Rheology and Structure-Rheology Relationship for Thermoplastics

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FUNDAMENTALS

Rheology of polymer melts [4, 35]

Strain and stress

The mechanical behavior of a material is described by the constitutive equation which relates stress and deformation history. The state of stress is given by the stress tensor:

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

(1)

σ_{ij} is the stress component which acts on the surface i in direction j.

For $i \# j$, σ_{ij} are shear stress components, for $i = j$ σ_{ij} are normal stress components. Tension stresses are positive, pressure stresses is negative. The stress tensor is symmetric, ie. $\sigma_{ij} = \sigma_{ji}$.

The deformation state at infinitesimal deformation is defined by the strain tensor on a surface i in direction j:

$$\underline{\underline{\varepsilon}} = \begin{pmatrix} \dfrac{\partial u_1}{\partial X_1} & \dfrac{1}{2}\left[\dfrac{\partial u_2}{\partial X_1} + \dfrac{\partial u_1}{\partial X_2}\right] & \dfrac{1}{2}\left[\dfrac{\partial u_3}{\partial X_1} + \dfrac{\partial u_1}{\partial X_3}\right] \\ \dfrac{1}{2}\left[\dfrac{\partial u_1}{\partial X_2} + \dfrac{\partial u_2}{\partial X_1}\right] & \dfrac{\partial u_2}{\partial X_2} & \dfrac{1}{2}\left[\dfrac{\partial u_3}{\partial X_2} + \dfrac{\partial u_2}{\partial X_3}\right] \\ \dfrac{1}{2}\left[\dfrac{\partial u_1}{\partial X_3} + \dfrac{\partial u_3}{\partial X_1}\right] & \dfrac{1}{2}\left[\dfrac{\partial u_2}{\partial X_3} + \dfrac{\partial u_3}{\partial X_2}\right] & \dfrac{\partial u_3}{\partial X_3} \end{pmatrix}$$

(2)

$X(X_1, X_2, X_3)$ is the position of a material particle at time $t=0$; $u(u_1, u_2, u_3)$ is the displacement vector.

The strain tensor is symmetric. The main components describe the extension; the off-diagonal elements describe the shear deformations.
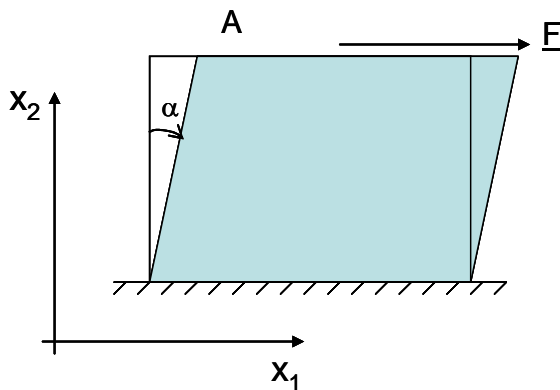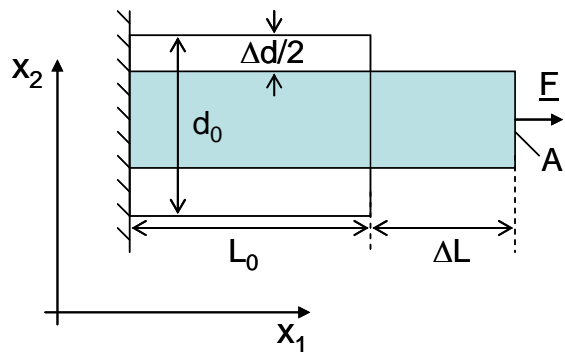

Figure 1.1 simple shear

Figure 1.2 simple extension

In simple shear (Figure 1.1), a force $\underline{F}$ is applied tangentially at the surface A of a body. The shear stress is defined as $\sigma_{21} = F/A$. The stress tensor for infinitesimal simple shear simplifies to:

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

(3)

with $\sigma_{ii} = -p^*$ the hydrostatic pressure.

The material generates normal stresses if subjected to finite shear deformations:

$$N_1 = \sigma_{11} - \sigma_{22} \neq 0 \quad \text{and} \quad N_2 = \sigma_{22} - \sigma_{33} \neq 0$$

(4)

The strain tensor is defined for simple shear is:

$$\underline{\underline{\varepsilon}} = \begin{pmatrix} 0 & \frac{1}{2}\gamma_{12} & 0 \\ \frac{1}{2}\gamma_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

(5)

$$\varepsilon_{21} = \varepsilon_{12} = \frac{1}{2}\frac{\partial u_1}{\partial X_2} = \frac{1}{2}\gamma_{21}$$

$$\gamma_{21} = \tan \alpha$$

In simple extension (Figure 1.2) a force $\underline{F}$ acts perpendicularly on the surface A. The stress tensor is only defined by the normal stress components. All shear stress components are zero.

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

(6)

In directions X_2 and X_3, only the hydrostatic pressure is applied; as such $\sigma_{22} = \sigma_{33} = -p^*$. Since the hydrostatic pressure superposes on the normal stress components, the stress applied to a body is:

$$\sigma = \sigma_{11} + p^* = \sigma_{11} - \sigma_{22} = \underline{F}/A$$

(7)

For an infinitesimal extension, the component of the strain tensor ε_{11} is equivalent to the Cauchy strain ε_C.

$$\varepsilon_{11} = \frac{\partial u_1}{\partial X_1} = \frac{\Delta u_1}{\Delta X_1} = \frac{\Delta L}{L_0} = \varepsilon_C$$

(8)

If incompressibility can be assumed, the strain stress component normal to the main direction, become:

$$\varepsilon_{22} = \varepsilon_{33} = \frac{1}{2}\varepsilon_{11} = \frac{1}{2}\varepsilon_C$$

(9)

By combining (8) and (9), the strain tensor for simple strain reduces to:

$$\underline{\underline{\varepsilon}} = \begin{pmatrix} \varepsilon_C & 0 & 0 \\ 0 & -\frac{1}{2}\varepsilon_C & 0 \\ 0 & 0 & -\frac{1}{2}\varepsilon_C \end{pmatrix}$$

(10)

The constitutive equation for an incompressible Hookean body is given by:

$$\sigma = -p^*\underline{\underline{1}} + 2G\underline{\underline{\varepsilon}}$$

(11)

G is the shear modulus. With (4), (5), (11) the shear stress for a Hookean body in simple shear reduces to:

$$\sigma_{21} = G\gamma_{21}$$

(12)

In simple extension the applied stress is:

$$\sigma = \sigma_{11} - \sigma_{22} = 2G(\varepsilon_{11} - \varepsilon_{22}) = 2G(\varepsilon_C + \frac{1}{2}\varepsilon_C)$$
$$\sigma = 3G\varepsilon_C = E\varepsilon_C$$

(13)

$E = 3G$ is the elasticity modulus for an incompressible Hookean solid.

