From Gert Strobl, The Physics of Polymers 2'nd Edition, Springer 1997 p. 324-338.

Phenomenological Description of Polymer Flow:

At low shear rates the properties of polymeric liquids are described by two constitutive parameters, the zero shear rate viscosity, η_0, and the recoverable shear compliance, J_e^0, where the 0 sub/super-script reflects the low shear rate limit. The recoverable shear compliance reflects the elasticity of the fluid and describes recoil behavior for the fluid for instance.

At higher rates of strain the typical rheological features measured in a viscometer such as a cone-and -plate viscometer are the shear rate dependent viscosity, $\eta(\gamma')$, and the first normal stress difference, $\Psi_1(\gamma')$. The second normal stress difference is sometimes also measured, $\Psi_2(\gamma')$. These constitutive parameters are defined by the following equations,

$$\eta(\gamma') = \sigma_{zx}/\gamma'$$
$$\Psi_1(\gamma') = (\sigma_{xx} - \sigma_{zz})/(\gamma')^2$$
$$\Psi_2(\gamma') = (\sigma_{yy} - \sigma_{zz})/(\gamma')^2$$

Figure 7.15 from Strobl (below) shows typical behavior for $\eta(\gamma')$ and $\Psi_1(\gamma')$. The third curve in

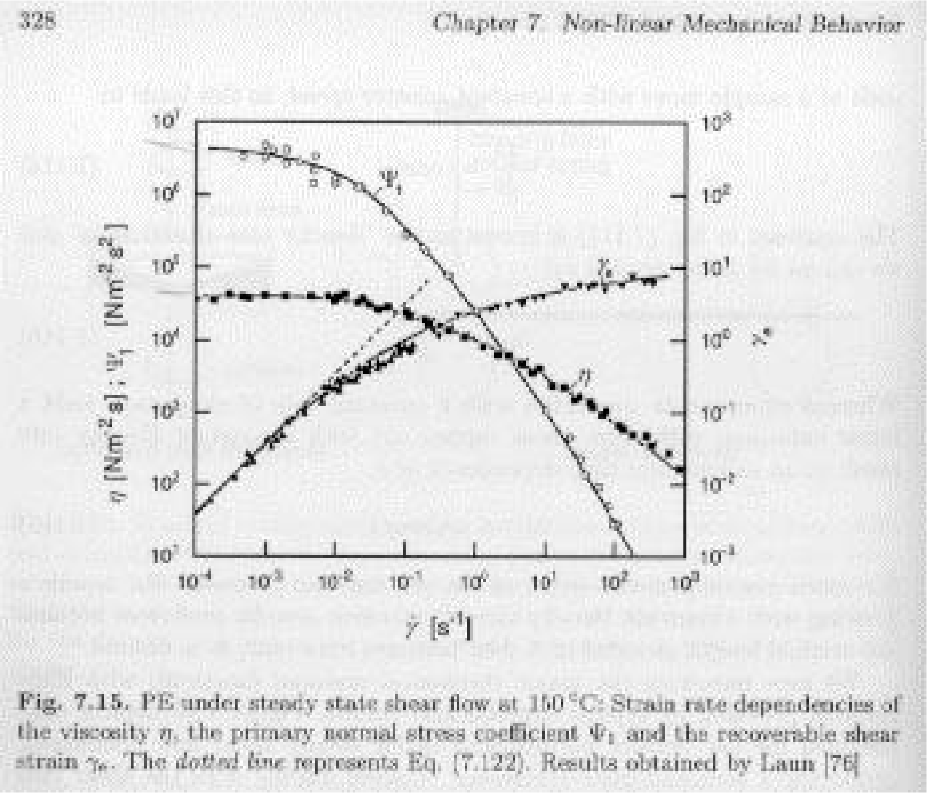
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Fig. 7.15. PE under steady state shear flow at 150 °C: Strain rate dependencies of the viscosity η, the primary normal stress coefficient Ψ_1 and the recoverable shear strain γ_e. The *dotted line* represents Eq. (7.122). Results obtained by Laun [76]

Figure 7.15 shows the recoverable shear strain, γ_e, that is proportional to the recoverable shear compliance, $J_e = \gamma_e/\sigma_{zx}$. At low strain rates the recoverable shear strain is just linear in the rate of strain as indicated by the dashed line. The linear behavior occurs in the regime where the viscosity and first normal stress coefficient are constant. In fact, the dashed line follows a linear function of the viscosity and first normal stress coefficient,

$$\gamma_e(\gamma'=>0) = (\Psi_1(\gamma'=>0) / \{2\ \eta(\gamma'=>0)\})\ \gamma' = (\sigma_{xx} - \sigma_{zz})/(2\ \sigma_{zx})$$

then,

$$J_e^0 = \gamma_e(\gamma'=>0)/\sigma_{zx} = \Psi_{1,0}/(2\ \eta_0^2)$$

At low shear rates there remain only two independent parameters that describe polymeric flow.

