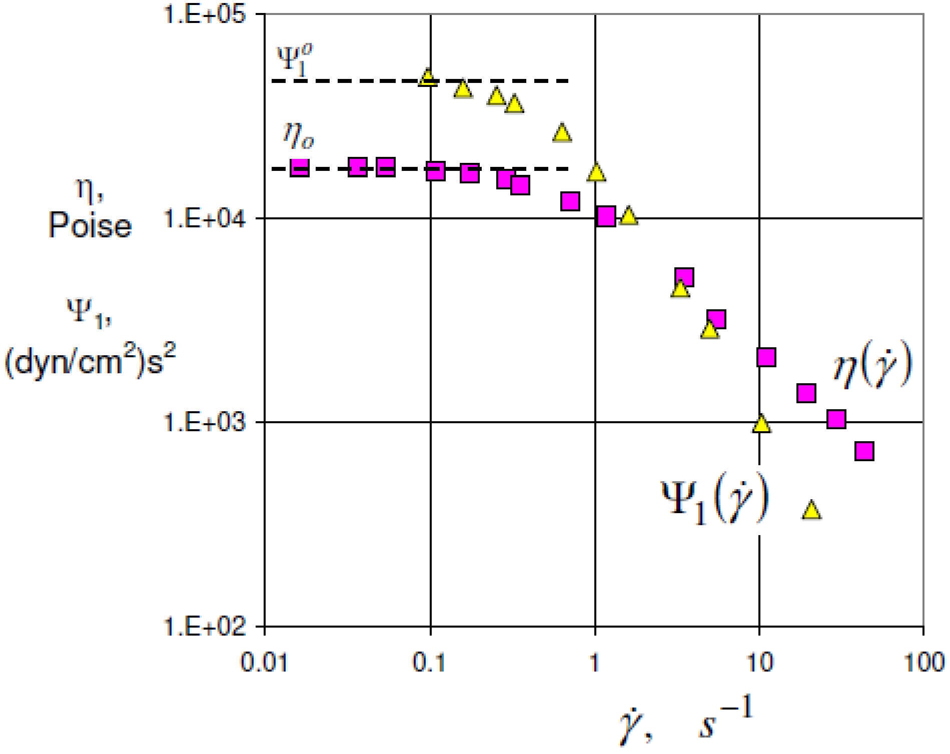
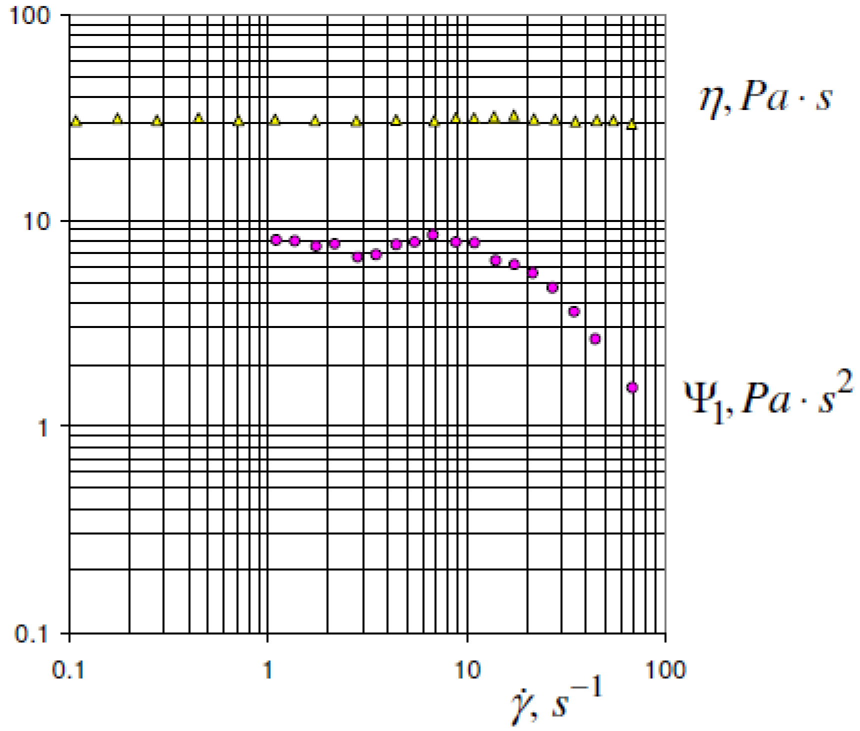
유변학