The constitutive equation of a Newtonian fluid an equation relating stress and strain rate:

$$\sigma = -p^*\underline{\underline{1}} + 2\eta\underline{\underline{\dot{\varepsilon}}}$$

(14)

η is the shear viscosity. $\dot{\varepsilon}$ is the time derivative of the strain tensor. For non curved stream lines, the components of the strain rate tensor simplify to:

$$\dot{\varepsilon}_{ij} = \frac{1}{2}\frac{\partial}{\partial t}\left(\frac{\partial u_j}{\partial X_i} + \frac{\partial u_i}{\partial X_j}\right) = \frac{1}{2}\frac{\partial}{\partial t}\gamma_{ij}$$

(15)

The stresses in shear and extension in simple shear resp. extension reduce to:

$$\sigma_{21} = 2\eta\dot{\varepsilon}_{21} = 2\eta\,\tfrac{1}{2}\,\frac{\partial}{\partial t}\gamma_{21} = \eta\dot{\gamma}_{21}$$

(16)

and

$$\sigma = \sigma_{11} - \sigma_{22} = 2\eta(\dot{\varepsilon}_{11} - \dot{\varepsilon}_{22}) = 2\eta(\dot{\varepsilon}_{11} + \tfrac{1}{2}\dot{\varepsilon}_{11})$$
$$\sigma = 3\eta\dot{\varepsilon}_C = \eta_E\dot{\varepsilon}_C$$

(17)

$\eta_E = 3\eta$ is incompressible the elongational viscosity for an Newtonian fluid. η is the shear viscosity

Polymer melts are viscoelastic fluids, i.e. their rheological behavior can be described by time-dependent material functions. For infinitesimal deformation, the response of the material to consecutive changes of the strain can be added linearly (superposition). The material behavior can be described by linear differential equations (linear viscoelasticity). The constants of proportionality of the Hookean body (*E; G*) and the Newtonian fluid (η_E; η) are extended to time dependent functions.

The constitutive equation for a linear viscoelastic body is:

$$\sigma = -p\underline{\underline{1}} + 2\int_{\infty}^{t} G(t-t')\frac{d\underline{\underline{\varepsilon}}(t')}{dt'}dt'$$

(18)

For a linear viscoelastic fluid, $G(\infty) = 0$, partial integration gives:

$$\sigma = -p\underline{\underline{1}} + 2\int_{\infty}^{t} m(t-t')\big(\varepsilon(t) - \varepsilon(t')\big)dt'$$

(19)

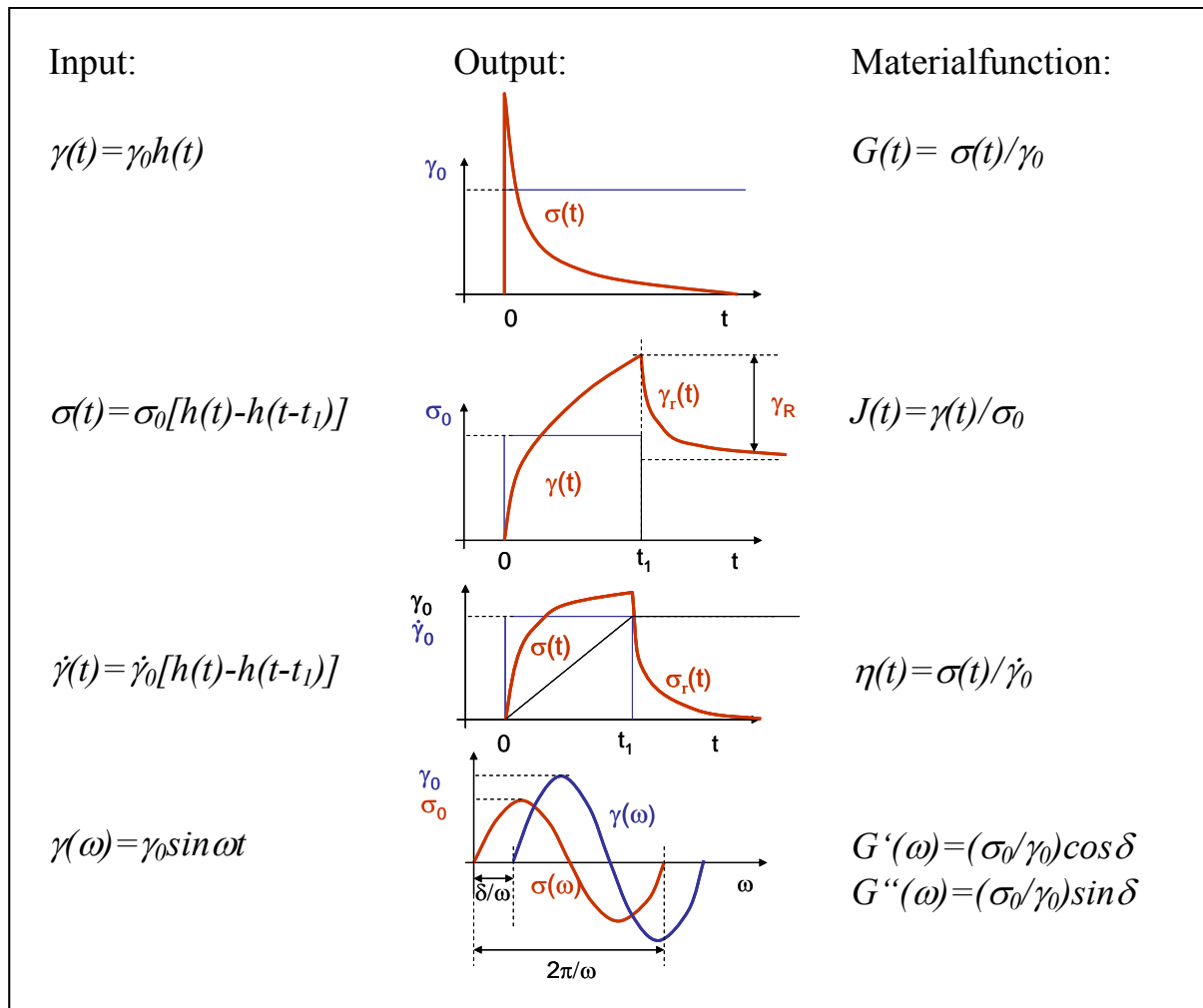| Input:	Output:	Materialfunction:
$\gamma(t)=\gamma_0 h(t)$	$\sigma(t)$	$G(t)= \sigma(t)/\gamma_0$
$\sigma(t)=\sigma_0[h(t)-h(t-t_1)]$	$\gamma_r(t)$, γ_R, $\gamma(t)$	$J(t)=\gamma(t)/\sigma_0$
$\dot{\gamma}(t)=\dot{\gamma}_0[h(t)-h(t-t_1)]$	$\sigma(t)$, $\sigma_r(t)$	$\eta(t)=\sigma(t)/\dot{\gamma}_0$
$\gamma(\omega)=\gamma_0 \sin\omega t$	$\gamma(\omega)$, $\sigma(\omega)$	$G'(\omega)=(\sigma_0/\gamma_0)\cos\delta$ $G''(\omega)=(\sigma_0/\gamma_0)\sin\delta$

Figure 1.3. Table with key basic test modes

$m(t - t') = dG(t -t')/dt'$ is a memory function.