The Lodge Liquid:

Consider a fluid composed of elements at positions **r** at time t. The full trajectory of the fluid elements for all times in the past can be described by the function **r***(**r**, t, t*) where **r** is the position at the present time, t, and **r*** is the position of the fluid element at time t* in the past. We would like to describe the stress tensor, σ(**r**, t), at time t for all positions **r** which is related to the function **r***. The Finger tensor, **B**(**r**, t, t*), is used to describe the stress tensor at time t based on all times in the past, t*, where,

$$B_{ij}(t, t^*) = (\delta r_i/\delta r^*_k)(\delta r_j/\delta r^*_k)$$

The stress at time t and position **r**, σ(**r**, t), is a functional of **B**(**r**, t, t*),

$$\sigma(\mathbf{r}, t) = \sigma(\mathbf{B}(\mathbf{r}, t, t^*)) \text{ for } t^*<t$$

which is a statement of the principle of causality as well as eliminating rigid body rotations and translations that are ignored through the use of the Finger tensor rather than the strain tensor.

The equation of state of an ideal rubber can be written in terms of the Finger tensor,

$$\sigma = G \bullet \mathbf{B} - p\ \mathbf{1}$$

where G is the shear modulus and p is the hydrostatic pressure. This can be combined with the Boltzmann superposition principle to yield,

$$\sigma(t) = -\int_{t^*=-\infty}^{t} G(t - t^*)\frac{d\mathbf{B}(t,t^*)}{dt^*}dt^*$$

where G(t) is the time dependent modulus.

For simple shear flow,

$$\mathbf{B}(t,t^*) = \begin{pmatrix} 1 + (\gamma(\mathbf{t}) - \gamma(t^*))^2 & 0 & \gamma(\mathbf{t}) - \gamma(t^*) \\ 0 & 1 & 0 \\ \gamma(\mathbf{t}) - \gamma(t^*) & 0 & 1 \end{pmatrix}$$

For the shear stress this yields,

$$\sigma_{zx}(t) = \int_{t^*=-\infty}^{t} G(t - t^*)\frac{d\gamma(t^*)}{dt^*}dt^*$$

and for the first normal stress difference,

$$(\sigma_{xx} - \sigma_{zz})(t) = 2\int_{t^*=-\infty}^{t} G(t - t^*)(\gamma(t) - \gamma(t^*))\frac{d\gamma(t^*)}{dt^*}dt^*$$

The second normal stress difference is zero.

The Lodge Liquid represents a combination of rubber elasticity and the Boltzmann superposition principle. For an Hookean elastic G(t - t*) is constant so the shear stress is linear in the shear strain and the first normal stress difference is $G\gamma^2(t)$. For a Newtonian liquid $G(t - t^*) = \eta\ \delta(t-t^*)$ so the normal stress difference is 0 and Newton's law of viscosity describes the shear stress.

Time Dependent Shear Stress Growth for a Lodge Liquid:

Consider the application of a constant rate of strain, γ', at time t = 0 to a Lodge liquid. The shear stress will develop in time following,

$$\sigma_{zx}(t) = \gamma' \int_{t^*=0}^{t} G(t - t^*)dt^*$$

The first normal stress difference will also develop in time following,

$$(\sigma_{xx} - \sigma_{zz})(t) = 2\gamma'^2 \int_{t^*=0}^{t} G(t - t^*)(t - t^*)dt^* = 2\gamma'^2 \int_{t^*=0}^{t} G(t^*)t^*dt^*$$

since γ(t) = t γ'. The steady state values for viscosity and first normal stress coefficient are reached when t => ∞, so,

$$\eta = \int_{0}^{\infty} G(t)dt$$

and

$$\Psi_1 = 2\int_{0}^{\infty} tG(t)dt$$

The Lodge liquid does not predict a shear rate dependent viscosity or first normal stress difference. Linear response theory yields a similar expression for the recoverable shear compliance,

$$J_e^o(\eta_0)^2 = \int_{0}^{\infty} tG(t)dt$$

so the Lodge liquid supports the idea of two parameters describing the zero shear rate behavior of a polymeric fluid,

$$\Psi_{1,0} = 2J_e^0(\eta_0)^2$$

which is the basis of the dotted line in Figure 7.15 from Strobl given above.

Then a simple combination of rubber elasticity and Boltzmann superposition can account for the zero shear rate behavior of polymeric fluids. Description of shear thinning behavior at higher strain rates would require substituting the Finger tensor for a functional of the Finger tensor that displays a decay at high strains or high strain rates. For polymer processing this is best accomplished by empirical functions that describe certain regimes of viscosity and normal stress coefficients as a function of strain rate such as power-law fluid laws. It is an interesting result of the Lodge liquid model that the first normal stress difference appears to be a direct consequence of fluid elasticity in the most elementary sense.