Experimental data

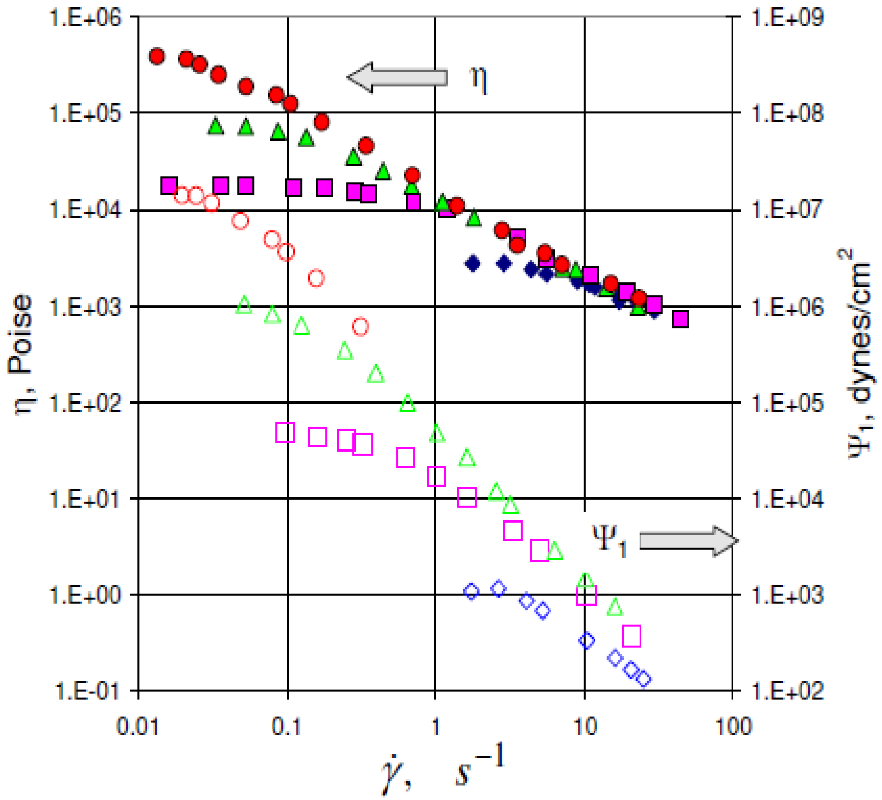
shear thinning



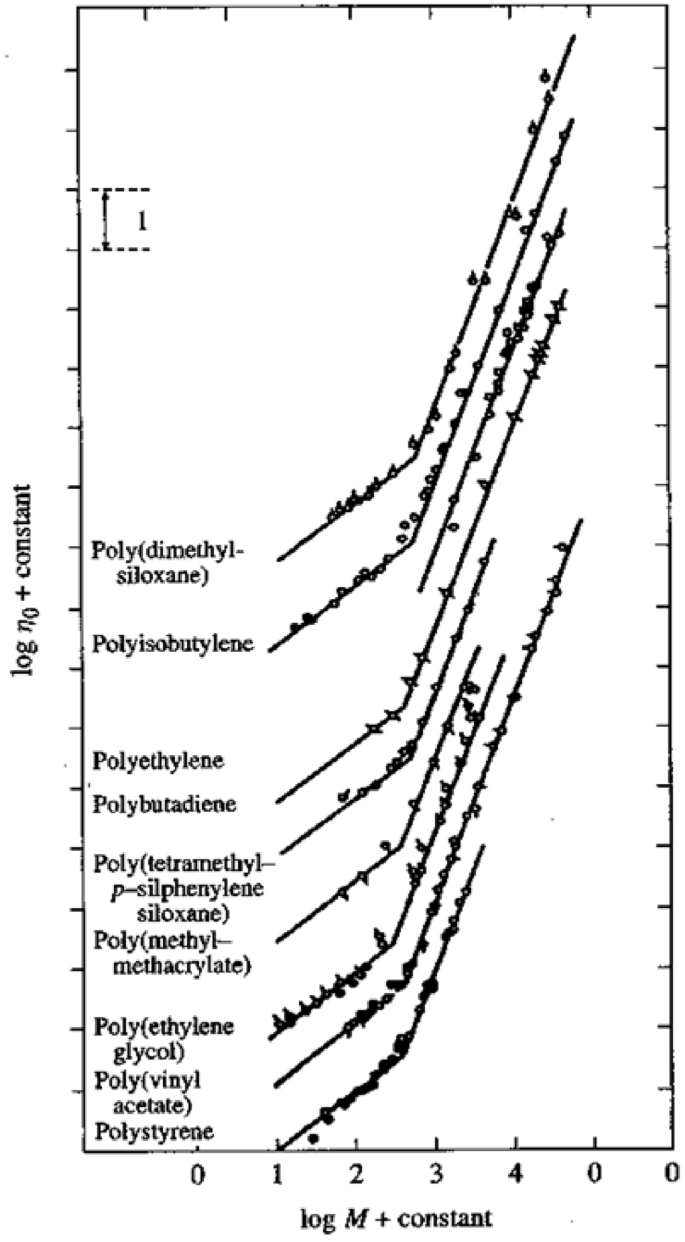
Boger fluid

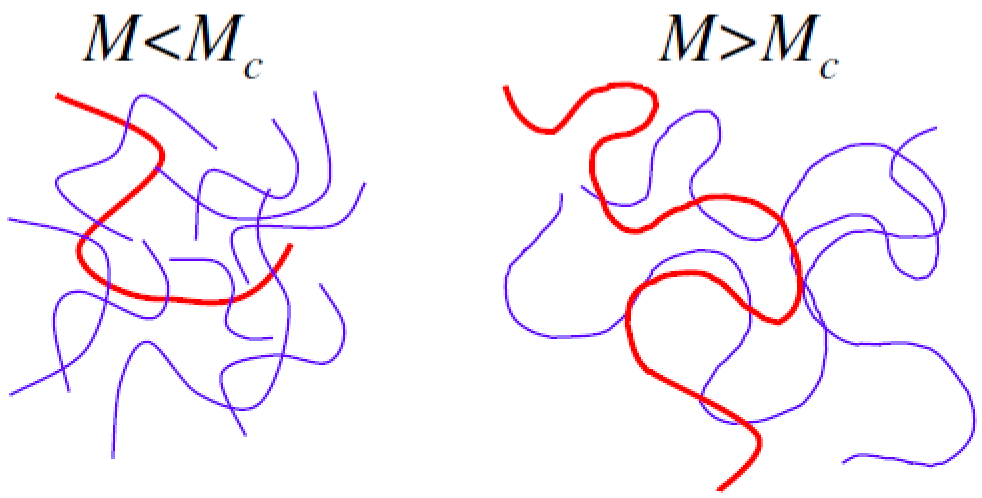


effect of MW



1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
η, Poise
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
Ψ1, dynes/cm2
η
Ψ1
0.01
0.1
1
10
100
$\dot{\gamma}$, s^{-1}