In order to determine the relation between deformation and stress a number of basic tests are performed. The response of the material to step and oscillatory deformation is measured. Figure 1.3 summarizes the key basic tests used to determine the linear viscoelastic material response. In the following, these tests are described in detail.

Relaxation

During a relaxation test, the material is subjected to a step shear strain at the time $t = 0$.

$$\gamma(t) = \gamma_0 h(t) \quad \text{with} \quad h(t) = \begin{cases} 0 & (t < 0) \\ 1 & (t > 0) \end{cases}$$
(20)

The response of the material, the stress σ(t), is a decreasing function with time. The relaxation modulus is defined as:

$$G(t) = \frac{\sigma(t)}{\gamma_0}$$
(21)

$G(t)$ is a monotonic function. $G(t \to o) = G_0$ is the glass modulus; $G(t \to \infty) = G_e$ is the equilibrium modulus which is zero for thermoplastic. For infinitesimal deformation, i.e. if $\gamma_o \to 0$, $G(t)$ becomes independent of γ_o.

Oscillatory shear

In oscillation experiments the material functions are frequency dependent. The material is subjected to a sinusoidal shear deformation:

$$\gamma_{21} = \hat{\gamma}_{21} \exp(i\omega t)$$
(22)

With γ_{21} representing the amplitude and ω the angular frequency (Figure 1.3). The shear stress response is given by :

$$\sigma_{21} = \hat{\sigma}_{21} \exp(i(\omega t + \delta))$$
(23)

with σ_{21} is the shear stress amplitude and δ the phase shift. The material function $G*(\omega)$ is defined as :

$$G^*(\omega) = \frac{\sigma_{21}(\omega)}{\gamma(\omega)} \qquad G^* = G' + iG''$$
(24)

G' is the storage modulus; G'' the loss modulus; $G''/G' = tg\delta$ is the loss factor.

Step strain rate

In a step strain rate test, the deformation rate is stepped from zero to γ_0 at $t = 0$ (Fig. 1.3).

$$\dot{\gamma}(t) = \dot{\gamma}_0 h(t) \qquad \text{with} \quad \gamma(t) = \dot{\gamma}_0 t$$
25)

The response of the material to the strain rate step is the stress σ(t). The material function is the time dependent viscosity :

$$\eta(t) = \frac{\sigma(t)}{\dot{\gamma}_0}$$
(26)

The linear viscoelastic viscosity function is independent of $\dot{\gamma}_0$.

Relaxation spectrum, Moments of the relaxation time spectrum

The relaxation behavior of polymers can be simulated using a Maxwell-model which is represented by a Hookean spring and a Newtonian damping element. The relaxation shear modulus described by this model is:

$$G(t) = \frac{\sigma(t)}{\gamma_0} = G \exp(-t/\tau)$$
(27)

τ is the time of relaxation and is the ratio of the viscosity of the damping element and the elasticity modulus G of the spring.

For an oscillation deformation, the loss and storage moduli to can be calculated according to:

$$G'(\omega) = G\frac{\omega^2\tau^2}{1+\omega^2\tau^2}$$

$$G''(\omega) = G\frac{\omega\tau}{1+\omega^2\tau^2}$$

(28)&(29)

The real relaxation behavior, however cannot be described by a single Maxwell-model. A general Maxwell model is obtained by combining *n* elements in parallel.

The relaxation modulus as well as the storage and loss moduli extend to:

$$G(t) = \sum_{i=1}^{N} G_i \exp(-t/\tau)$$

$$G'(\omega) = \sum_{i=1}^{N} G_i \frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2}$$

$$G''(\omega) = \sum_{i=1}^{N} G_i \frac{\omega\tau_i}{1+\omega^2\tau_i^2}$$

(3), (31), (32)

with $\{G_i, \tau_i\}$ the discrete relaxation spectrum.

Replacing $G_i(\tau_i) = g(\tau)d\tau$ and the summation with the integral, the relaxation modulus changes to:

$$G(t) = {E(t)}\big/{3} = \int_0^{\infty} g(\tau)\exp(-t/\tau)d\tau$$

(33)

As the relaxation time extends over a wide range, use of a logarithmic time axis is preferred:

$$d\ln\tau = d\tau/\tau; \qquad g(\tau)\tau = H(\ln\tau)$$

$$G(t) = \int_{-\infty}^{+\infty} H(\ln\tau)e^{-t/\tau}d\ln\tau$$

(34); (35)

The storage and loss moduli are:

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\ln\tau)\frac{\omega^2\tau^2}{1+\omega^2\tau^2}d\ln\tau$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\ln\tau)\frac{\omega\tau}{1+\omega^2\tau^2}d\ln\tau$$

(36); (37)

For $t\to 0$, (35) reduces to:

$$G(0) = G_0 = \int_{-\infty}^{+\infty} H(\ln\tau)d\ln\tau$$

(38)

G_0= zero moment of the relaxation spectrum.

Integration of the modulus *G(t)* gives a viscosity:

$$\eta(t) = \frac{p_{21}(t)}{\dot{\gamma}_0} = \int_0^t G(t)dt$$

$$= \int_{-\infty}^{+\infty} \tau H(\tau)(1-\exp(-t/\tau))d\ln\tau)d\ln\tau$$

(39);(40)

If $t\to\infty$; η $(t\to\infty)$ equals the zero shear viscosity:

$$\eta_0 = \lim_{\substack{t\to\infty \\ \dot{\gamma}_0\to 0}} \eta(t) = \int_{-\infty}^{+\infty} H(\ln\tau)\tau d\ln\tau$$

(41)

η_0 = first moment of the relaxation spctrum.

The step strain rate test is most advantageous for the determination of the relaxation time spectrum at long times as the spectrum is weighted with the relaxation time.

From (37), the first moment of the relaxation time spectrum is obtained for $\omega \to 0$:

$$\lim_{\omega\to 0} \frac{G''(\omega)}{\omega} = \int_{-\infty}^{+\infty} H(\ln\tau)\tau d\ln\tau = \eta_0$$

(42)

The second moment of the relaxation time spectrum is derived from the storage modulus (36) for $\omega\to 0$:

$$\lim_{\omega\to 0} \frac{G'(\omega)}{\omega^2} = \int_{-\infty}^{+\infty} H(\ln\tau)\tau^2 d\ln\tau = A_G$$

(45)

Creep test

The response of a material to a shear stress $\sigma(t) = \sigma_o h(t)$ at time $t = 0$, is the shear deformation $\gamma(t)$ (Fig. 1.3). The material function is the compliance *J(t)*:

$$J(t) = \frac{\gamma(t)}{\sigma_0}$$

(44)

$J(t)$ can be separated into three parts:

$$J(t) = J_0 + J_d \Psi(t) + \frac{t}{\eta_0}$$

(45)

With J_o = time independent elastic compliance; J_d = retarded compliance; $\Psi(t)$ = creep function with $\Psi(0) = 0$ and $\Psi(\infty) = 1$ and η_0 the zero shear viscosity.

