

Rheometry

Clases 6

Capillary Rheometry Review (1)

Suppose the software in the capillary rheometer computer crashes and the only thing you can read is load and piston speed velocity.

At that moment a customer has a problem and it requires capillary viscosity data. What would you do to report the viscosity with the information you get from the Instrument?

Summarize the methodology

Capillary Rheometry Review (2)

Please, answer the following questions:

- ❑ The apparent viscosity (Γ) is obtained by multiplying the volumetric flow Q by:
- ❑ Suppose you work all day doing some viscosity tests in the Instron and then you realized that while the instrument is set up for a $L/D = 40$ with a 0.05 in diameter, unadvertedly you use a $L/D = 40$ with a 0.03 in diameter.
- ❑ How would that affect your results?
- ❑ What would you do?
- ❑ Would you throw the results away and start all over again?
- ❑ What other use you can think of for the entrance pressure data?

Capillary Rheometry Review (3)

What information can be obtained from a capillary rheometer?

Answers

1) *The shear viscosity (η),*

2) _____

3) _____

4) _____

5) _____

Questions and Reflections

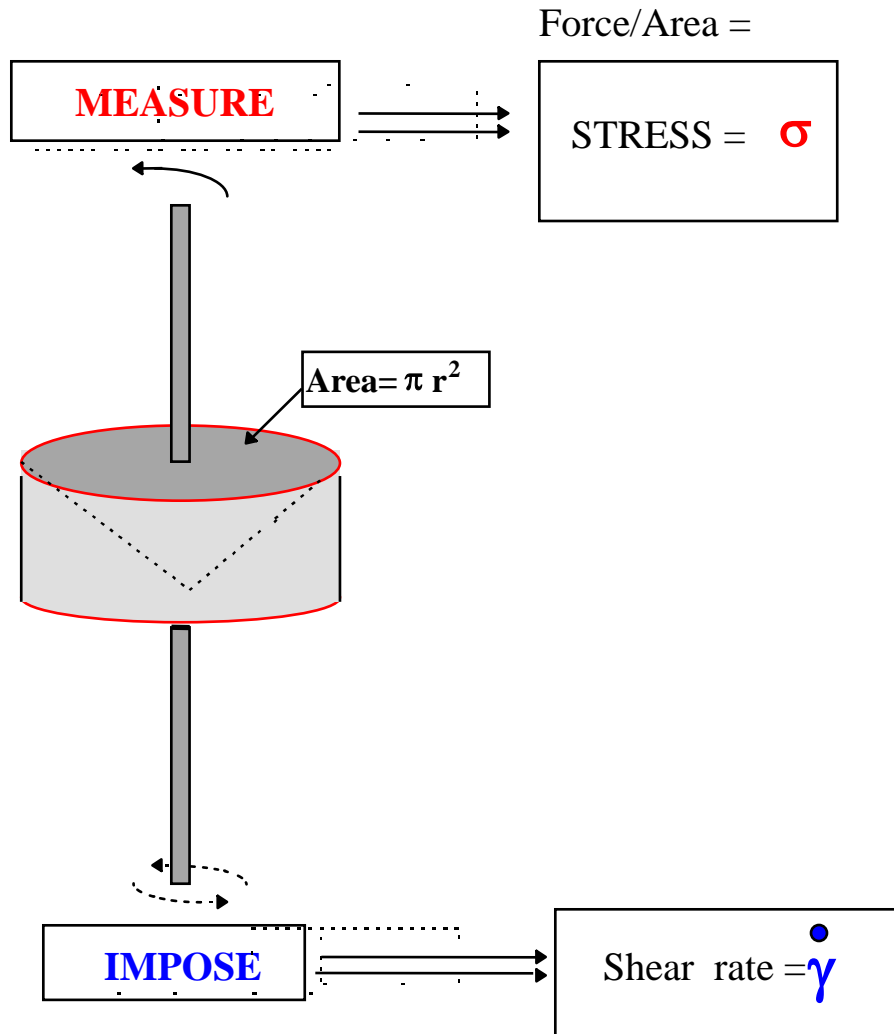
- ❑ Besides of the capillary test, are there some other ways to measure the viscosity?
- ❑ What other moduli exist for solid and liquids?
- ❑ Are those moduli dependent from each other?
- ❑ If they are dependent, how can a given moduli be calculated from another one?

Other rheological tests:

- ❑ **Constant shear rate** (viscosity moduli)
- ❑ **Constant stress** (Creep and recovery compliance)
- ❑ **Constant strain** (Relaxation Moduli)
- ❑ **Dynamic mechanical analysis** (complex moduli)