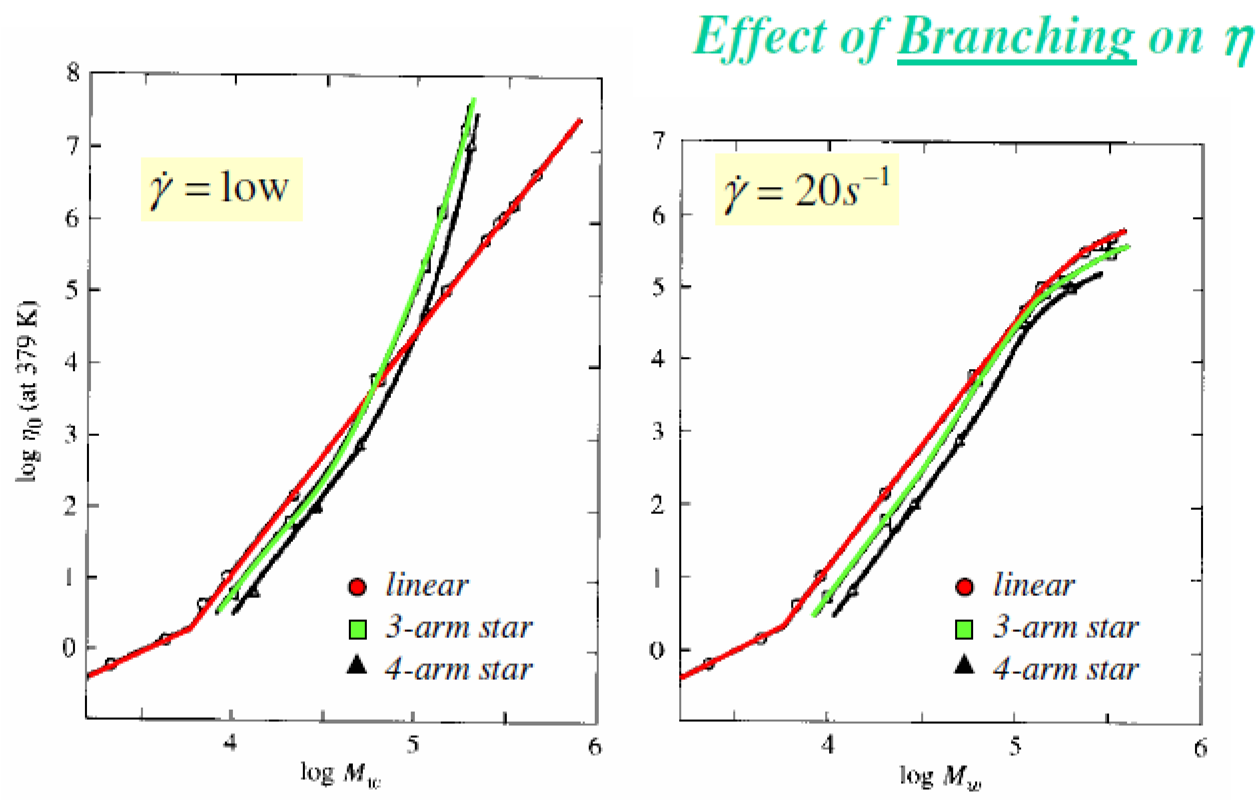




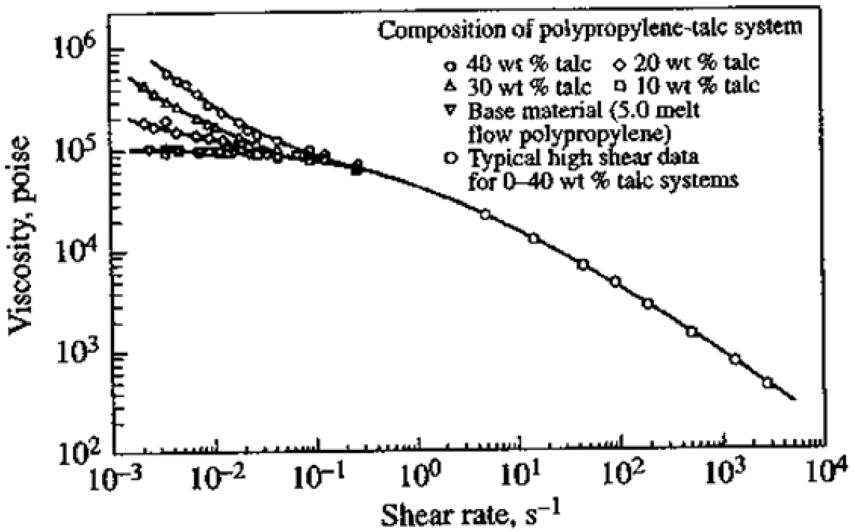
Unentangled
relaxation is rapid

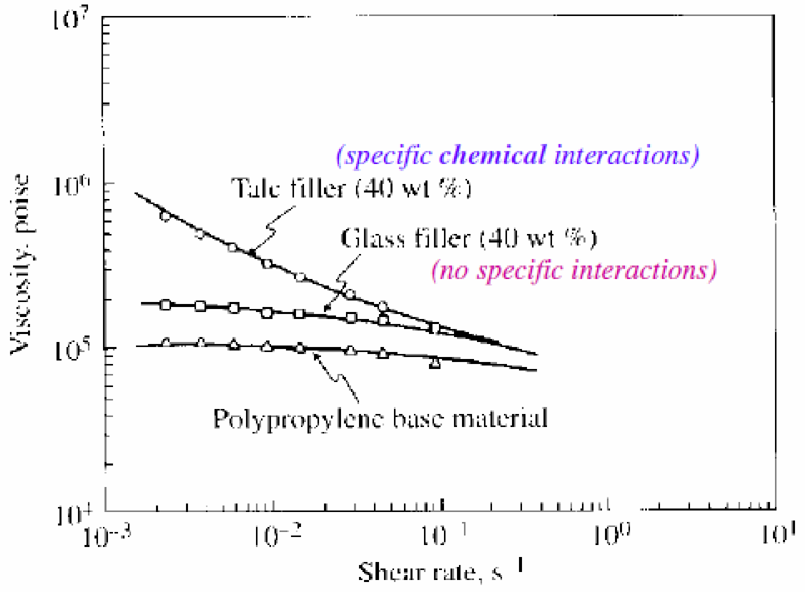
Entangled
relaxation is retarded

effect of branching

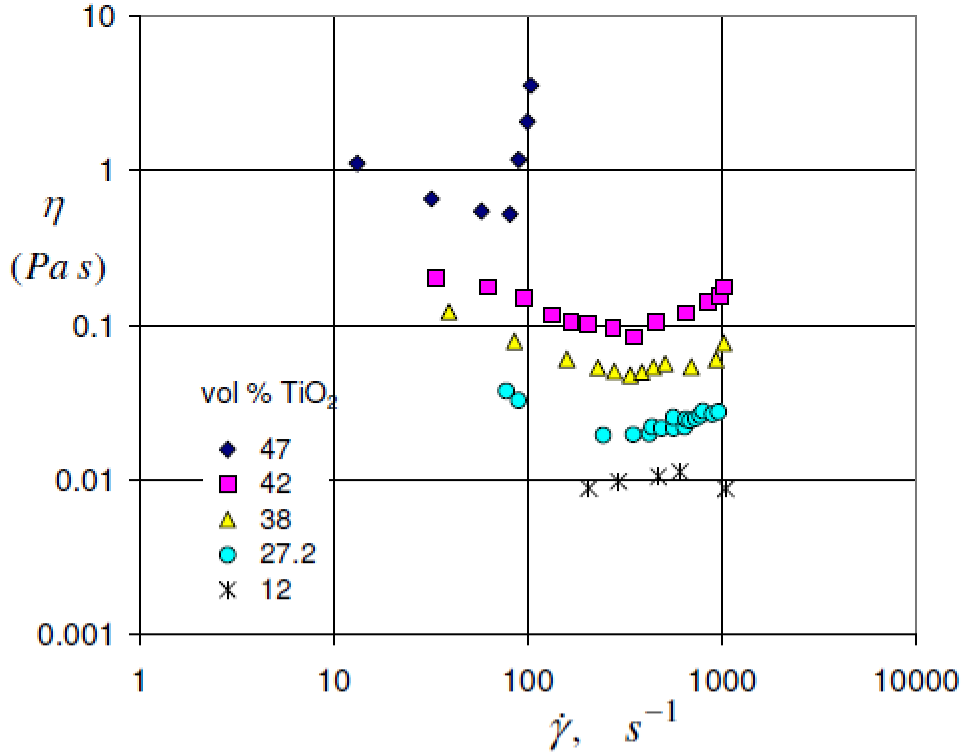


effect of filler

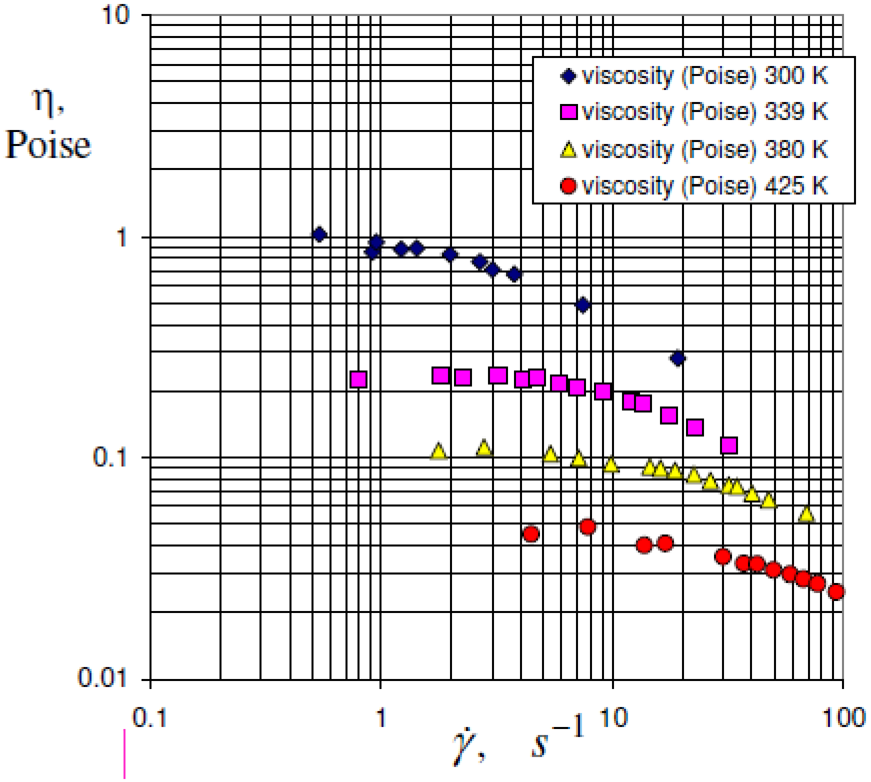




shear thickening

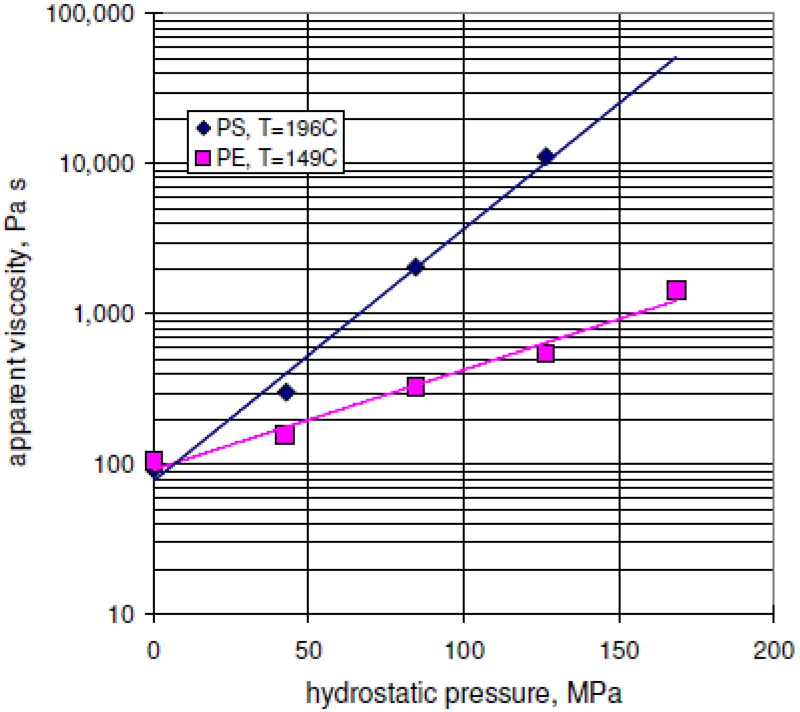