Recovery

If a linear viscoelastic material is subjected to a constant stress σ_o at the time $t=0$ and unloaded at $t = t_1$ the recovered deformation $\gamma_r(t)$(Figure 1.3) [31] is:

$$\gamma_r(t) = \sigma_0 J(t_1) - (\sigma_0 J(t) - \sigma_0 J(t - t_1))$$
$$J(t_1) = J_0 + J_d \Psi(t_1) + t_1 / \eta_0$$
$$J(t) = J_0 + J_d \Psi(t) + t / \eta_0$$
$$J(t - t_1) = J_0 + J_d \Psi(t - t_1) + (t - t_1) / \eta_0$$
$$\gamma_r(t) = \sigma_0(J_0 + J(\Psi(t_1) - \Psi(t) + \Psi(t - t_1)))$$

(46), (47), (48), (49), (50)

If steady state flow has been obtained in creep, i.e. $\Psi(t_1) = \Psi(t) = 1$, equation (50) reduces to:

$$\gamma_r(t) = \sigma_0(J_0 + J_d \Psi(t_1))$$

(51)

The recovered strain for $t \rightarrow \infty$ is the total recoverable strain $\gamma_R(t_1)$ at time t_1: If no steady state flow has been obtained during creep ($\Psi(t_1) \neq 1$), γ_R reduces for $t \rightarrow \infty$

$$\gamma_R(t_1) = \lim_{t \rightarrow \infty} \gamma_r(t - t_1)$$
$$\gamma_R = \sigma_0(J_0 + J_d \Psi(t_1))$$

(52)

If steady state flow is obtained during creep, $\gamma_R(t_1)$ reduces for $t \rightarrow \infty$ to:

$$\gamma_R = \sigma_0(J_0 + J_d) = \sigma_0 J_e$$

(53)

The steady state compliance J_e is the sum of J_d and J_o.

Retardation time spectrum

The creep behavior of the material can be represented by the general Voigt-Kelvin model. The compliances for elongation and shear can be derived as follows:

$$J(t) = J_0 + \sum_{i=1}^{n} J_i (1 - \exp(-t / \tau_i) + t / \eta_0$$

(54)

τ_i is the retardation time of the element i of a series of n elements.

All $\{J_i; \tau_i\}$ pairs represent the discrete retardation spectrum. $f(\tau)d\tau$ is the continuous function of the retardation time spectrum. Equation (54) can be rearranged:

$$J(t) = J_0 \left(\int_0^\infty f(\tau)(1 - \exp(-t / \tau))d\tau \right) + t / \eta_0$$

(55)

Introducing a logarithmic time scale, $d\ln\tau$ goes to $L(d\ln\tau)$ and (55) can be rearranged to:

$$J(t) = J_0 + \left(\int_{-\infty}^{+\infty} L(\ln \tau)(1 - \exp(-t / \tau))d\ln\tau \right) + t / \eta_0$$

(56)

This equation defines the continuous retardation spectrum $L(\ln\tau)$. The total recoverable compliance is $J_R(t) = J(t) - t/\eta_o$.

If $t \rightarrow \infty$ and $J = 0$:

$$J_R(t \rightarrow \infty) \equiv J_e = \int L(\ln \tau)d\ln\tau$$

(57)

J_e is the steady state compliance.

J_e is the zero moment of the retardation time spectrum.

J_e can also be determined from the moments of the relaxation spectrum [4]:

$$J_e = \frac{\int_{-\infty}^{+\infty} H(\ln\tau)\tau^2 d\ln\tau}{\left(\int_{-\infty}^{+\infty} H(\ln\tau)\tau d\ln\tau \right)^2} = \frac{A_G}{\eta_0^2}$$

(58)

Non-viscoelastic behavior

The linear viscoelasticity is only valid for infinitesimal deformations. In order to describe finite deformations, the relative Finger tensor $\underline{\underline{C}}^{-1}(t')$ is used:

$$\left(\underline{\underline{C}}_t^{-1}(t')\right)_{ik} = \sum_j \frac{\partial x_i(t)}{\partial x_j'(t')} \frac{\partial x_k(t)}{\partial x_j'(t')}$$

(59)

x_i and x'_j are material coordinates of the same element at time $t' > t_0$ and at the reference time t.

For finite deformations, Lodge introduced the rubber-like liquid model described by the following constitutive equation :

$$\underline{\underline{p}} = -p * \underline{\underline{1}} + \int_0^t m(t-t')\underline{\underline{C}}_t^{-1}(t')dt'$$

(60)

For simple shear, the relative Finger tensor is reduced to:

$$\underline{\underline{C}}_t^{-1}(t') = \begin{pmatrix} 1+\gamma^2(t',t) & \gamma(t',t) & 0 \\ \gamma(t',t) & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(61)

with the relative shear:

$$\gamma(t',t) = \gamma(t) - \gamma(t')$$

(62)

This model exhibits a first normal stress difference $N_1 = \tau_{11} - \tau_{22}$ which varies with the shear deformation squared.

The first normal stress function $\theta_1(t)$ can be obtained using (60):

$$\theta_1(t) = \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}^2} = 2\int_0^t G(t)t\,dt$$

$$\theta_1(t) = 2\int_{-\infty}^{+\infty} H(\ln\tau)\tau^2\left(1-(1+t/\tau)\exp(-t/\tau)\right)d\ln\tau$$

(63) (64)

The first normal stress function $\theta_1(t)$ reduces for $t\to\infty$ (steady state flow) to:

$$\theta_1(t\to\infty) = \theta_0 = 2\int_{-\infty}^{+\infty} H(\ln\tau)\tau^2 d\ln\tau$$

(65)

θ_0 is independent of shear rate and is proportional to the second moment of the relaxation spectrum. Comparing (65) and (43) gives:

$$\theta_0\big/2 = A_G$$

(66)

A_G is obtained from the theory of linear viscoelasticity. $\theta_o = 0$ for the linear viscoelasticity.

$\theta_1(t) \neq 0$ and especially $N_1 \sim \dot{\gamma}^2$ are valid for second order fluids like the rubber like liquid model.

For a simple elongation, the relative Finger tensor is:

$$\underline{\underline{C}}_t^{-1}(t') = \begin{pmatrix} \exp 2\varepsilon_H(t,t') & 0 & 0 \\ 0 & \exp(-\varepsilon_H(t,t')) & 0 \\ 0 & 0 & \exp(-\varepsilon_H(t,t')) \end{pmatrix}$$

(67)

$\varepsilon_H(t' t)$ is the relative Hencky elongation between time t and t'. The constitutive equation by Lodge is an extension of linear viscoelasticity and describes the first normal stress difference in simple shear and the extensional viscosiy in simple elongation. In the limit of infinitesimal deformation, it reduces to the constitutive equation of the linear viscoelasticity.

