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On network models of molten polymers: Loss of junctions due to stretching of material planes

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With 2 figures

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1. Introduction

During the last two decades a considerable amount of research has been devoted to finding rheological constitutive equations (also called "models") of polymeric liquids. Depending on the assumptions made in the derivation of these models, they can be classified into certain groups, see for instance (1).

One group of these are the so-called network models. It consists of the rubberlike liquid equation by *Lodge* (2) and its modifications. If the memory function m is assumed to depend on the strain history, the constitutive equation has the form

$$\sigma(t) = -p\mathbf{1} + \int_{-\infty}^{t} m(t,t',C^{-1})C^{-1}(t')\,dt', \quad [1]$$

σ = stress at time t, Pa; p = pressure level, Pa; $m(t,t',C^{-1})$ = memory function, Pa s^{-1}; $C^{-1}(t')$ = Finger tensor; t' = time previous to time t.

The stress at time t is assumed to depend on the strain history previous to time t. Network theory assumes that temporary junctions are formed between the macromolecules. The junctions which are formed at time t' (also called state t' of the material) change their relative distances during the deformation from state t' to state t. Consequently there is a contribution to the stress from these junctions; the contribution is proportional to the deformation from state t' to state t. The total stress at state t then is the integral of the stress contributions from all past times t' up to the present time t.

The Finger tensor $C^{-1}(t')$ is a measure of the strain involved in the deformation from t' to t. It is the contravariant metric of an embedded coordinate system that becomes orthonormal at state t. The state t is not mentioned explicitly in describing the strain between t' and t by means of the Finger tensor. However, by choosing the embedded coordinate system to be orthonormal at state t, the components of $C^{-1}(t')$ also depend on t.

In polymer melts and concentrated polymer solutions, temporary junctions such as entanglements are created and lost at finite rates. The stress contribution of a deformation $t' \to t$ is the larger, the more junctions of the past state t' are still functioning at the present state t. In a first mechanism, junctions may break due to the thermal mobility of the macromolecules at rates determined by *time constants* λ_i; the same time constants are also assumed to determine the rate of creation of junctions. In a second mechanism, junctions may also break due to *large deformations* $t' \to t$. The creation and the loss of junctions is described in the memory function $m(t,t',C^{-1})$.

In the rubberlike liquid equation, the memory function depends just on the time interval $(t - t')$

$$m(t,t',C^{-1}) \equiv \mu(t-t') = \sum_{i=1}^{N} \frac{G_i}{\lambda_i}\exp\left(-\frac{t-t'}{\lambda_i}\right), \quad [2]$$

G_i = moduli of linear viscoelasticity, Pa; λ_i = time constants of linear viscoelasticity, s, at constant temperature and pressure.

An alternative formulation of eq. [2] would be by means of a continuous relaxation spectrum. μ is the memory function of *linear viscoelasticity*. The moduli and relaxation times are assumed to be time *in*dependent.

If the relaxation times are time dependent (due to temperature changes with time, for instance), the memory function contains a time integral (3)

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$$\mu(t,t') = \sum_{i=1}^{N} \frac{G_i}{\lambda_i} \exp\left(-\int_{t'}^{t} \frac{dt''}{\lambda_i(t'')}\right). \qquad [3]$$

In the derivation of this memory function it is assumed that junctions in the network break in a first-order reaction.

Eqs. [1] and [2] describe, as experiments show, the rheological behavior at strains of magnitude $1-3$ and below (4). This is a great success of the network theory. However, the deformation of molten polymers in industrial processes exceeds this value by orders of magnitude and it has been a task in recent years to modify the rubberlike liquid equation, so that it also may be valid for flows with large deformations.