effect of temperature



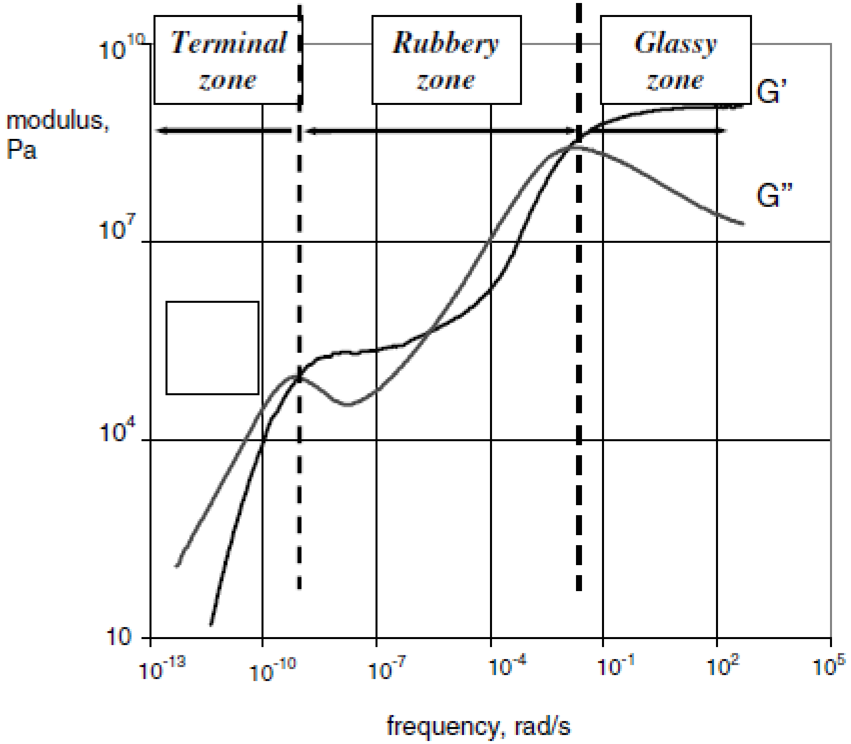
$$\eta_0 = Ae^{B/T}$$

effect of pressure

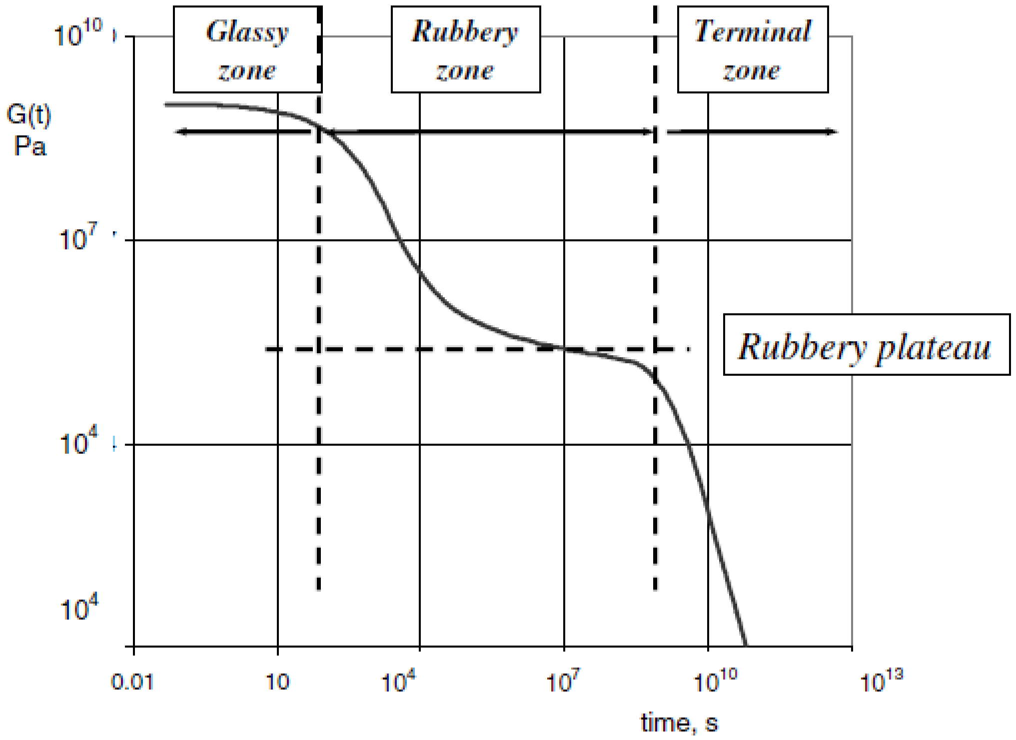


$$\eta_0 = K e^{aP}$$

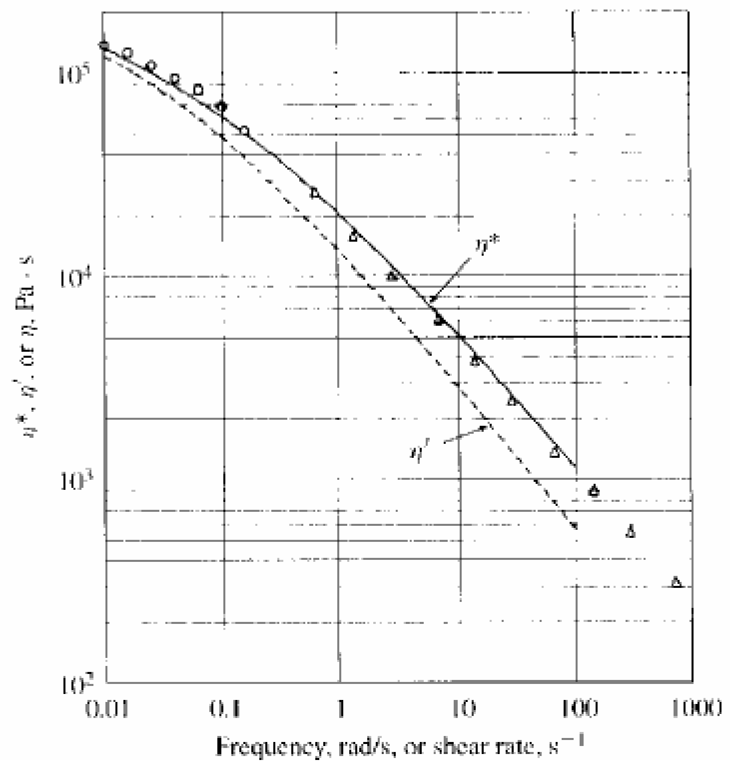
G′ & G″


Terminal zone
Rubbery zone
Glassy zone
G'
G"
modulus, Pa
10^{10}
10^{7}
10^{4}
10
10^{-13}
10^{-10}
10^{-7}
10^{-4}
10^{-1}
10^{2}
10^{5}
frequency, rad/s