Temperature dependence[4]

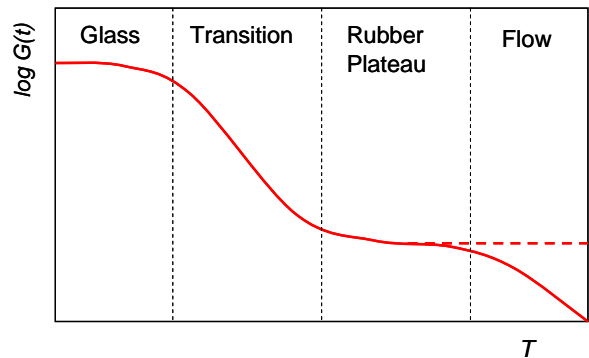Viscoelastic functions are not only functions of time, but also of temperature.

Figure 1.4 Modulus as a function of temperature

Below the glass transition temperature, the configuration of the polymer chain backbones are largely immobilized and the viscoelastic properties characterizing the polymer system do not change significantly with time or frequency. In the transition zone between glass-like and rubber-like consistency, the dependence of viscoelastic functions on temperature is most remarkable. In the rubber and flow region, linear viscoelastic functions are strongly dependent on frequency and time. Cross-linked materials don't exhibit a flow region.

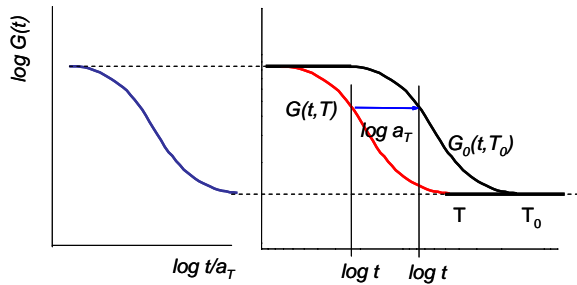Any attempt to analyze the temperature dependence at constant frequency or time

Fig. 1.5 Comparison of time and temperature dependence of the modulus G(t)

by seeking an analytical form for the modulus $G(T)$ resp. $G*(T)$ would lead to very complicated results. Instead, the method of reduced variables is used.

This method, very often referred to as Bolzman superposition principle or t-T superposition principle, has been developed empirically.

The shear modulus $G(t)$ at T = constant shows similar behavior as the shear modulus $G(T)$ at a given time t in the logarithmic plot of figure 1.5. If $G(log\ t)$ curves are shifted along the time axis, the curves obtained at different temperatures superpose.

The shift along the logarithmic time axis generates a shift factor a_T resp. *log a_T*.

For a thermo-rheological simple body, all relaxation times shift by the same amount and a_T is defined as:

$$a_T = \frac{\tau_i(T)}{\tau_i(T_0)} \cong \frac{\eta_0(T)}{\eta_0(T_0)}$$

(68)

Instead of representing $G(t,T)$ in a three dimensional plot, the two curves $G(t,T_o)$ and $a_T(T)$ are sufficient to describe the material behavior as a function of time and temperature.

The practical advantage of the t-T superposition is the possibility to determine a wide range of frequency resp. time dependence at a constant temperature which would never be accessible experimentally at a single temperature.

For amorphous materials, Williams, Landel and Ferry developed an empirical equation to predict a_T This equation holds for most unfilled materials.

$$\log a_T(T) = -8.86 \frac{T - T_s}{101.6 + T - T_s}$$

$$T_s \cong T_g + 50$$

(69)

Note: Because of the temperature dependence of the specific volume, the modulus has to be corrected for T-effects:

$$G(\frac{1}{a_T}, T_0) = \frac{\rho_0 T_0}{\rho T} G(t, T)$$

(70)

This correction can very often be neglected. For semi- crystalline materials, the Arrhenius relation holds for a_T at higher temperatures:
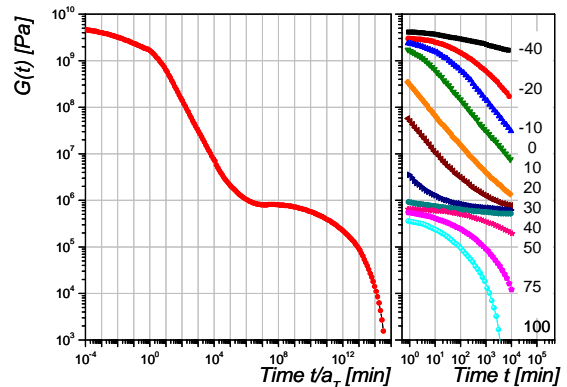

Fig. 1.6 Master curve and shift factor

$$a_T(T) = K \exp(E_a / RT) \tag{71}$$

E_a is an activation energy describing the temperature dependence of the material.

Characterization of polymer structure[3 12, 37]

Molecular weighting molecular weight distribution

The molecular weight distribution $w(M)$ of a polymer represents the mass of the macromolecules with a molecular weight M relative to the total mass of all molecules.

The average molecular weight M_w of the molecular weight distribution is the arithmetic mean of the molecular weights:

$$\overline{M}_w = \frac{\sum_i m_i M_i}{\sum_i m_i} \tag{72}$$

m_i= mass of all molecules with the molecular weight M_i

Instead of the mass the number of molecules with the molecular weight M can be used. The number average molecular weight M_n of the molecular weight distribution is defined:

$$\overline{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\sum_i m_i}{\sum_i m_i / M_i} \tag{73}$$

n_i = number of molecules with the molecular weight M_i

N_A = Avogadro number

Using (72) and (73) , M_w can be rearranged to:

$$\overline{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \tag{74}$$

Other averages are the average z molecular weight distribution:

$$\overline{M}_z = \frac{\sum_i z_i M_i}{\sum_i z_i} = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2} \tag{75}$$

and the viscosity average:

$$\overline{M}_{[\eta]} = \left(\frac{\sum_i m_i M_i^a}{\sum_i m_i} \right)^{1/a} \tag{76}$$

For a monodisperse distribution, all averages of the molecular weight distribution are the same. For polydisperse distributions, the values of the averages increase as follows:

$$\overline{M}_n < \overline{M}_{[\eta]} < \overline{M}_w < \overline{M}_z \tag{77}$$

The ratio of the different averages of the molecular weight distribution are used to characterize the polydispersity. The most important parameter of polydispersity is:

$$U = \frac{\overline{M}_w}{\overline{M}_n} - 1 \tag{78}$$

When U→0 for monodisperse polymers $(M_w = M_n)$, the zero moment of the molecular weight distribution is:

$$\int_0^\infty w(M)dM = 1 \tag{79}$$

The first and second moments of the molecular weight distribution are:

$$\int_0^\infty M w(M)dM = \overline{M}_w$$
$$\int_0^\infty M^2 w(M)dM = \overline{M}_z \overline{M}_w \tag{80}\,(81)$$