The rubberlike liquid equation overemphasizes the non-linear effects in large deformations. In molten polymers, there seems to be an additional mechanism for losing memory of previous states of strain, i.e. for breaking junctions. It has been suggested by *Kaye* (5) and by *Bernstein, Kearsley* and *Zapas* (6) that this additional breaking of junctions depends on the invariants II, I of the stress at time t or of the strain between t' und t. Several authors (7–10) specifically assumed that the memory function is a product of two functions

$$m(t,t',C^{-1}) = h(I_{C^{-1}}, II_{C^{-1}}) \cdot \mu(t,t'), \qquad [4]$$

where h is the *damping function* and μ is the memory function of linear viscoelasticity as shown in eq. [2] or eq. [3]. The scalar damping function depends on the first and second invariant of the Finger tensor C^{-1}. At the limit of small strains, h will approach unity.

The question now arises as to what is the appropriate formulation of the damping function. There are several plausible simple combinations of the two strain invariants. *Wagner* (10) uses published experimental data on simple shear and on uniaxial extension of low density polyethylene to find that a damping function of the form

$$h = \exp(-n\sqrt{II_{C^{-1}} - 3}) \qquad [5]$$

describes the experiments best, at least in shear. For uniaxial extension it seems difficult to decide to what degree the first invariant $I_{C^{-1}}$ has an influence on the damping function of eq. [4].

Note that the damping function h describes an instantaneous loss of junctions, i.e. the loss supposedly does not require time as would a rate process. A transient strain (impuls strain) of magnitude ε_0 then has the same effect on existing network junctions as a strain ε_0 of long duration (step strain), for instance.

This procedure of finding an appropriate damping function is rather arbitrary. It would be helpful to know which combination of the strain invariants should be used to define the strain-dependence of the memory function. The applicability of the constitutive equation would then not be restricted to certain types of flow rich as shear or uniaxial extension. The goal of this study, therefore, shall be to define the damping function in a more specific way. It will be shown that the invariants of the Cauchy tensor $C(t')$ or the equivalent invariant of the Finger tensor $C^{-1}(t')$ have a geometrical meaning, which makes it possible to relate the loss of junctions to the maximum *stretch of material planes* instead to the strain in general.

2. Stretch of material planes

During the deformation from state t' to state t, material planes within the bulk of the material change their area. If the area of a plane decreases, the junctions positioned in that plane move closer together and a stress correspondingly builds up. If the area of a plane increases during the deformation, the distance between the junctions also increases. From the transient nature of the junctions one should assume, that the distance between junctions cannot be increased indefinitely without breaking them or without increasing the probability of breakage. If the material planes with maximum stretch would be known for a flow, their stretch could be used as a measure for breaking junctions.

In a deformation, material planes do not only stretch, but they also move parallel to each other. This parallel displacement will not be used in the following study, although it might cause some additional increase of distance between junctions.

2.1. Stretch measure

A small element in an isotropic continuum is deformed uniformly from state t' to state t. The deformation is described by the covariant metric

$$C_{ij} = \boldsymbol{e}_i \cdot \boldsymbol{e}_j \qquad [6]$$

of a material coordinate system $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$, which is orthonormal at state t. At state t the metric tensor reduces the unit tensor, $C(t) = \mathbf{1}$. Tensor C is called the *Cauchy tensor*.

A gradient of the deformation is assumed to have no influence, i.e. the neighborhood of a material point P is taken to be so small, that the deformation is practically uniform. Material planes then remain plane during the deformation.

To demonstrate the stretching of arbitrary material planes, we mark a material surface S around a material point P in the small material element, see figure 1. Point P is the origin of the embedded coordinate system e_i. At state t, the material surface S is chosen to be a *sphere of unit radius*. During the deformation at states prior to state t, surface S had the shape of an *ellipsoid*.

Now we chose an arbitrary material plane through P, which cuts the ellipsoid at state t' and, correspondingly, the sphere at state t into two equal parts. The area of the cut changes from the area $A(t')$ of an ellipse to an area $A(t)$ of a circle of unit radius. While at state t' the area $A(t')$ depends on the direction of the cut and on the strain, the area $A(t)$ is the same for all possible cuts.