relaxation modulus

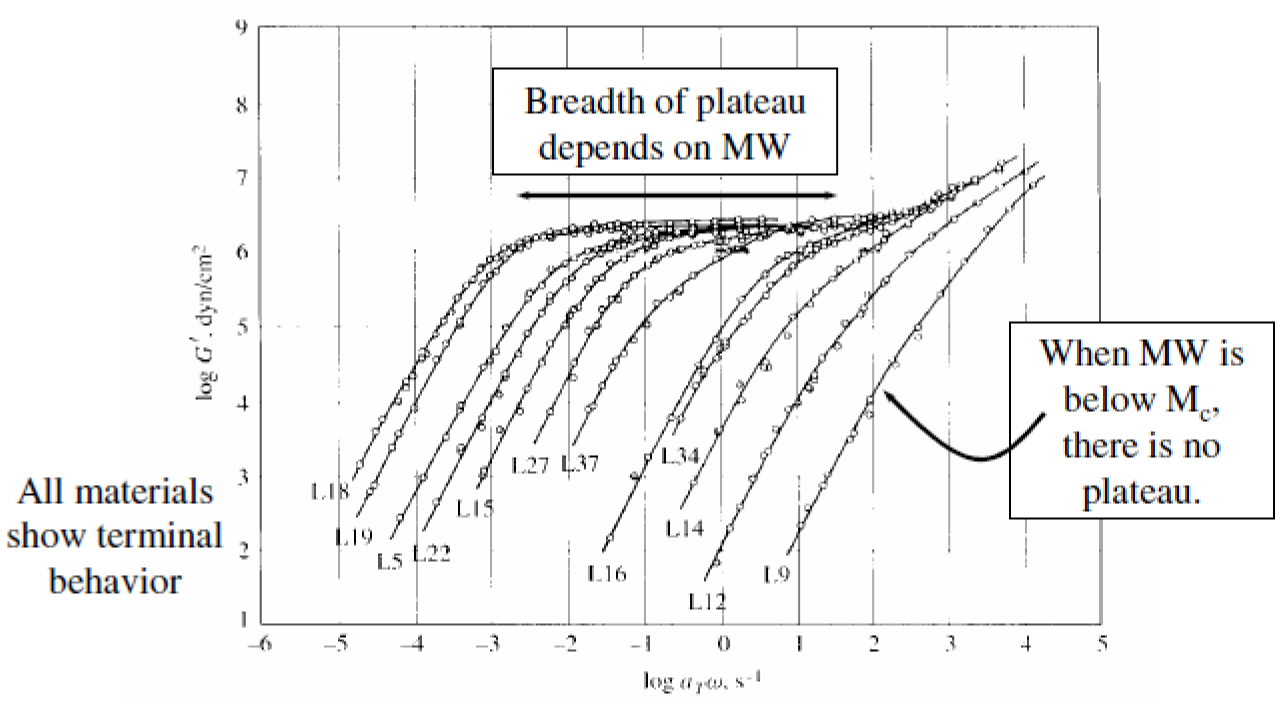


Cox-Merz rule

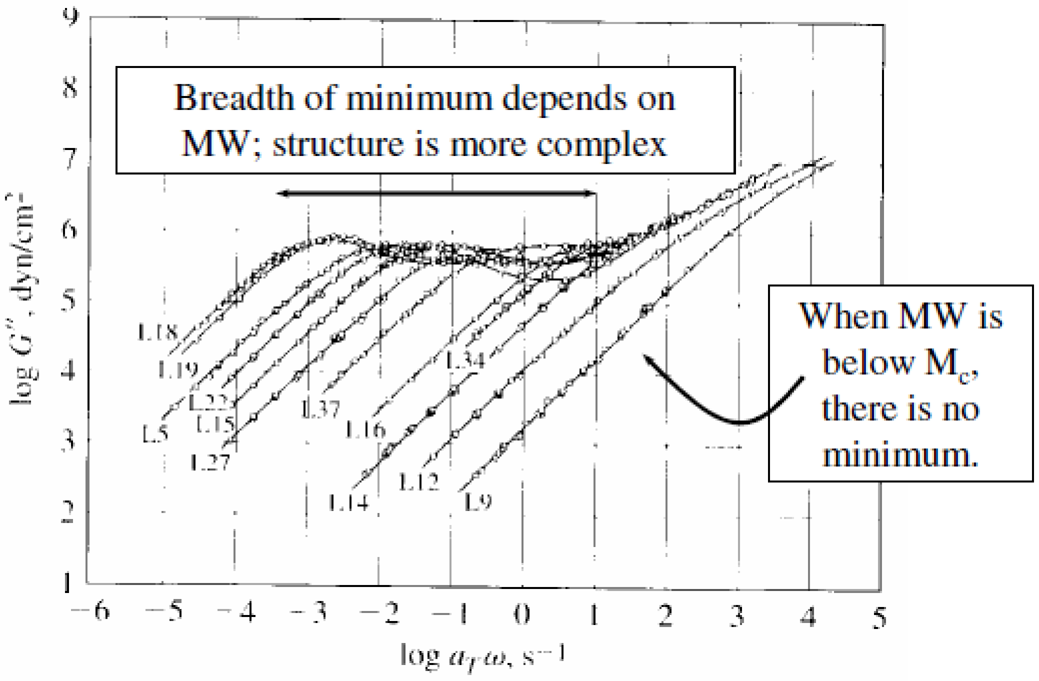


$$\eta(\dot{\gamma}) = \left|\eta^*(\omega)\right|_{\dot{\gamma}=\omega}$$

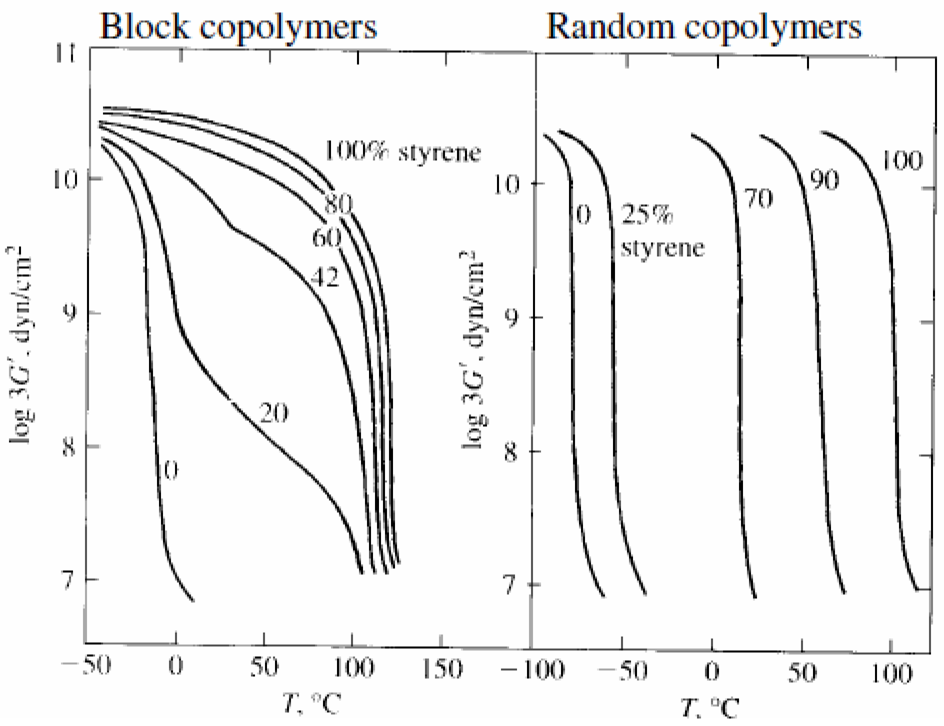
effect of MW


Breadth of plateau depends on MW
When MW is below M_c, there is no plateau.
All materials show terminal behavior
log G', dyn/cm²
log $a_T\omega$, s⁻¹
L18
L19
L5
L22
L15
L27
L37
L34
L16
L14
L12
L9
1
2
3
4
5
6
7
8
9
−6
−5
−4
−3
−2
−1
0
1
2
3
4
5