The (-1) moment is the inverse of the number average molecular weight:

$$\int_0^\infty M^{-1} w(M)dM = 1/\overline{M}_n \tag{82}$$

The shape and the width of the molecular weight distribution are determined by the kinetics of the polymerization reaction.
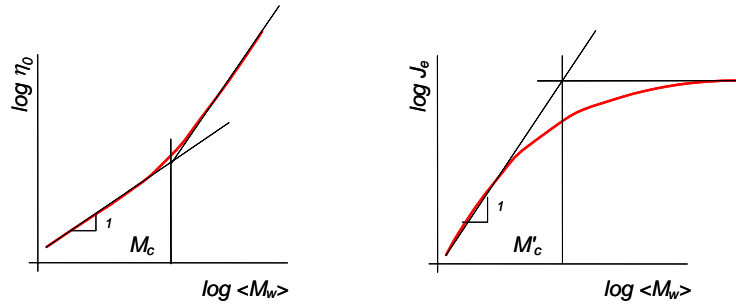
Figure 2.1 Variation of the zero shear viscosity and the steady state compliance with the weight average molecular weight M_w for narrow-distributed

The most important distribution functions $w(M)$ describing experimentally found molecular weight distributions are:

The Schultz-Flory normal distribution with the coupling ratio k':

$$w(M) = \frac{a^{k'+1} M^{k'} \exp(-aM)}{\Gamma(k'+1)}$$

(83)

with $a = k'/M_n$ and Γ being the gamma function.

If $k' = 1$, the polymerization is started by monfunctional initiators. The termination occurs only through disproportion reactions. The broadness of distribution is U = 1

If $k' = 2$, the termination is caused by recombination and U = 0.5

The Poisson distribution:

$$w(M) = \frac{v'^{M-1} M \exp(-v')}{(M-1)!(v'+1)}$$

(84)

v' is the kinetic chain length.

The Poisson distribution is the result of a polymerization with constant number of growing chains. The reactivity of the chain is independent of chain length. All chains start growing at the same time and no chain termination occurs i.e. anionic polymerization). The broadness of the distribution follows as:

$$U = \left(\frac{\overline{M}_w}{\overline{M}_n} - 1\right) = \frac{1}{P_n}$$

(85)

With increasing extent of polymerization P_n, the distribution becomes narrower

Table 2.1 M_c, M'_c and M_e for different polymers [10]

Polymer	M_c	M'_c	M_e
PS	31200	130 000	18 100
poly(a-methyl-stryrol)	13 500	104 000	13 500
PE	3 800	(14 400)	–
PMMA	27 500	>150 000	5 900
			(10 000)
PIB	15 200	-	8 900
PVAc	24 500	86 000	12 000

M_c, M'_c = critical molecular weights M_e = molecular weight between entanglements $M_e = g_N RT/G_{eN}$ g_N being a front factor /4/ .

RELATION OF POLYMER STRUCTURE AND RHEOLOGICAL BEHAVIOR OF THERMOPLASTICS

Molecular weight distribution of linear polymers

Influence on zero-shear viscosity and steady state compliance

A) Polymers with narrow molecular weight distribution (quasi mono/disperse $M_w = M_n$)

Figure 2.1 represents the zero shear viscosity and the steady state compliance as a function of the weight average molecular weight for narrow-distributed polymers. The double logarithmic plot shows the zero shear viscosity increasing linearly with a slope of 1 as a function of M_w before continuing the ascent above M_c on a straight line with a slope of 3.4 [2, 10, 17, 32]. The intersection of the two extrapolated straight lines is the critical molecular weight M_c (cf. Table 2.1).

M_c is independent of temperature and for most polymers is equivalent to a molecular weight corresponding to a chain length of 300 to 500 main chain atoms [10]. The strong increase of the zero shear viscosity with the molecular weight above M_c is due to strong interactions (entanglements) between the polymer chains.

The steady state compliance of narrow-distribution polymers is proportional to M_w below a critical molecular weight M'_c. Beyond M'_c, J_e is independent of the molecular weight (Figure 2.1.)

The value of J_e for polystyrene with a polydispersity of $M_w/M_n - 1 = 0.1$ is 1.6×10^5 m^2/N [10,27]. Critical molecular weight values M'_c for various polymers are compiled in table 2.1.

B) Polydisperse polymers ($M_w > Mn$)

For polydisperse polymers, the zero shear viscosity varies with the weight average molecular weight M_w for narrow-distributed polymers. Tests with PMMA, PS and PE show that the zero shear viscosity is independent of the breath of the distribution. More careful comparison of the zero shear viscosity for different distributions (i.e. bimodal, bimodal) shows that the dependence on molecular weight M_w is only approximate. It has to be concluded that no average molecular weight is able to describe the dependence of the zero shear viscosity for all kinds of distributions [32].

Contrary to the zero shear viscosity is the steady state compliance highly dependent on the polydispersity of polymers.

Table 2 .2 lists some relations between the steady state *compliance J_e* and the molecular weight distribution, proposed by various authors. Ferry [5] developed the relation (1) based on the Rouse-theory. J_e is dependent on molecular weight. This is in the range beyond M'_c contradictory to experimental results

Mills[18] and Zosel[45] correlated the steady state compliance with the relation of the second moment and the first moment squared of the molecular weight distribution ($M_z M_w/M_w{}^2$). This relation between the moments of molecular weight distribution corresponds to the same relation between

Table 2 .2 Correlation between the steady state compliance and the average values of molecular

(1) Ferry [5]	$J_e \approx \dfrac{\overline{M}_y \bullet \overline{M}_{y]1}}{\overline{M}_w}$
(2) Mills [18]	$J_e \approx \left(\dfrac{\overline{M}_y}{\overline{M}_w}\right)^{3.7}$
(3) Zosel [43]	$J_e \approx \left(\dfrac{\overline{M}_y}{\overline{M}_w}\right)^{2.5}$
(4) Agarwal [1]	$J_e \approx \dfrac{\overline{M}_y \bullet \overline{M}_{y]1}}{\overline{M}_n \bullet \overline{M}_w}$

the moments of the relaxation spectrum. The difference between he exponents of the relations (2) and (3) indicate that the correlation of J_e with the average molecular weights has only restrictive validity. This is also true for the relation (4) developed by Agarwal [1] although he uses a large number of published results to support the empirical relation.

Influence on linear viscoelastic moduli and compliances

The modulus $G(t)$ as well as the compliance $J(t)$ are linear viscoelastic functions in time. The frequency dependence is represented by the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$. In the double logarithmic plot (Fig. 2 .2) , the shear modulus $G(t)$ decreases starting from the glass transition temperature (modulus G_o), leveling off into the rubbery plateau which is independent of time and molecular weight for polymers with $M_w > M_c$ [19, 20, 36].

