model! It is thus seen that the enhancement of the viscosity upturn due to the presence of longchain branches can indeed be represented by a molecular stress function derived from the junction fluctuation theory of rubber networks.

To model the steady-state extensional viscosities at large deformations, a limiting value of the molecular stress has

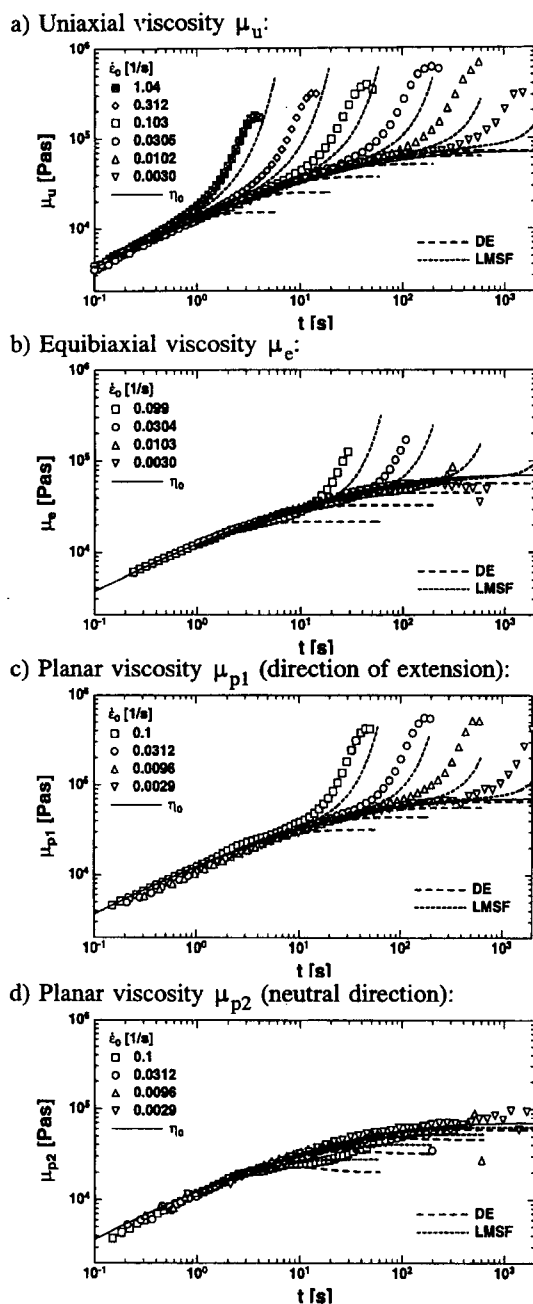


Fig. 8. Time-dependent extensional viscosities (symbols) of LDPE. Lines are predictions using the Doi-Edwards (DE) model, eq. (18), and the Linear Molecular Stress Function (LMSF) theory, eq. (40).

again to be considered, e.g. by

$$f^2 = 1 + (f_{\max}^2 - 1) \left[1 - \exp \left(- \frac{e^{2(\ln(u))} - 1}{2f_{\max}^2 - 1} \right) \right] \quad (43)$$

For small deformations, eq. (43) reduces to eq. (41). Using eq. (43) and a value of $f_{\max}^2 = 100$ corresponding to an average stretch of the macromolecules by a factor of 10, the steady-state viscosities can be modelled qualitatively. However, there is a systematic discrepancy between the