All materials show terminal behavior

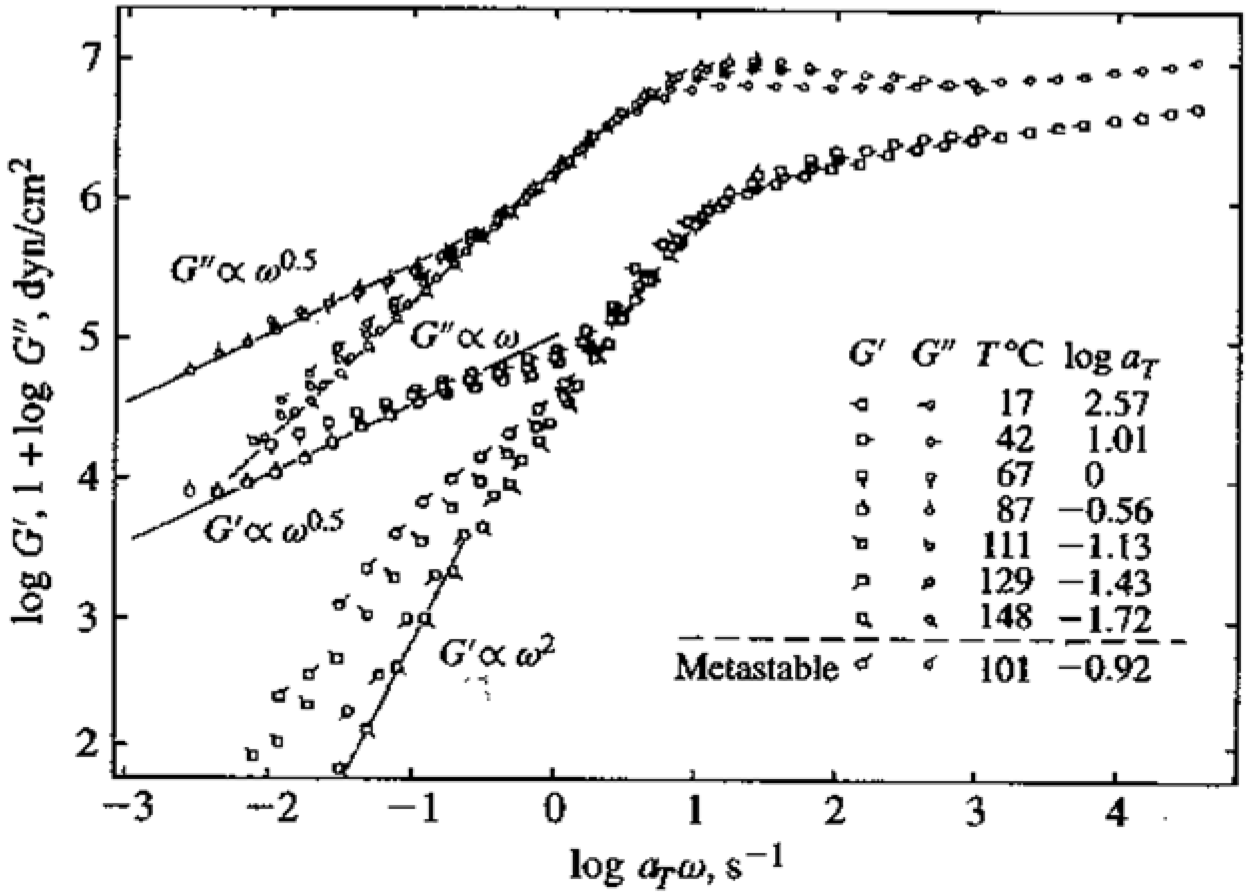


copolymers

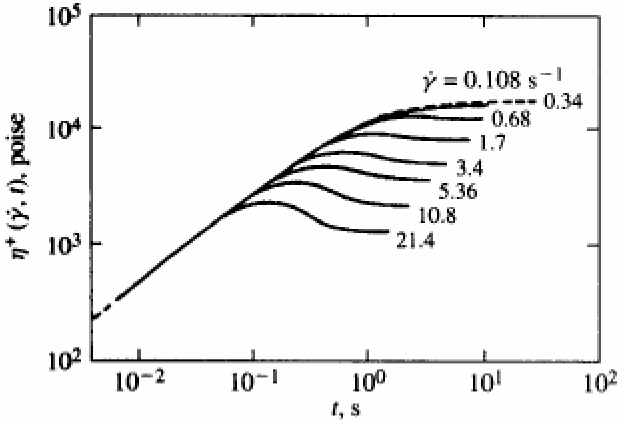


Block copolymers
Random copolymers
100% styrene
80
60
42
20
0
25%
styrene
70
90
100
log 3G′, dyn/cm²
T, °C

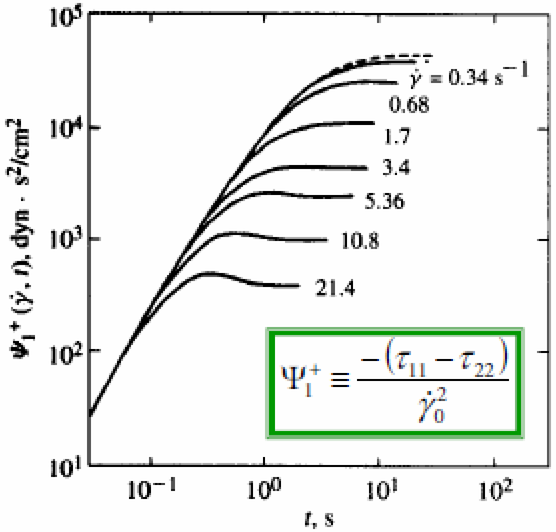
block copolymer



start-up of steady shear

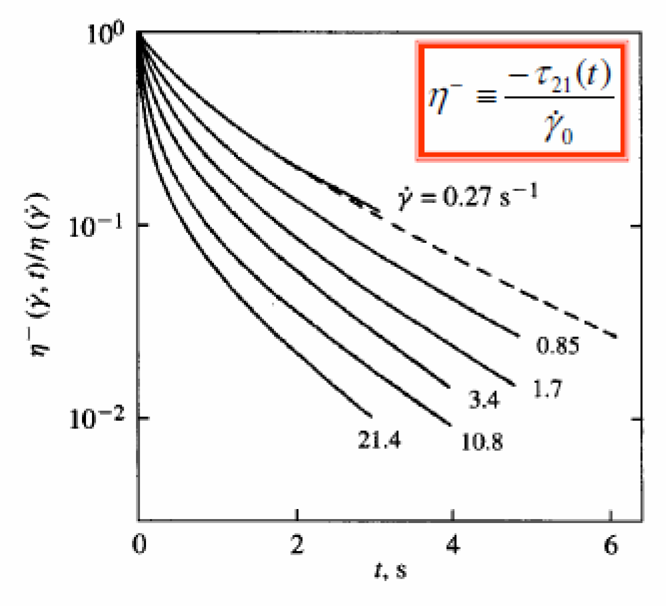


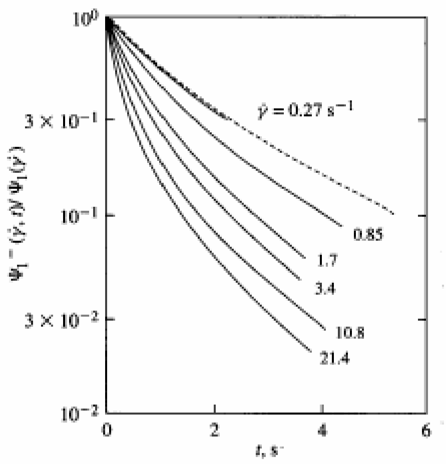
$$\eta^+ \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$



$$\Psi_1^+ \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

cessation of steady shear





$$\Psi_1^{-} \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

step strain experiment

Linear viscoelastic limit

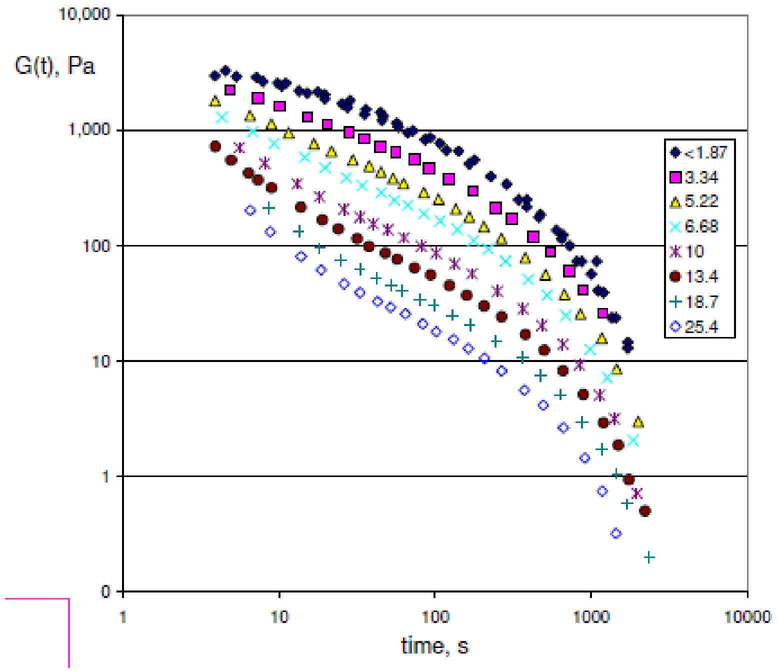
$$\boxed{\lim_{\gamma_0 \to 0} G(t, \gamma_0) = G(t)}$$

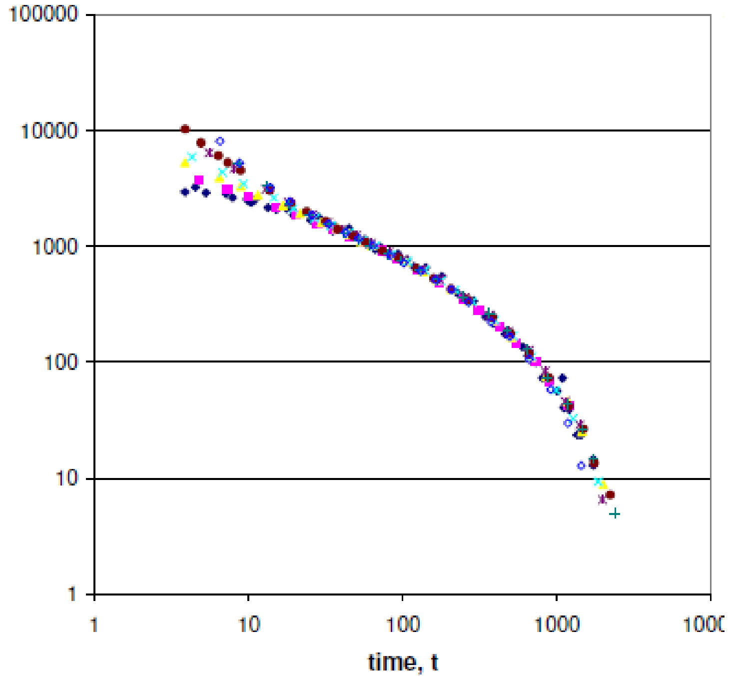
At small strains the relaxation modulus is independent of strain.