The planes perpendicular to the three principal axes of the ellipsoid are called the principal planes. If a, b, c are the lengths of the three principal axes of the ellipsoid ordered proceeding from the largest to the smallest, the areas of the ellipses on the principal planes are πab, πbc, πca. The areas πab and πbc are the largest and the smallest areas, respectively, of all possible cuts through P.

The plane which is stretched the most is the one with the smallest ellipse. The maximum relative increase of area in any material plane through P would be

$$\left(\frac{A(t)}{A(t')}\right)_{\max} = \frac{1}{bc}. \qquad [7]$$

The largest principal axis, a, is not used here, but it must be known to be able to distinguish the two smallest principal axes.

For formulating a constitutive equation, it would be more convenient to define a stretch measure without explicitly distinguishing between the different lengths of the principal axes. This can be done by averaging the relative increase of area of the three primary planes. The average value is dominated by the plane which stretches the most, if the square of the areas is taken:

$$\left\langle\frac{A^2(t)}{A^2(t')}\right\rangle = \frac{1}{3}\left[\left(\frac{1}{ab}\right)^2 + \left(\frac{1}{bc}\right)^2 + \left(\frac{1}{ca}\right)^2\right] = \frac{a^2+b^2+c^2}{3a^2b^2c^2}; \qquad [8]$$

a *stretch measure*

$$\varepsilon_p(t,t') = \left\langle\frac{A^2(t)}{A^2(t')}\right\rangle^{1/2} - 1 \qquad [9]$$

can be defined. This stretch measure describes the average increase of distances between material points or between junctions, when the material deforms from state t' to state t. The index p shall emphasize that the average is taken with a preference to the plane of *maximum stretch*. The 1/2th power is chosen, to that ε_p can be explained to be a relative change in area.

2.2. *Principal axes of the strain ellipsoid*

The ellipsoid in figure 1 is completely described by the Cauchy tensor ((2), p. 46). It is called the strain ellipsoid. The principal values a^2, b^2, c^2 of

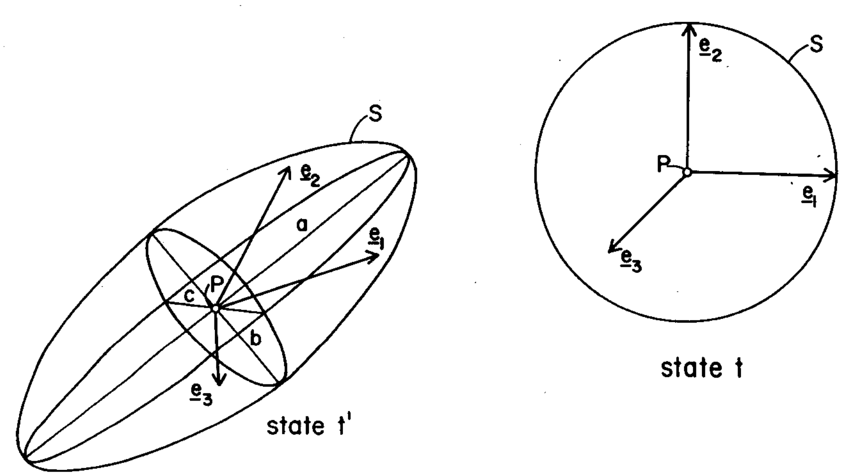

Fig. 1. Strain ellipsoid at state t', which changes into a sphere of unit radius at state t. The three ellipses are on the principal planes of the ellipsoid

the ellipsoid are also the principal values of the Cauchy tensor $C(t')$; they are functions of its three invariants

$$I_C = C_{11} + C_{22} + C_{33}, \quad [10]$$

$$II_C = C_{11}C_{22} + C_{22}C_{33} + C_{33}C_{11} - C_{12}^2 - C_{23}^2 - C_{31}^2, \quad [11]$$

$$III_C = \det C. \quad [12]$$

From these equations, it can be derived that

$$a^2 + b^2 + c^2 = I_C, \quad [13]$$

$$(abc)^2 = III_C. \quad [14]$$

With these expressions, the scalar stretch measure becomes

$$\varepsilon_p(t,t') = \left(\frac{I_C}{3\,III_C}\right)^{1/2} - 1. \quad [15]$$