VISCOUS MODULUS

Viscous modulus (1): the material's response to a constant shear rate



$$\text{MODULUS} = \frac{\text{STRESS}}{\text{SHEAR RATE}}$$

Viscous modulus

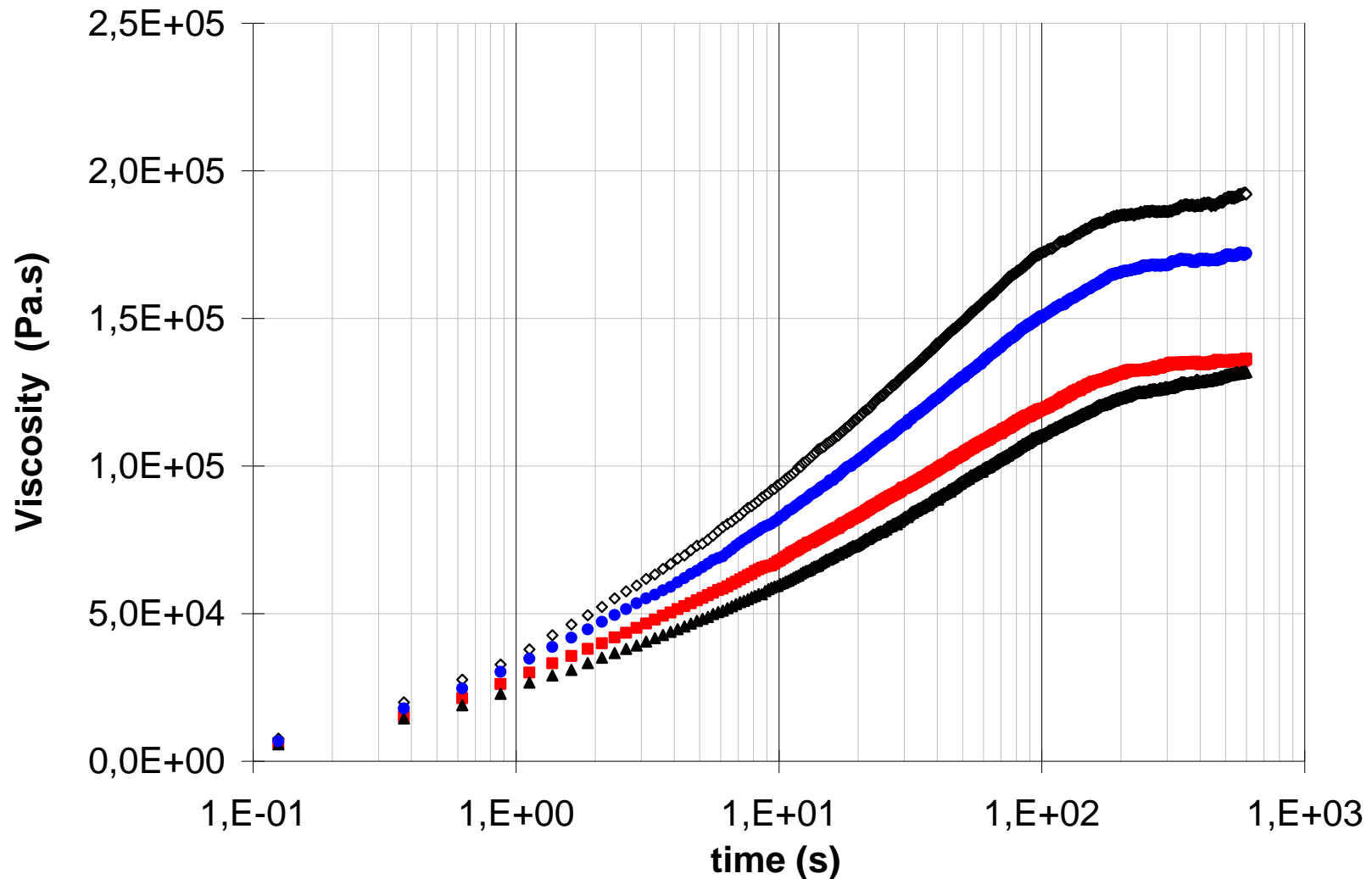
$$\eta = \sigma / \dot{\gamma}$$

$$\dot{\gamma} = dv_{\theta} / dz$$

σ in Pa
and
shear rate in 1/s

η in Pa.s

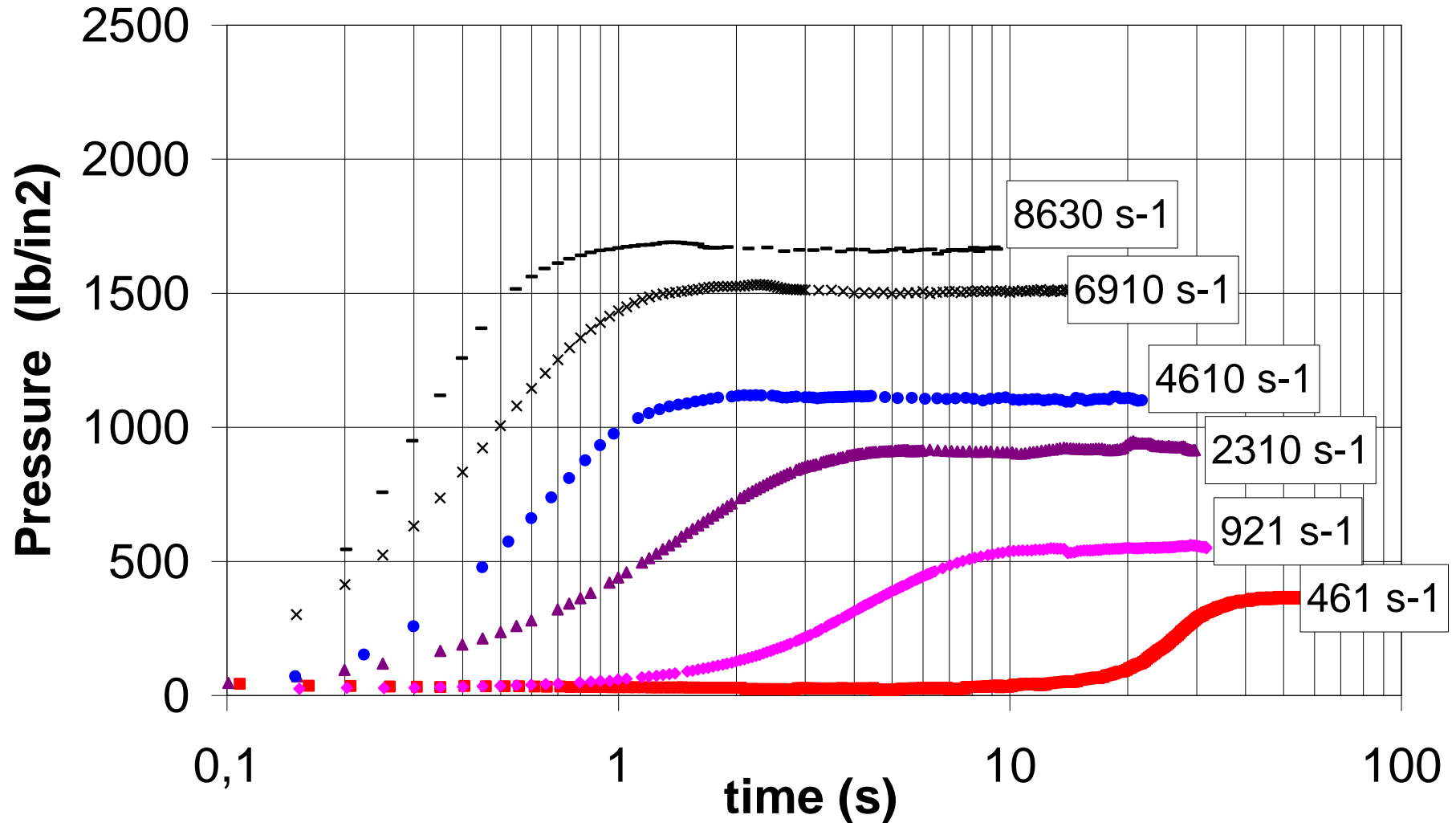
Viscosity versus time for HDPE resins when a sudden shear rate of 0.01 1/s is imposed in a parallel plate rheometer



Pressure drop versus time.