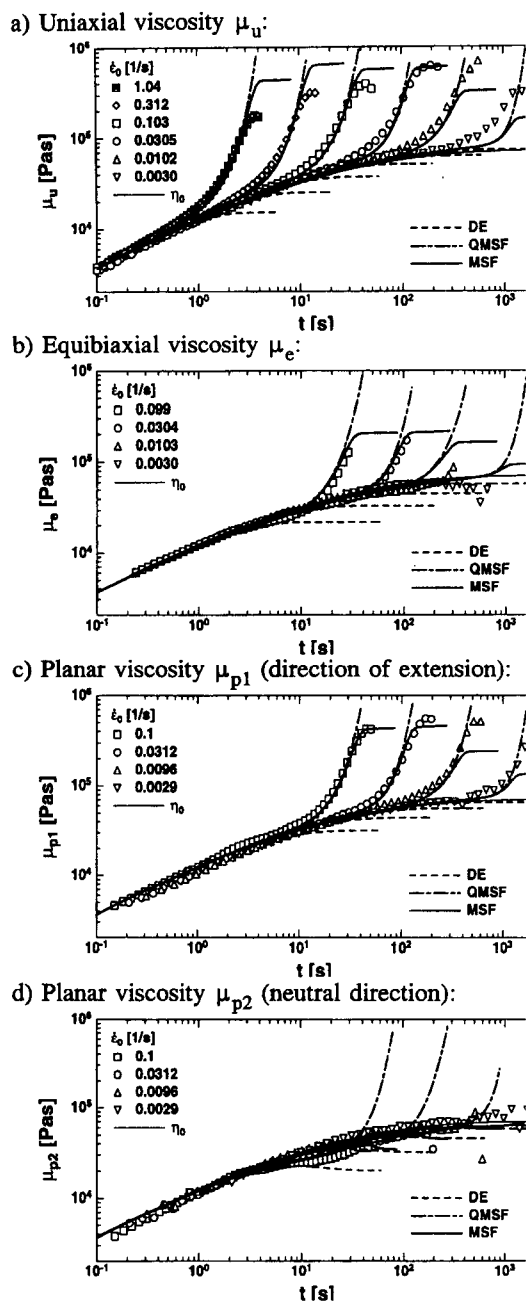


Fig. 9. Time-dependent extensional viscosities (symbols) of LDPE. Lines are predictions using the Doi-Edwards (DE) model, eq. (18), the Quadratic Molecular Stress Function (QMSF) theory, eq. (41), and the one-parameter Molecular Stress Function (MSF) theory, eq. (43).

steady-state viscosities predicted and observed, which is probably outside experimental uncertainty. This means that the upturn of the extensional viscosities is time-deformation separable, while the ultimate steady-state value is not, i.e. the strain measure is the same for all relaxation modes up to a value of f_{\max} , which might not be a strict constant but might depend on the relaxation time.

The uniaxial elongational viscosity h_u and the damping

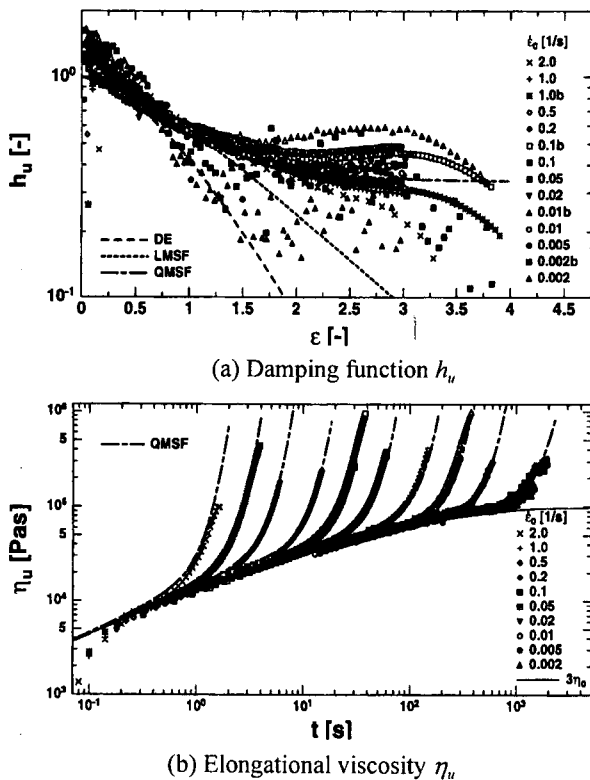


Fig. 10. Damping function h_u and elongational viscosity η_u of long-chain branched PP. Lines are predictions using the Doi-Edwards (DE) model, eq. (18), the Linear Molecular Stress Function (LMSF) theory, eq. (40), and the Quadratic Molecular Stress Function (QMSF) theory, eq. (41).