Damping function, h

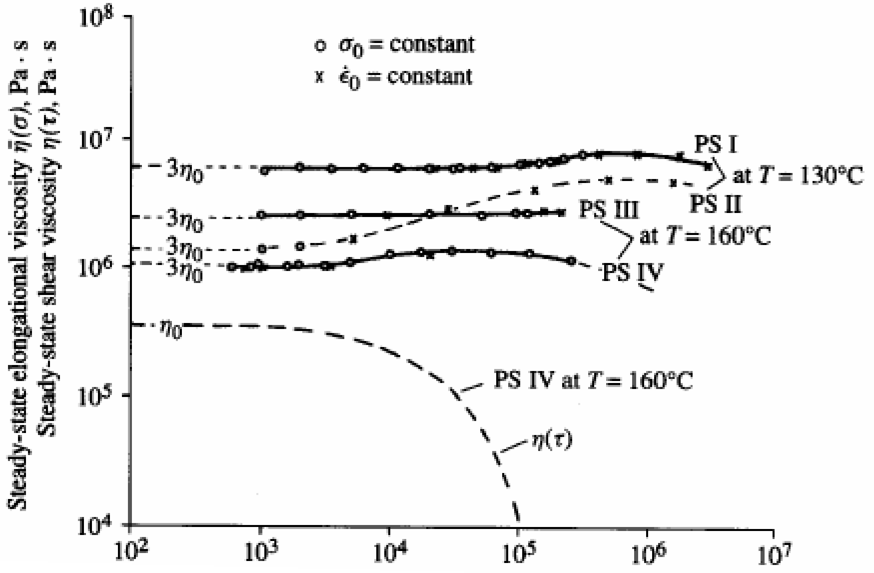
$$\boxed{h(\gamma_0) \equiv \frac{G(t, \gamma_0)}{G(t)}}$$

The damping function summarizes the non-linear effects as a function of strain amplitude.





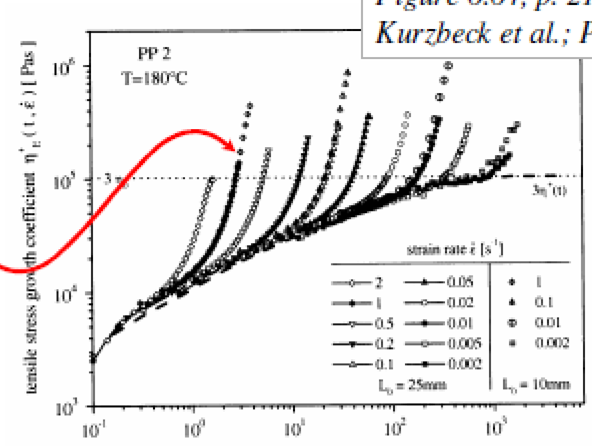
steady elongational viscosity



Start-up of Steady Elongation

Figure 6.64, p. 218
Kurzbeck et al.; PP

Strain-hardening



Fit to an advanced constitutive equation (12 mode pom-pom model)

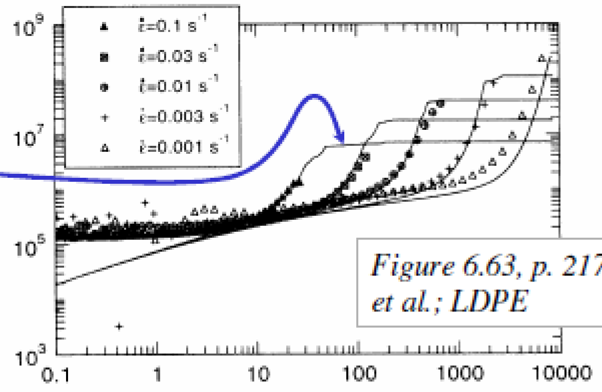
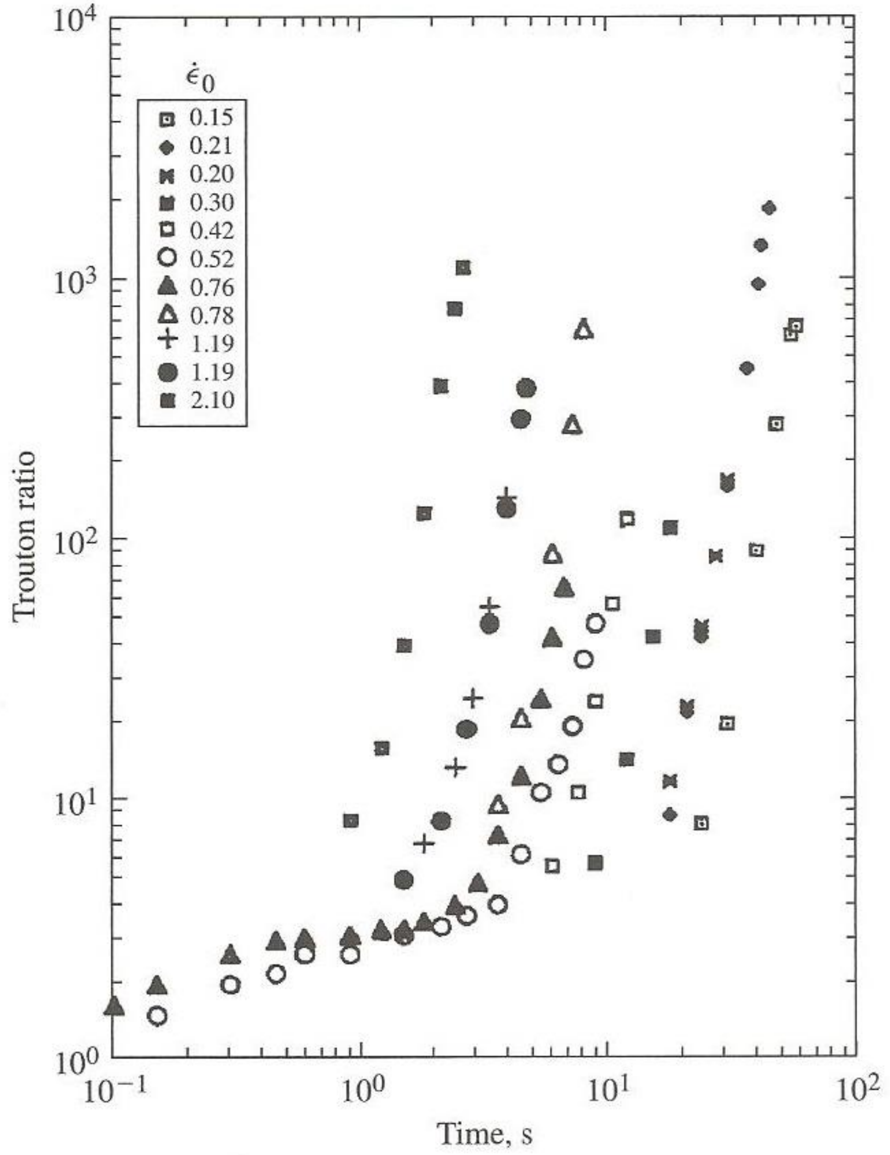
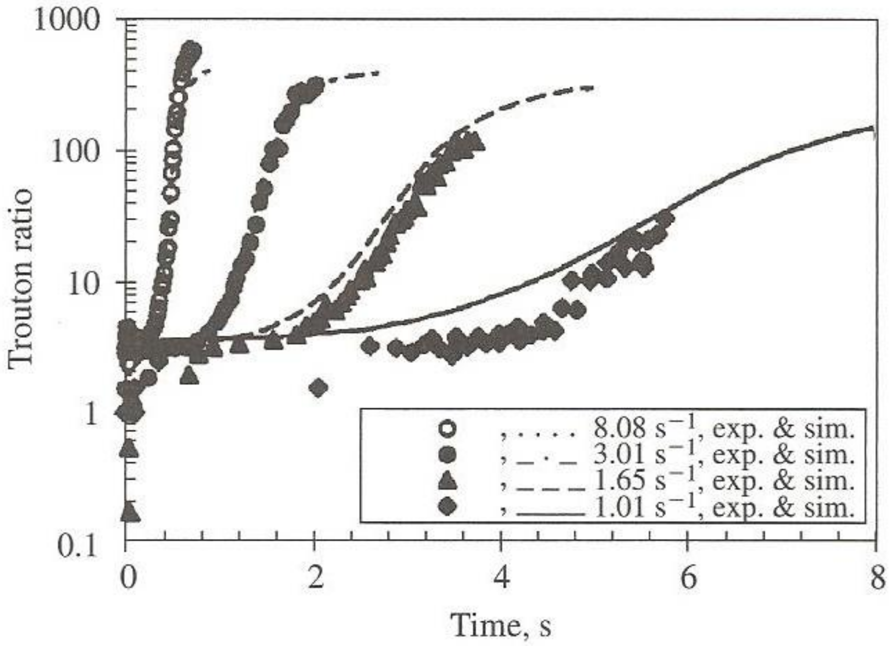