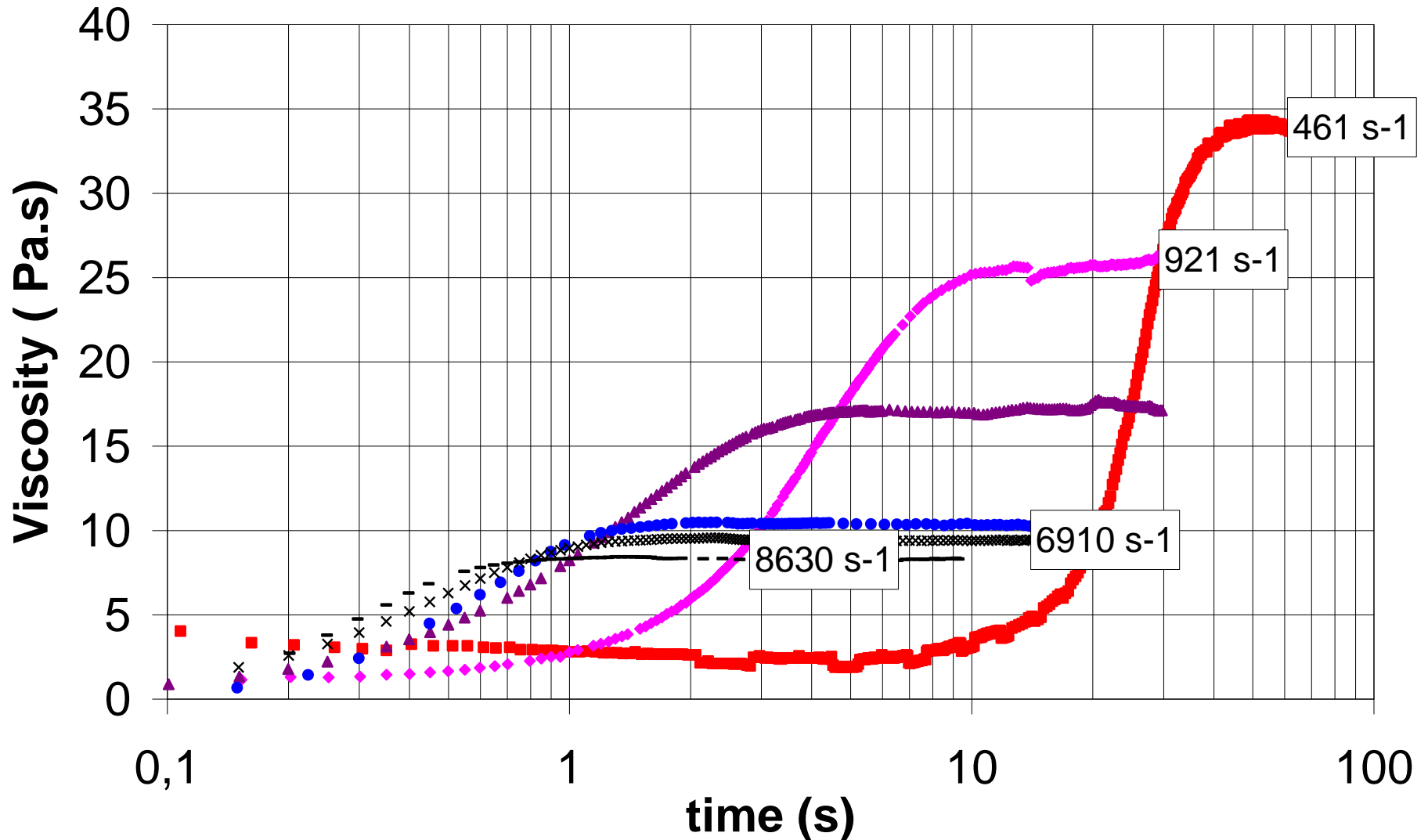
Temperature 200°C. Die: L/D =40, diameter=0.03 in.

High MFI PP resin. (Capillary rheometer)

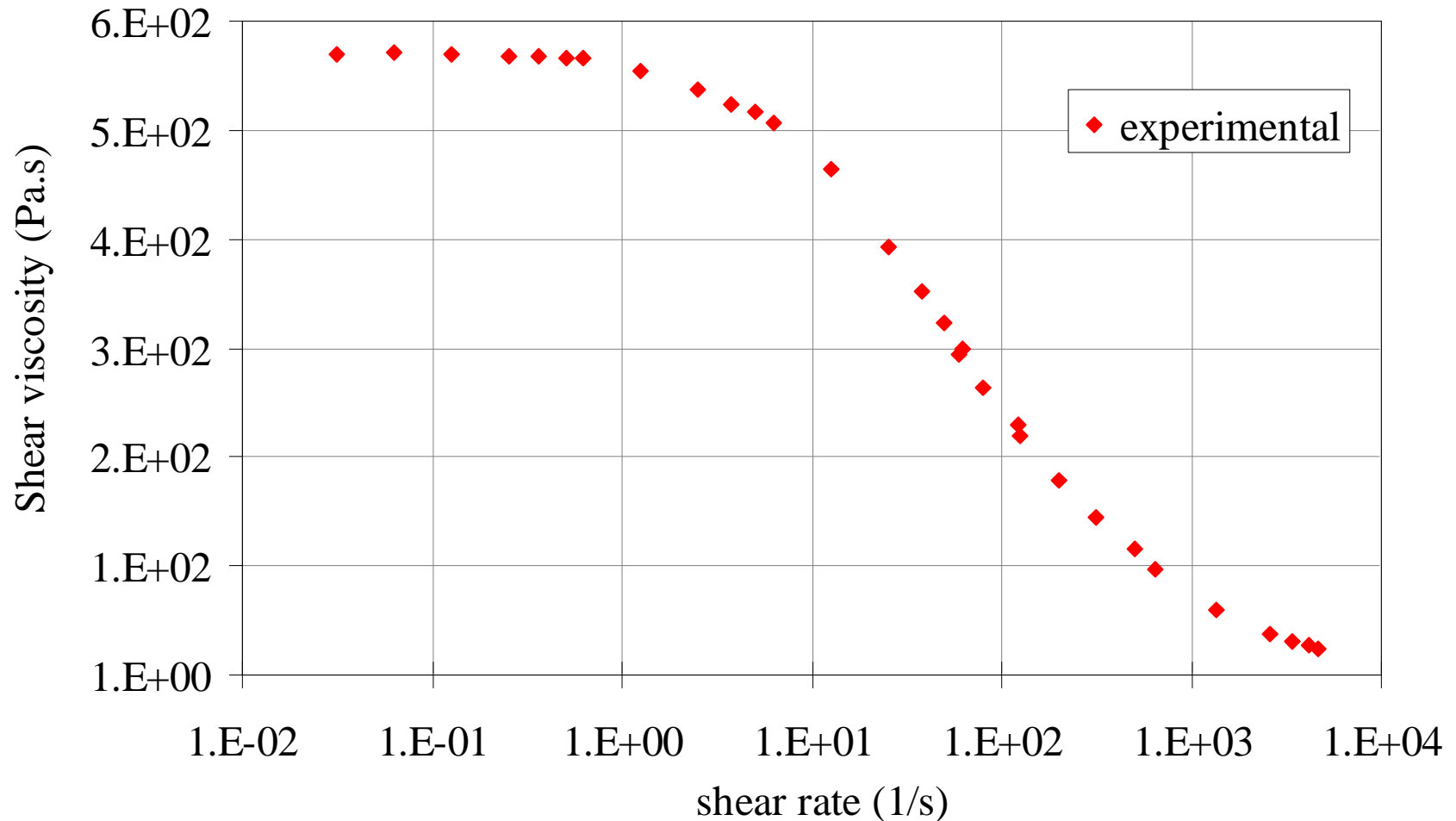


Viscosity versus time

(Capillary rheometer)