If the density is constant, the third invariant assumes the value 1. The stretch measure of eq. [15] can also be determined from the invariants of the Finger tensor

$$[\tfrac{1}{3} II_{C-1}]^{1/2} - 1. \quad [16]$$

Note that there is something arbitrary about defining the stretch measure by means of stretching *planes* instead of stretching *lines*. A stretch measure for stretching of lines could be derived using the above procedure. If $l(t')$ and $l(t)$ are lengths between two material points at states t' and t, a stretch measure could be defined as

$$\varepsilon_l = \left\langle \frac{l^2(t)}{l^2(t')} \right\rangle^{1/2} - 1 = \left[\frac{1}{3}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)\right]^{1/2} - 1 = \left[\frac{1}{3} I_{C-1}\right]^{1/2} - 1. \quad [17]$$

The first and the second invariant of the Finger tensor describe the maximum stretch of material lines and of material planes, respectively. The third invariant describes volume changes.

3. Constitutive equation with stretch dependent memory

The derivation of the constitutive equation does not prescribe a specific formulation of the damping function. The most simple damping function is

$$h(t,t') = \exp[-n\,\varepsilon_p(t,t')] \quad [18]$$

where n is a material constant to be determined from experiments. This simple damping function should be examined before one choses more complicated relations.

The damping function of eq. [18] is practically the same as to the damping function of eq. [5], which has been determined from experimental data. The success of this type of damping function, as shown by *Wagner* (10), suggests that stretching of material planes is responsible for the increased loss of junctions in flows with large deformations.

The complete constitutive equation as described above would be the rubberlike liquid equation, eq. [1], with a memory function

$$m(t,t',C^{-1}) = [\exp(-n(II_{C-1}/3)^{1/2} + n)] \cdot \sum_{i=1}^{N} \frac{G_i}{\lambda_i} \exp\left(-\int_{t'}^{t} \frac{dt''}{\lambda_i(t'')}\right). \quad [19]$$

In the following, the stretch measure will be calculated for three types of flow. While in shear the planes of maximum stretch change during the deformation, at irrotational flow such as uniaxial extension or biaxial extension, the material planes of maximum stretch are the same during the whole deformation.

3.1. Unidirectional simple shear

The material is deformed with a shear rate $\dot\gamma(t')$. The shear between state t' and state t is

$$\gamma(t') = -\int_{t'}^{t} \dot\gamma(t')\,dt'. \quad [20]$$

If the shear rate is constant in the whole time interval, the shear is proportional to the time difference.

$$\gamma(t') = -\dot\gamma(t - t'). \quad [21]$$

An embedded coordinate system is chosen, which at state t is defined by e_1 in the direction of shear, e_2 perpendicular to the shear surfaces, and e_3 perpendicular to e_1 and e_2. The components of the Cauchy tensor with respect to the orthonormal frame are

$$(C(t')) = \begin{pmatrix} 1 & \gamma & 0 \\ \gamma & 1+\gamma^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad [22]$$

The value of the stretch measure of uniaxial simple shear

$$\varepsilon_p(t',t) = (1 + \gamma^2/3)^{1/2} - 1 \qquad [23]$$

depends on the shear. The volume is assumed to be constant. For large strains, the stretch measure approaches $(0.574|\gamma| - 1)$.