function h_u of a longchain-branched polypropylene PP are presented in Fig. 10 (Kurzbeck *et al.*, 1999). This polymer shows extreme strain-hardening, which can be described quantitatively by the Quadratic Molecular Stress Function model of eq. (41) up to the maximum strains investigated. Also shown in Fig.10 are the damping functions for the Doi-Edwards model as well as for the Linear Molecular Stress Function theory. Neglecting the scatter at small Hencky strains, which is due to experimental difficulties, the LMSF theory is seen to give a good description of the experimentally determined damping function up to a Hencky strain of about $\epsilon = 1$; at larger strains, the data indicate a plateau, which is well described by the Quadratic Molecular Stress Function model. No steady-state value was reached for the elongational viscosity in constant strain-rate elongation. However, three experiments with Hencky strains up to $\epsilon = 4$ indicate that f^2 approaches saturation at high strains.

In summary, long-chain branched polymer melts show a more severe upturn of the extensional viscosities with increasing deformation than linear polymer melts (Wagner *et al.*, 1999). We can quantify this by use of the Quadratic Molecular Stress Function theory which has a quadratic dependence on the scalar stretch field L/L_0 , and is derived

from the junction fluctuation theory of Flory (1977) for polymer networks. While for the upturn of the extensional viscosities time-deformation separability is well observed, the maximum value f_{\max} of the molecular stress function might depend on the relaxation mode and seems to increase with longer relaxation times.

10. Open questions

Besides questions mentioned or discussed in this paper, like irreversibility of strain effects or the relation of the maximum value of the molecular stress function, f_{\max} , or the minimum value of the tube diameter, a_{\min} , to molecular parameters, the most pressing question is certainly a unifying description of irrotational (extensional) and rotational (shear) flows. Constitutive equations discussed so far are all of the Rivlin-Sawyers or K-BKZ-type. It is well established by now that single-integral equations of this type are unable to describe irrotational and rotational flows by use of the same strain measure (see e.g. Wagner *et al.* (1998), and references therein). Integro-differential equations of the type suggested e.g. by Pearson *et al.*, (1989), Mead *et al.*, (1998) and Mcleish and Larson (1998) seem to offer a way out or around this problem. These equations are of the form

$$\sigma = -p\mathbf{E} + 5\lambda^2 \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} \left\langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \right\rangle dt' \quad (44)$$

where λ is a chain stretch parameter which is modelled by a differential equation. The structure of these equations with the square of the chain stretch parameter in front of the integral do not seem to be commensurable with experimental evidence in planar extension of polymer melts (Rubio and Wagner, 2000): the same ratio of strain-hardening is predicted for the planar viscosities μ_{p1} and μ_{p2} , while experimentally very little strain-hardening in the 2-direction is observed as seen in Figs. 6, 8 and 9. However, defining chain stretch by a rate equation might allow to differentiate between strain measures for simple shear and pure shear.

11. Lessons from the 20th Century

At the end of this century, we have to admit that we still do not know a constitutive equation describing irrespective of the type of flow, the nonlinear rheological behaviour of "simple" polymer melts like polyethylene or polystyrene, which are produced commercially by the millions of tons. However, some basic features became apparent: the importance of topological constraints, the advantage of the orientation tensor over the classical strain measures, allowing the modelling of all types of irrotational flows, the similarities of the strain measures for polymer melts and rubbers. The quest goes on to find the most simple but

unifying picture to model the complex nonlinear material behaviour of polymer melts and rubbers. Clearly, the tube model proposed by Doi and Edwards has been of tremendous help. But as Albert Einstein once said: "We should simplify as much as possible, but not further."

Acknowledgement

Financial support from the European Commission (Brite-Euram BRTR-CT96-0278), from the German Science Foundation (DFG) through various grants, and from the Korean Society of Rheology is gratefully acknowledged.

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