Shear viscosity versus shear rate for a polypropylene resin

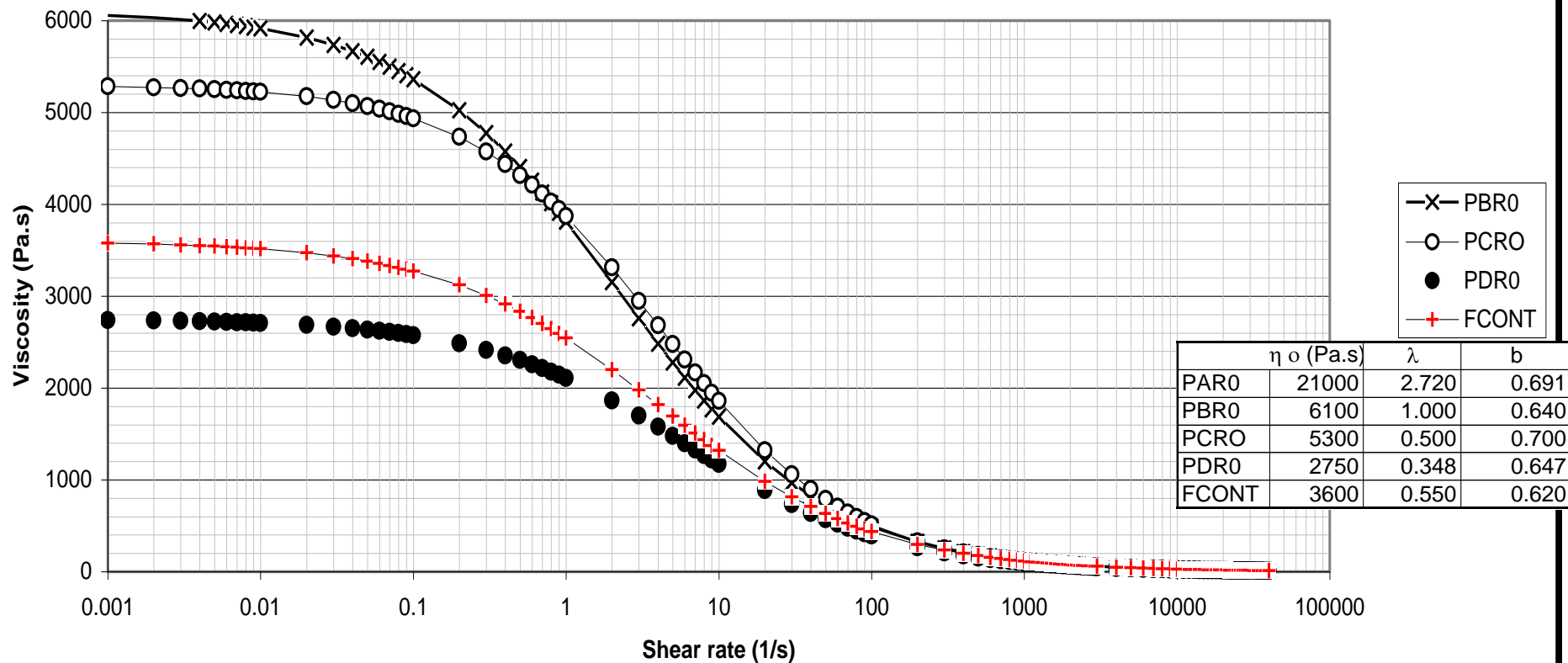


Shear viscosity vs. shear rate

(steady state shear viscosity vs. constant shear rate)

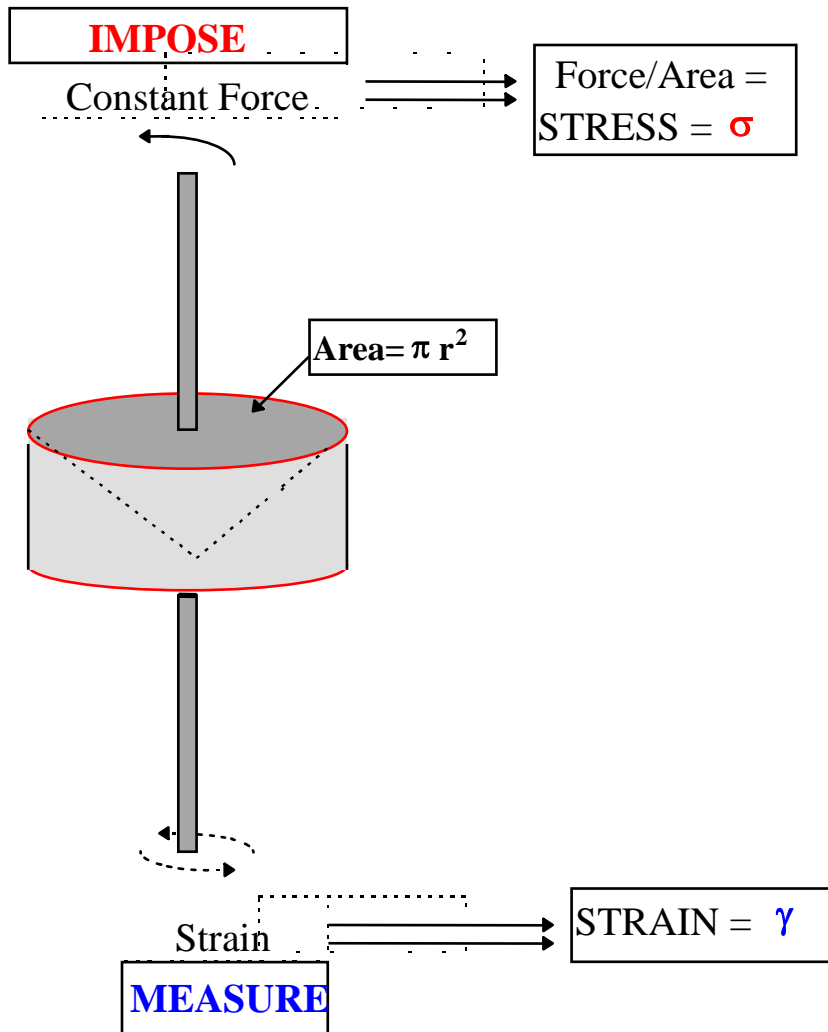
for a set of reactor grade polypropylene resins