3.2. Uniaxial extension

A material is extended in one direction at a rate

$$\frac{1}{e_1}\frac{de_1}{dt'} = \dot{\varepsilon}(t') \qquad [24]$$

and can deform freely in the plane perpendicular to the direction of extension:

$$e_2(t') = e_3(t'). \qquad [25]$$

The volume is assumed to stay constant during the deformation. An embedded coordinate system is chosen along the principal axes of strain. The values of the embedded coordinate vectors are

$$e_1(t') = \exp\varepsilon, \qquad [26]$$

$$e_2(t') = e_3(t') = \exp(-\varepsilon/2), \qquad [27]$$

where the elongation ε is given by the integral

$$\varepsilon(t') = -\int_{t'}^{t} \dot{\varepsilon}(t')\,dt'. \qquad [28]$$

The components of the Cauchy tensor are

$$(C(t')) = \begin{pmatrix} \exp 2\varepsilon & 0 & 0 \\ 0 & \exp(-\varepsilon) & 0 \\ 0 & & \exp(-\varepsilon) \end{pmatrix}. \qquad [29]$$

The stretch measure of uniaxial extension is

$$\varepsilon_p(t',t) = [\tfrac{1}{3}\exp 2\varepsilon + \tfrac{2}{3}\exp(-\varepsilon)]^{1/2} - 1. \qquad [30]$$

3.3. Biaxial extension

A material is extended in two directions

$$\frac{1}{e_1}\frac{de_1}{dt'} = \dot{\varepsilon}_1(t'); \qquad \frac{1}{e_2}\frac{de_2}{dt'} = \dot{\varepsilon}_2(t') \qquad [31]$$

while it can deform freely in the third direction.

The length of the three embedded vectors along the principal axes of strain are

$$e_1(t') = \exp\varepsilon_1,$$

$$e_2(t') = \exp\varepsilon_2,$$

$$e_3(t') = \exp(-\varepsilon_1)\cdot\exp(-\varepsilon_2). \qquad [32]$$

The volume is assumed to remain constant. The elongational strains are

$$\varepsilon_1(t') = -\int_{t'}^{t} \dot{\varepsilon}_1(t')\,dt';$$

$$\varepsilon_2(t') = -\int_{t'}^{t} \dot{\varepsilon}_2(t')\,dt'. \qquad [33]$$

The components of the Cauchy tensor are

$$(C(t')) = \begin{pmatrix} \exp 2\varepsilon_1 & 0 & 0 \\ 0 & \exp 2\varepsilon_2 & 0 \\ 0 & 0 & \exp(-2\varepsilon_1)\exp(-2\varepsilon_2) \end{pmatrix}.$$

The stretch measure of biaxial extension is

$$\varepsilon_p(t',t) = [\tfrac{1}{3}\{\exp 2\varepsilon_1 + \exp 2\varepsilon_2 + \exp(-2\varepsilon_1)\exp(-2\varepsilon_2)\}]^{1/4} - 1. \qquad [35]$$

If the rate of extension is the same in the two directions, $\varepsilon_1 = \varepsilon_2 = \varepsilon$, the stretch measure becomes

$$\varepsilon_p(t',t) = [\tfrac{2}{3}\exp 2\varepsilon + \tfrac{1}{3}\exp(-4\varepsilon)]^{1/4} - 1. \qquad [36]$$

4. Conclusion

The stretch measure ε_p for unidirectional simple shear, for uniaxial extension and for biaxial extension (with $\varepsilon_1 = \varepsilon_2$) is shown in figure 2.