Beyond the plateau – the modulus further decreases (terminal zone). The latter depends on molecular weight and with increasing molecular weight shifts towards longer time. The value of the plateau modulus G_{eN} is independent of molecular and, in the case of polystyrene, amounts to 2×10^5 N/m^2 [2, 5]. The theory of rubber elasticity allows the calculation of an average molecular weight M_e between entanglements from G_{eN} [4]. Table 2.1 gives values of G_{eN} for various polymers.

Starting from a glassy state, the compliance $J(t)$ increases, and for polymers exhibits a rubber plateau when $M_w > M_c$. The value of rubber plateau J_{eN} is equivalent to the inverted value of G_{eN} [3, 27].

Beyond the plateau zone, $J(t)$ further increases towards a straight line with slope 1 (terminal zone). In the terminal zone, the polymer undergoes a purely viscous deformation with a constant viscosity η_o.

The recoverable compliance $J_R(t)$ (cf. Chapter 1, equation (57)) increases with time and for $t \to \infty$ equals the steady state compliance J_e. With increasing molecular weight, the terminal zone for the compliance $J(t)$ shifts towards longer times. With increasing polymer polydispersity, the transition from the rubber to the terminal zone becomes wider. Furthermore, as shown by figure 2.2, the steady state compliance J_e is much larger for polydisperse than for monodisperse polymers. For the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ the increase in molecular weight results in a shift of the terminal zones towards smaller frequencies (Figure. 2.2) [6,15,18]. A rubber plateau appears for $G'(\omega)$, independently of molecular weight beyond M_c. The loss modulus shows a molecular weight dependent maximum [25].

With polymers having a broad molecular weight distribution, the shape and the height of the rubber plateau is less well defined and the transition into the terminal zone covers a larger frequency range.

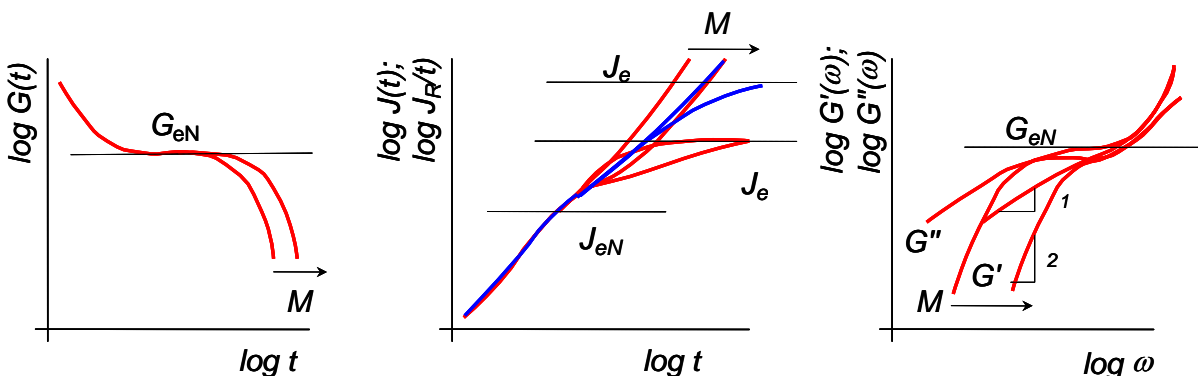## Influence on non-linear behavior (viscosity function)

Figure 2.2 Typical evolution of modulus, compliance, storage and loss moduli for polymer melts.

At large deformation, resp. deformation rates polymer melts do not exhibit linear viscoelastic behavior any more. Above a critical shear rate, the steady state viscosity decreases. Dividing the steady state viscosity with the zero shear viscosity and multiplying the shear rate with the zero shear viscosity, reduces the viscosity curves for narrow-distributed polymers to a single master curve , independently of molecular weight $\eta(\dot{\gamma}\eta_o/\eta_o)t$ [9,39]. This master curve, however is not independent of molecular weight distribution. For broad-distributed polymers, the viscosity function deviates from the linear behavior at lower shear rates. At high shear rates, the curves tend to meet again, independently of the molecular weight distribution.

Mendelson et al. [16] defined a second shift factor $X_M=1/(\eta_o\dot{\gamma})^{0.35}$ for commercial polymers. The reduced viscosity function $\eta(\eta_o \dot{\gamma}X_M)/\eta o$ describes the material behavior independently of molecular weight and molecular weight distribution.

The extensional viscosity is three times the shear viscosity at low deformation rates. Whereas the shear viscosity decreases above a critical strain rate, the elongation viscosity increases first and shows a maximum before decreasing.

The maximum of the elongational viscosity function $\eta_E(\dot{\varepsilon})$ depends strongly on branching. With increasing branching, the value of the maximum in $\eta_E(\dot{\varepsilon})$ for a LDPE increases. No maximum appears at all for HDPE. A clear differentiation of branching and molecular weight distribution influences cannot be made.

Influence of branching

The influence of long-chain-branching on the zero shear viscosity and the steady state compliance has been systematically analyzed with comb and star shaped polymers [7,11,13,14,40]. For polymers with low molecular weight, the zero shear viscosity is lower for branched polymers than for linear polymers with the same molecular weight M_w. The zero shear viscosity of the branched polymers increases with molecular weight according to $\eta_o\approx\bar{M}_w^{3.4}$ [14], of linear polymers according to $\eta_o\approx\bar{M}_w^{3.4}$.

Because of the stronger dependence on molecular weight of the zero shear viscosity of the branched polymers, the zero shear viscosity for these polymers becomes larger than the one for the linear polymers having the same molecular weight M_w /7/.

The lower viscosity of the branched polymers with small molecular weight is due to lower drag flow of the polymer coils, due to the smaller radius of gyration of the branched molecule, compared to the linear molecule with the same molecular weight. At higher molecular weight, the branches cause a stronger entanglement resistance which explains the stronger dependence of the viscosity on molecular weight.

The steady state compliance J_e is also independent of molecular weight M_w starting from a critical molecular weight for narrow-distributed branched polymers. The absolute value of J_e however, is much higher than for linear polymers.

Contrary to long-chain-branches, short-chain-branches have hardly any influence on rheological behavior [39]. It has to be noted, however, that short-chain-branched polymers are much more dependent on temperature than long-chain-branched polymers[4].

Blending rules

<u>Binary blends</u>

In 1957, Ninimyia and Fujito[20] developed a blending rule for the relaxation spectrum with the following assumptions:

a) the molecular weight distribution is approximated by a multi-component blend

b) the relaxation spectrum of the components is approximated by a box distribution;

c) the relaxation spectrum of the blend is the sum of the spectra of the components weighted with their volume fraction.

This simple blending rule, however, does not describe the real behavior of the polymer as it neglects the interactions between the various components.

In order to analyze the non-linear behavior experimentally, Ninimyia[2] measured the relaxation moduli of binary blends of narrow-distributed poly-vinylacetates and compared them with the moduli of the original components. To be able to describe the relaxation modulus of the blend $E_b(t)$ he had to introduce a shift factor for the moduli of the components as well as a weighting factor w_i (weight fraction). The shift factor λ_i of each component i was determined experimentally.