Viscosity Curves for the reactor grade resins as fitted by a model proposed by Cross (1) for linear polymers:

$$\eta = \eta_0 / (1 + 0.6(\lambda \dot{\gamma})^b)$$


CONSTANT STRESS RHEOMETRY

Constant stress rheometry: creep and recovery compliance



$$\text{MODULUS} = \text{STRAIN} / \text{STRESS}$$

Compliance modulus

$$J = \gamma / \sigma$$

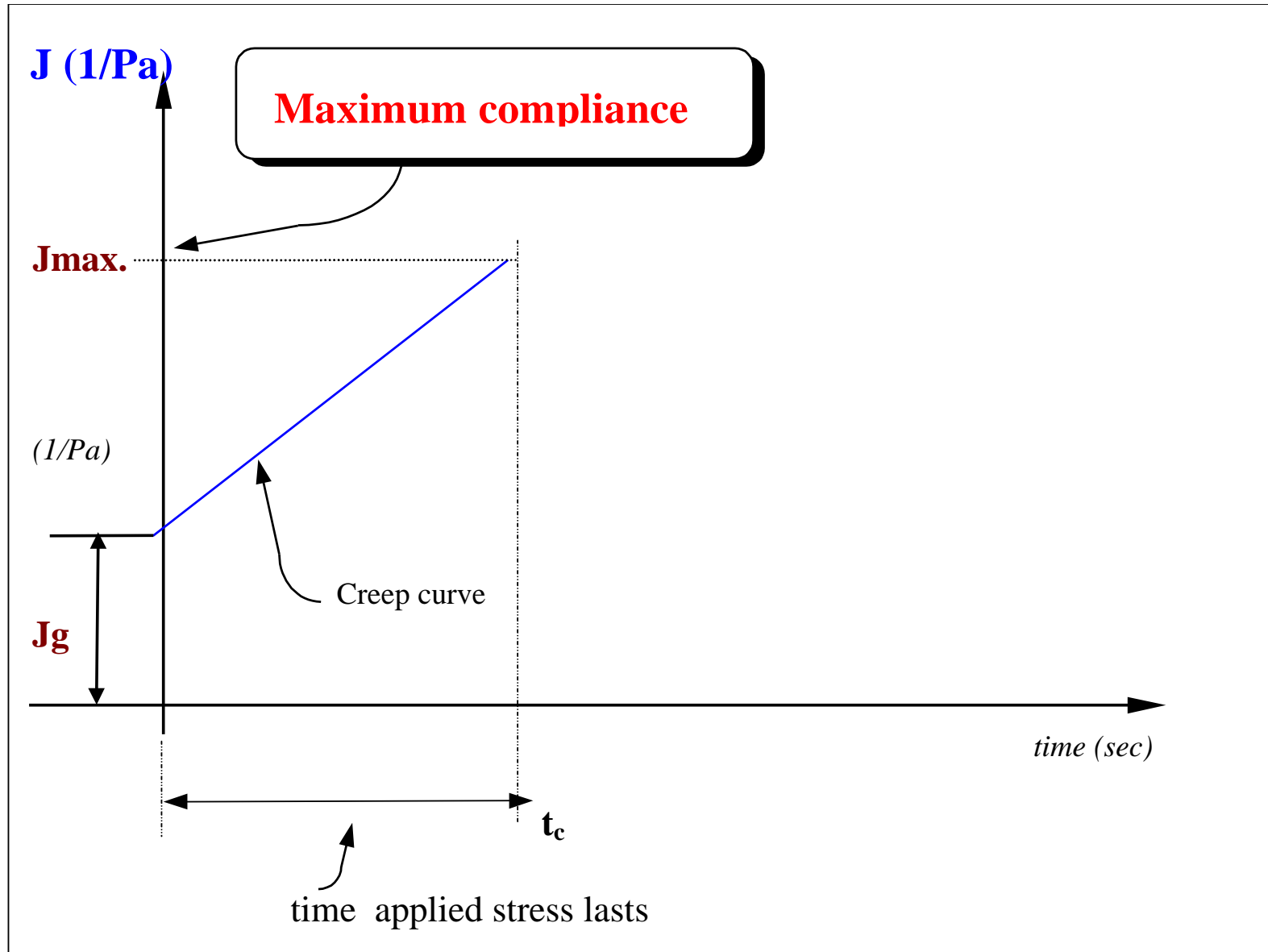
$$\gamma = (L - L_0) / L_0$$

σ in Pa

then

J en unidades de 1/Pa

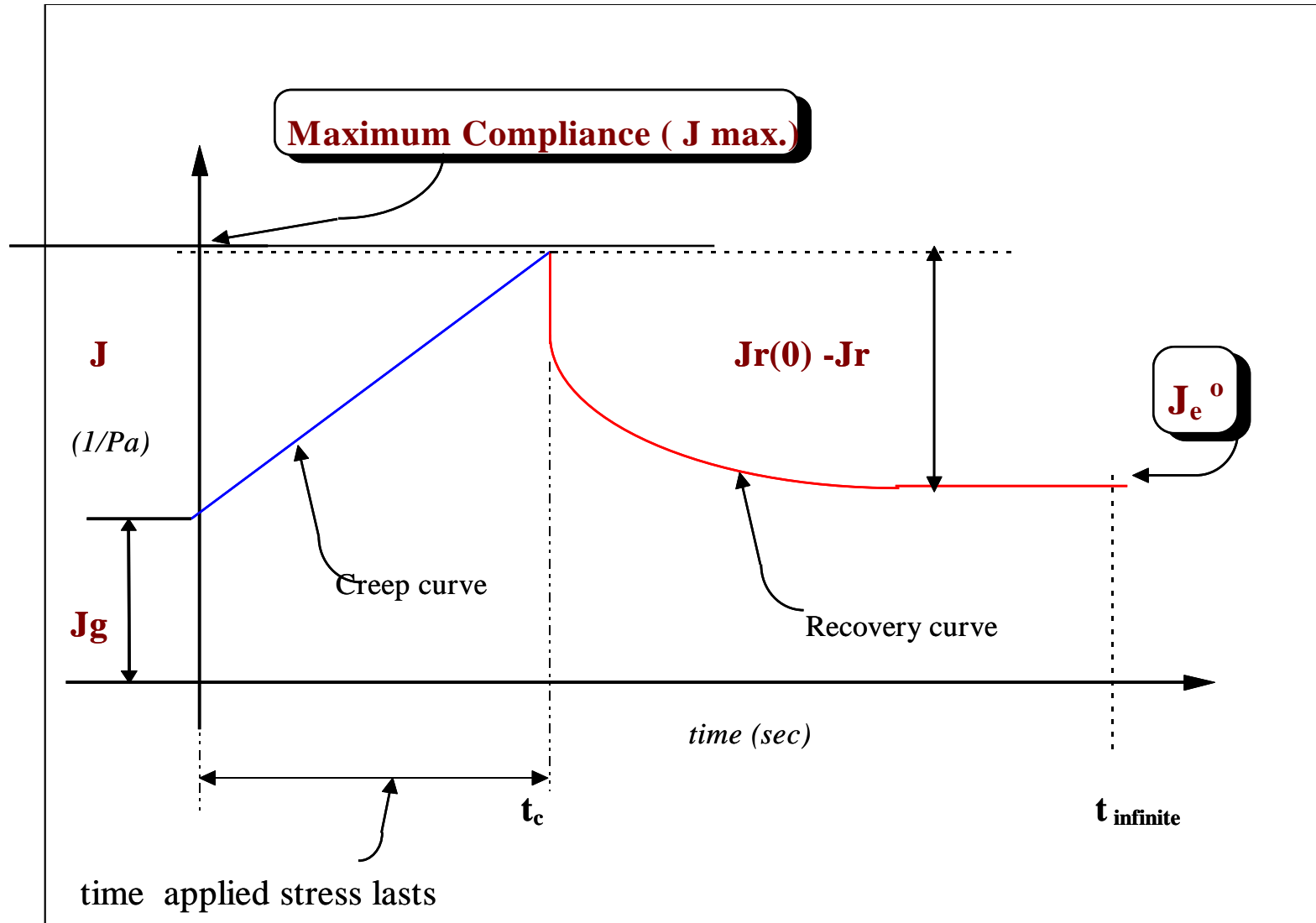
Constant stress rheology:



But, once the stress ceases
the material...