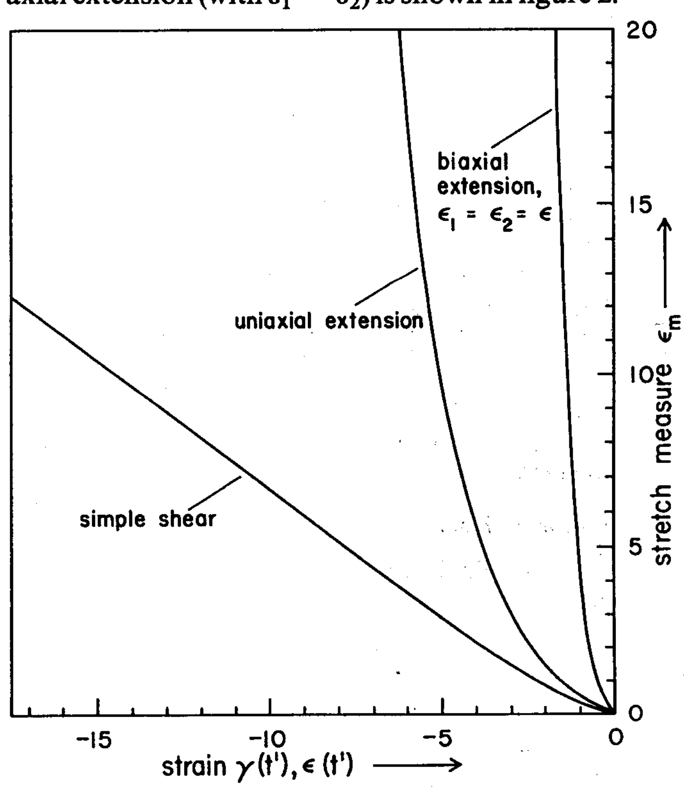

Fig. 2. The value of the stretch measure ε_p as a function of the strain in unidirectional simple shear, in uniaxial extension, and in biaxial extension with $\varepsilon_1 = \varepsilon_2 = \varepsilon$

In shear, the stretch measure increases linearly and in elongation it increases exponentially with the value of the strain. With figure 2 and eq. [18], the value of the damping function can be calculated. A comparison with measured damping functions for shear and elongation will show whether the selected form of the damping function is adequate or a new one should be tried. If it describes the behavior of the polymer in shear and in elongation, it has to be further tested in more general types of flow. It is hoped that by means of the stretch measure a single form of the damping function can be found.

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Summary

In a deforming continuum, material surfaces change their area. If material points are members of a surface which stretches during the deformation, these material points increase their relative distances. The continuum is modeled by a network of macromolecules which form temporary junctions between each other. Junctions on a stretching material surface increase their distance. As a consequence, the probability of *junction breakage* is increased.

The stretching of material planes through a material point is described by means of an embedded coordinate system. The metric of this coordinate system is the Cauchy tensor *C*. A *stretch measure* ε_p is defined for arbitrary flows. The stretch measure is used to formulate a memory function in a rheological constitutive equation for large strain. Specific applications are made to unidirectional simple shear, uniaxial extension and biaxial extension.

In a consecutive study, comparison with experiments will demonstrate to what degree the selected memory function can describe the actual behavior of the polymer.

Zusammenfassung

Materie-Flächen in einem Kontinuum ändern ihren Flächeninhalt, wenn sich das Kontinuum deformiert. Punkte auf einer Materie-Fläche vergrößern ihre Abstände, wenn die Fläche gedehnt wird. Das Kontinuum stellt man sich als ein Netzwerk von Makromolekülen mit temporären Knotenpunkten vor. Knotenpunkte in einer sich vergrößernden Fläche vergrößern während der Deformation ihren Abstand. Als Folge davon erhöht sich die Wahrscheinlichkeit, daß sich diese *Knoten lösen.*

Mit einem eingeprägten Koordinatensystem wird beschrieben, wie sich ebene Materie-Flächen, die durch einen Punkt der Materie gehen, vergrößern oder verkleinern. Mit der Metrik des Koordinatensystems, dem Cauchy-Tensor *C*, wird ein Dehnungsmaß ε_p für Strömungen beliebiger Art definiert. Dieses Dehnungsmaß wird dazu verwendet, die Gedächtnisfunktion einer rheologischen Stoffgleichung für große Deformationen zu formulieren. Das Dehnungsmaß wird für besondere Strömungen wie die einfache Scherung, die einachsige Dehnung und die zweiachsige Dehnung berechnet.

In einer späteren Arbeit soll durch Vergleich mit Experimenten gezeigt werden, inwieweit die gewählte Gedächtnisfunktion das Verhalten von Polymerschmelzen wiedergibt.

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