Figure 6.63, p. 217 Inkson et al.; LDPE



$\dot{\epsilon}_0$
0.15
0.21
0.20
0.30
0.42
0.52
0.76
0.78
1.19
1.19
2.10
Trouton ratio
Time, s



Trouton ratio
Time, s
8.08 s^{-1}, exp. & sim.
3.01 s^{-1}, exp. & sim.
1.65 s^{-1}, exp. & sim.
1.01 s^{-1}, exp. & sim.

time-temperature superposition

Material functions depend on g_i, λ_i

relaxation times

relaxation moduli

$$G' = G'(\omega, \lambda_i, g_i)$$
$$G'' = G''(\omega, \lambda_i, g_i)$$

g_i, λ_i are in turn functions of <u>temperature</u> and <u>material</u> properties

> *Theoretical result*: in the linear-viscoelastic regime, material functions are a function of $\omega\lambda_i$ rather than of ω and λ_i individually.

•Relaxation times decrease strongly as temperature increases

•Moduli associated with relaxations are proportional to absolute temperature; depend on density

Empirical observation: for many materials, all the relaxation times and moduli have the same functional dependence on temperature

$$\lambda_i(T) = \tilde{\lambda}_i \underbrace{a_T(T)}_{\text{temperature dependence of all relaxation times}}$$

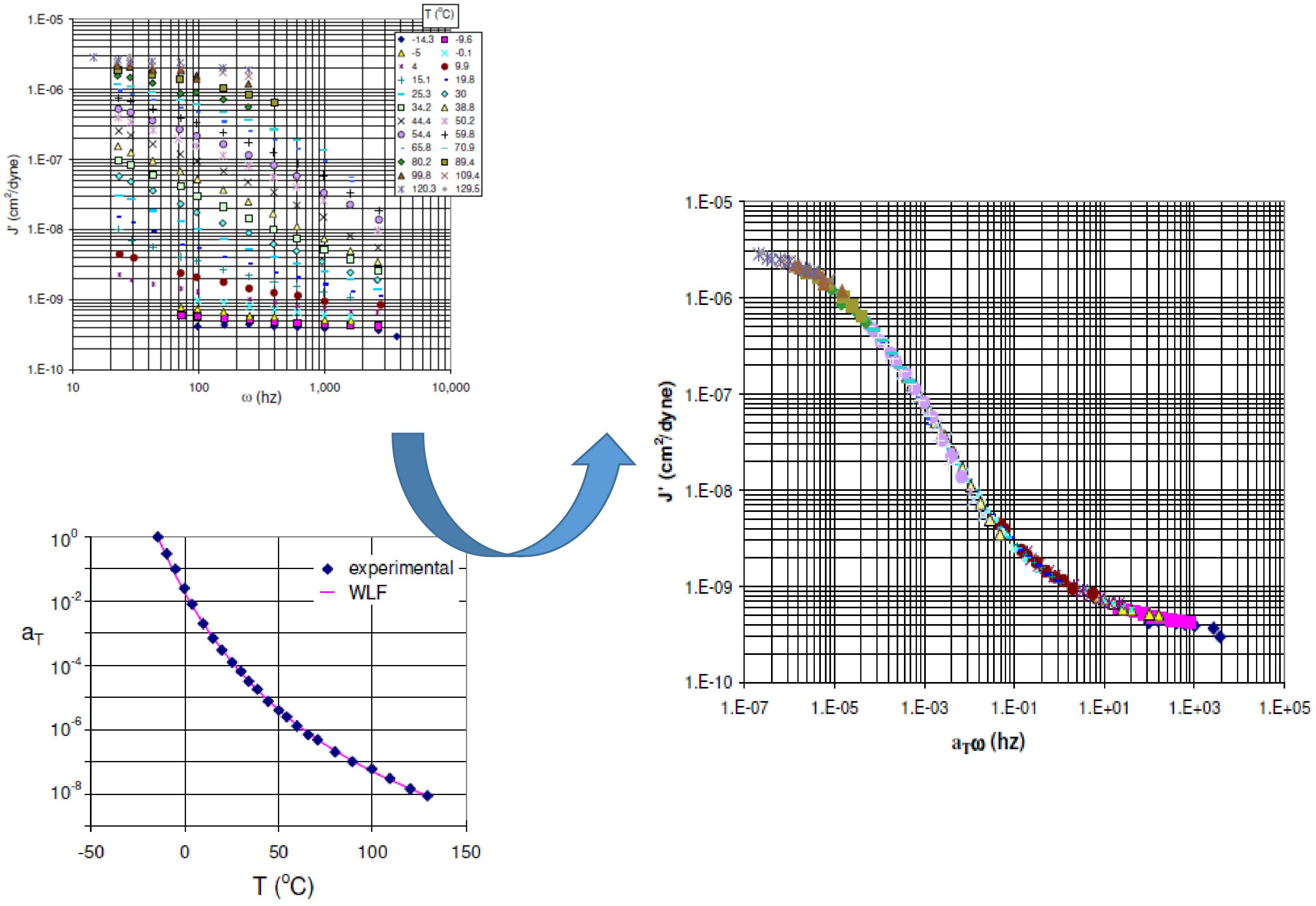
$$g_i(T) = \tilde{g}_i \underbrace{T\rho(T)}_{\text{temperature dependence of all moduli}}$$

Therefore if we plot reduced variables, we can suppress all of the temperature dependence of the moduli.

$$G_r' \equiv \frac{G'(T) T_{ref} \rho_{ref}}{T\rho} = f(a_T \omega, \tilde{\lambda}_i)$$

$$G_r'' \equiv \frac{G''(T) T_{ref} \rho_{ref}}{T\rho} = h(a_T \omega, \tilde{\lambda}_i)$$

Plots of G_r', G_r'' versus $a_T\omega$ will therefore be independent of temperature.



T (°C)
-14.3
-9.6
-5
-0.1
4
9.9
15.1
19.8
25.3
30
34.2
38.8
44.4
50.2
54.4
59.8
65.8
70.9
80.2
89.4
99.8
109.4
120.3
129.5
J' (cm²/dyne)
ω (hz)
experimental
WLF
a_T
T (°C)
J' (cm²/dyne)
$a_T\omega$ (hz)

shift factor

Arrhenius equation

$$a_T = \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

found to be valid for
$T > T_g + 100^oC$

Williams-Landel-Ferry (WLF) equation

$$\log a_T = \frac{-c_1^0 (T - T_{ref})}{c_2^0 + (T - T_{ref})}$$

found to be
valid *w/in*
100^oC of T_g