*recoils and the extent of recoil
with respect to the extent of
deformation under constant
stress is called the the recovery
compliance*

Constant stress rheology: creep and recovery compliance



where:

J is the compliance: Strain/ Stress

J_r (0) is the compliance at the time at which the stress ceases (t_c)

J_r is the compliance at any time after the stress ceases.

J_r(0)-J_r is the recoverable compliance at a given time ($t - t_c$)

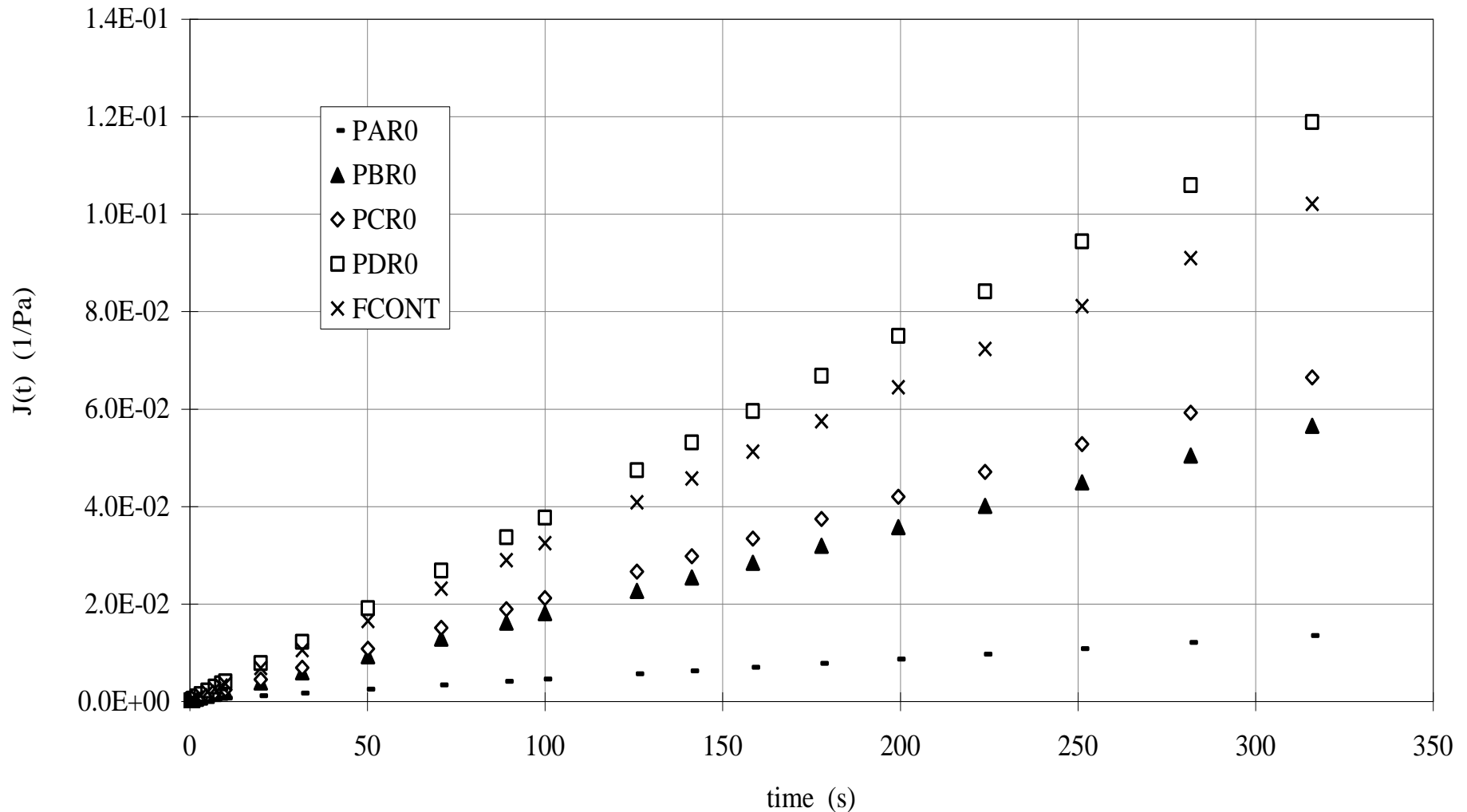
J_e⁰ is the steady state recoverable compliance
 $J_r(0) - J_r(t_{\text{infinite}})$ (at $t \gg t_c$).

J_g instantaneous or glassy compliance.

Creep compliance vs. time

(strain under constant stress vs time)