The analysis of the shift factors in relation to molecular weight distribution yielded a proportionality between λ_i and $(M_w/M_i)^a$, a = 1, if the molecular weight of the component $i < M_c$ and $a = 2.4$ for $M_i > M_c$[22]. From the blending rule for $E(t)$ the blending rules for the zero-shear viscosity and the steady state compliance D_{eb} can

be derived. The viscosity η_{Eob} calculated from the blending rule shows a the steeper increase for $w_2 << 1$ than for $w_2 \rightarrow 1$, which is also in the experiment (table 2.3). The experimentally found steady state compliance of the blend $D_{eb}(w_2)$ shows a well-defined maximum for $w_2 \sim 0.2$ and in the logarithmic plot a slope -2 if $w_2 \rightarrow 1$. This result is contrary to the linear blending rule which gives a slope -1 for $w_2 \rightarrow 1$.

Prest and Porter [28,29,30], Murakami and Bogue et al. established blending rules of a higher order which aim at a better overlapping between experimental and calculated steady state compliance.

Multicomponent blends.

Ninimyia and Yasuda [24, 41] extended the linear blending rule for binary blends (table 2/3) to multicomponent blends. The resulting equation contains as variables the shift factors λ_m and the relaxation time spectra H_m of the monodisperse polymer component m.

Zosel[43] changed Ninomiya's blending rule substituting λ_m with $(M_w/M_n)^2$. The relaxation time spectrum H_m was approximated by a box distribution with the parameters H_o and $\tau_{max.}$. Furthermore, he introduced the empirical relation $\tau_{max} \sim M^{3.4}$ which means that each molecular weight is

Table 2.3 Determination of the shift factors and prediction of the blending rule for the zero-shear viscosity and the steady state compliance.
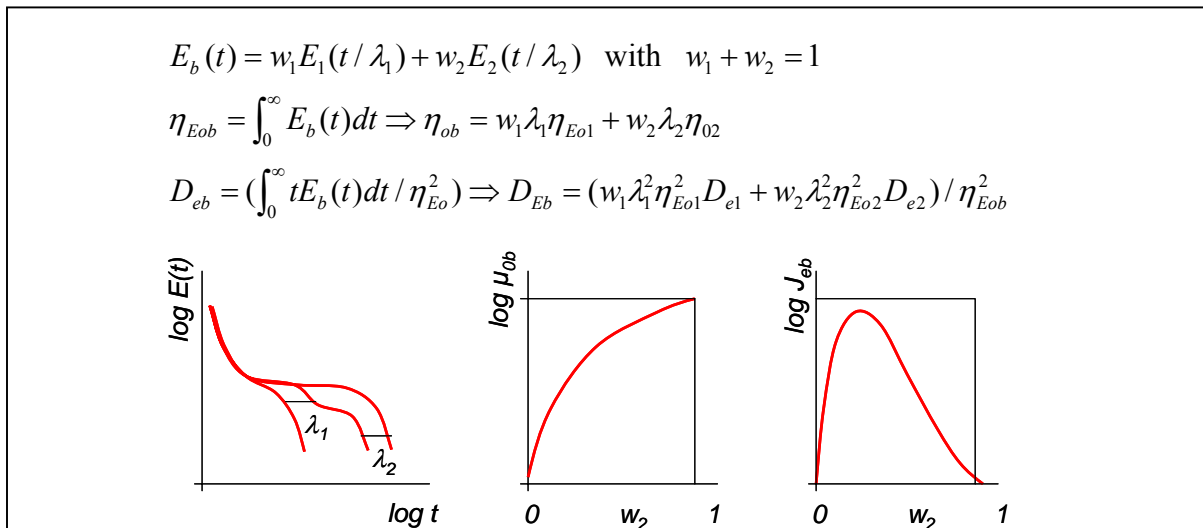
$$E_b(t) = w_1 E_1(t/\lambda_1) + w_2 E_2(t/\lambda_2) \quad \text{with} \quad w_1 + w_2 = 1$$

$$\eta_{Eob} = \int_0^\infty E_b(t)dt \Rightarrow \eta_{ob} = w_1 \lambda_1 \eta_{Eo1} + w_2 \lambda_2 \eta_{02}$$

$$D_{eb} = (\int_0^\infty t E_b(t)dt / \eta_{Eo}^2) \Rightarrow D_{Eb} = (w_1 \lambda_1^2 \eta_{Eo1}^2 D_{e1} + w_2 \lambda_2^2 \eta_{Eo2}^2 D_{e2})/\eta_{Eob}^2$$

Table 2.4 Multicomponent blends: relation between linear viscoelastic functions and molecular weight distribution

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a) NINOMIYA and YASUDA

$$H(\ln\tau) = \int_0^\infty w(M)H_m(\ln(\tau/\lambda_m))dM \quad \text{with} \int_0^\infty w(M)sM = 1$$

b) ZOSEL [88]

$$H(\ln\tau) = \int_0^\infty w(M)H_m(\ln(\tau/\lambda_m))dM \quad \text{with} \int_0^\infty w(M)sM = 1$$

Assumption:

$$\lambda_m = \left(\overline{M}_w \middle/ \overline{M}_m\right)^2$$

and H_m is a box distribution with parameters H_o and τ_{max}

$$H(\ln\tau) = H_o\int_0^\infty w(M)dM = H_o/1 - W(M(\tau)))$$

with $\log M(\tau) = a(\log\tau + b + 2\log\overline{M}_w)$ and $W(M) = \int_0^\infty w(M')dM'$

---

related to one characteristic relaxation time. Zosel thus calculated the relaxation time spectrum as a function of the cumulative molecular weight distribution (table 2.4). To verify this blending rule, the molecular weight distribution was calculated from the experimentally measured relaxation spectrum and compared with data from GPC measurements. The agreement between experimentally and theoretically determined molecular weight distribution was unsatisfactory. This is a very rudimentary model to calculate the molecular weight distribution from rheology.

REMARKS

The determination of the mechanical behavior of homologous polymer blends from the behavior of each component can only be approximative with these simple blending rules. Multi-component blending rules, using a box distribution with the parameters H_o and t_{max} to characterize the relaxation spectra of the monodisperse component are to much of a simplification of the real fact.

A blending rule predicting the mechanical behavior of a polydisperse polymer starting from the molecular weight distribution has to take into account a relation be-

tween relaxation time and molecular weight. The experimentally determined maximum relaxation time is $\tau_{max} \sim M^{3.4}$. If a blending rule is based on this relation, the assumption is implicitly made that each relaxation time is uniquely correlated to one molecular weight.

This assumption however is only a rough approximation as the behavior of a monodisperse polymer cannot be described by only one relaxation time, but by a spectrum of relaxation times. In this case, each time constant characterizes a defined motion of the chain.

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