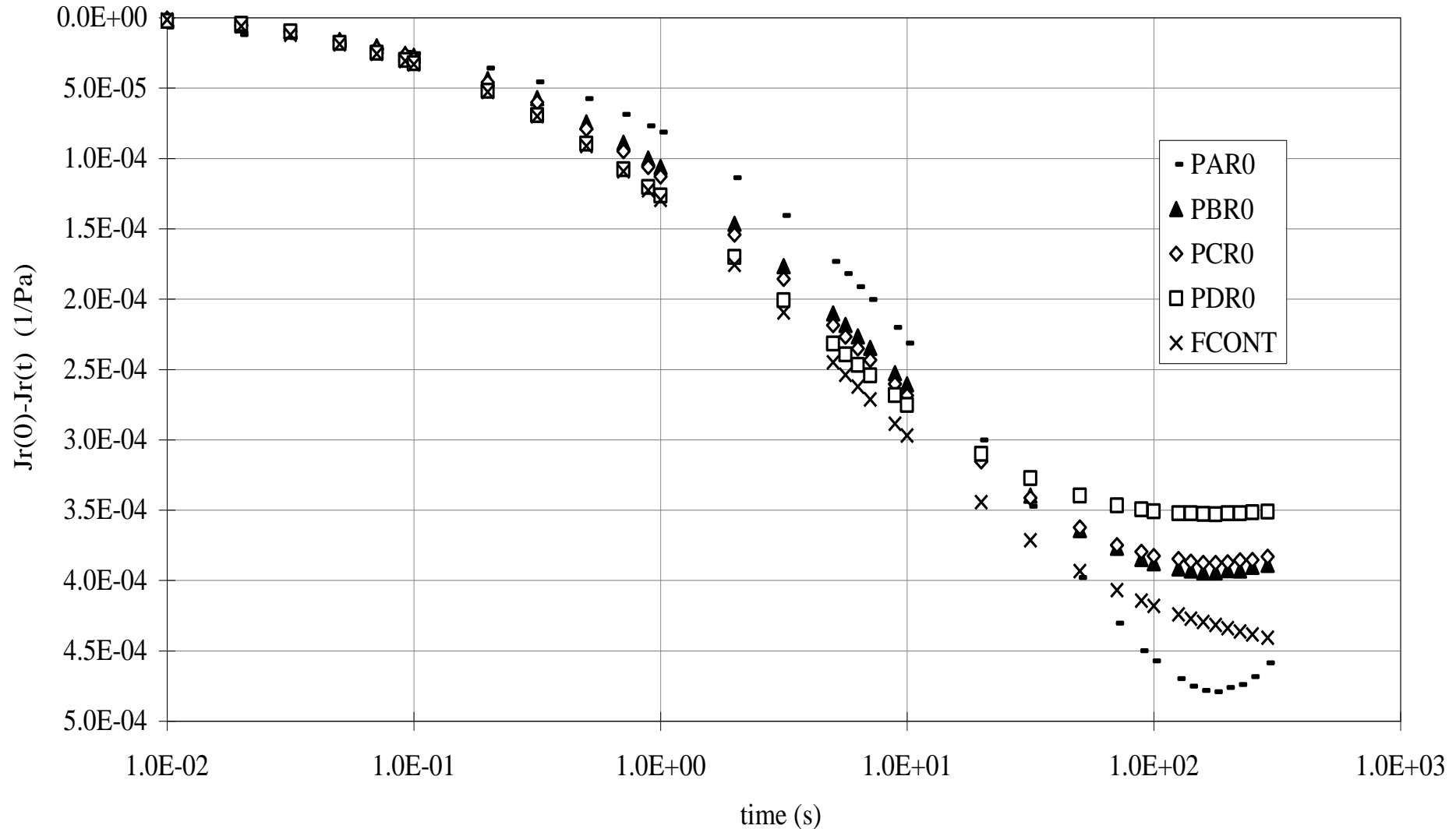
for a set of reactor grade polypropylene resins



Recovery compliance vs. time

(strain under constant stress vs time)

for a set of reactor grade polypropylene resins

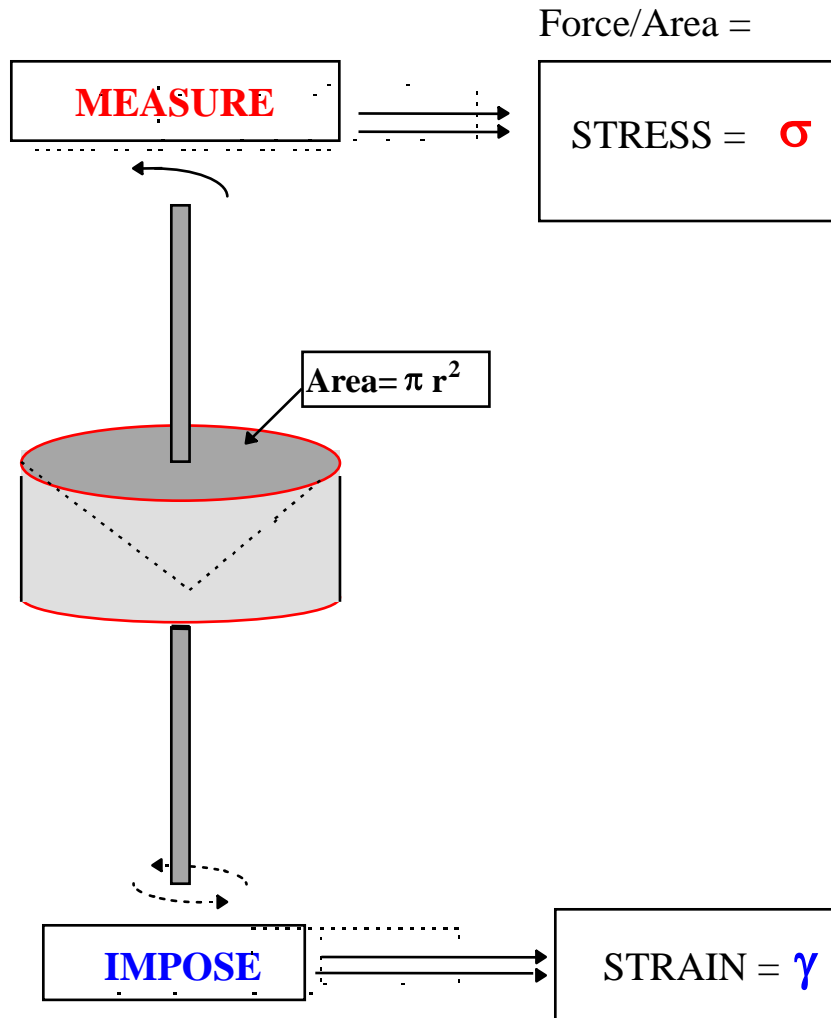


*Creep and recovery compliance data
for the RGPP resins
applied constant stress: 300 Pa*

resin	time	strain	$J_{\max} \times 10^{-5}$ at 300 s	shear rate	eta	$J_e^0 \times 10^{-4}$ at 300 s
par0	316	4.05	1351	1.24E-02	24200	4.95
pbr0	316	16.98	5660	5.34E-02	5620	3.89
pcr0	316	19.95	6650	6.28E-02	4780	3.86
pdr0	316	35.70	11900	1.11E-01	2710	3.51
pcont	316	30.63	10210	9.55E-02	3140	4.41

RELAXATION MODULUS

Relaxation modulus: the material's response to a sudden strain



$$\text{MODULUS} = \text{STRESS} / \text{STRAIN}$$

Relaxation modulus

$$G = \sigma / \gamma$$

$$\gamma = (L - L_0) / L_0$$

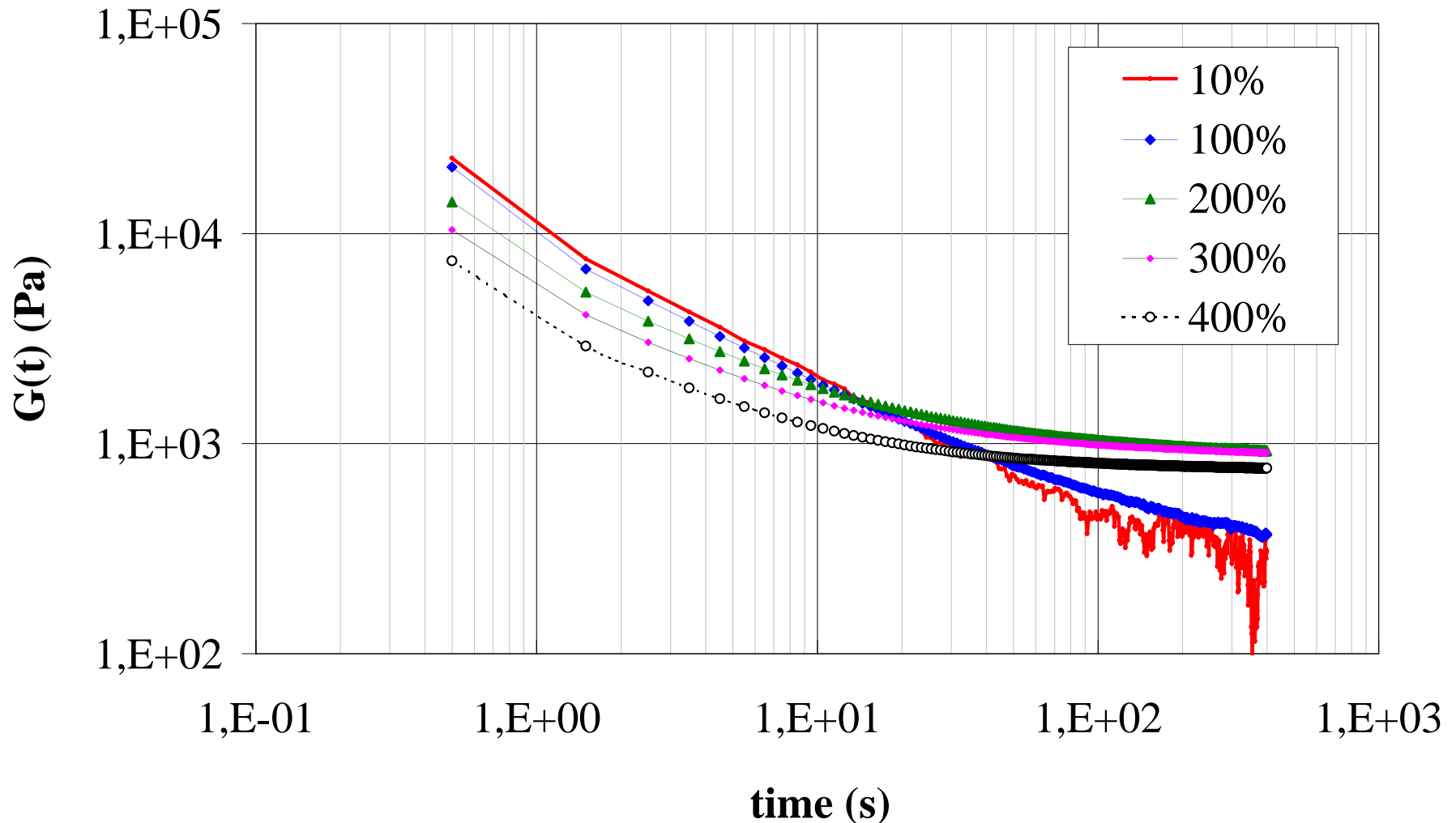
σ in Pa

then

G in Pa

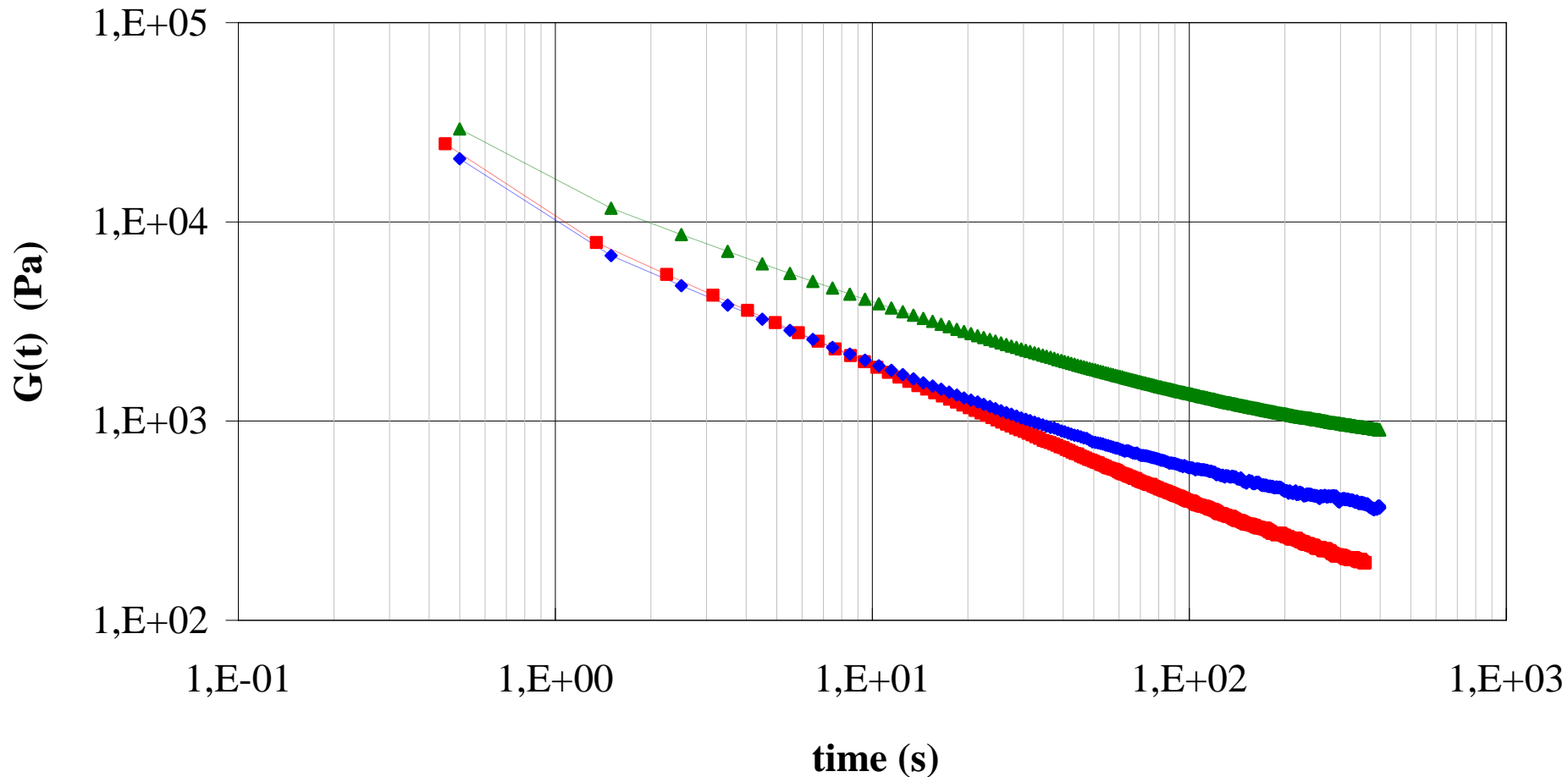
Typical Relaxation Moduli

Relaxation moduli at different % strain for a HDPE resin at
 $T=210^{\circ}\text{C}$



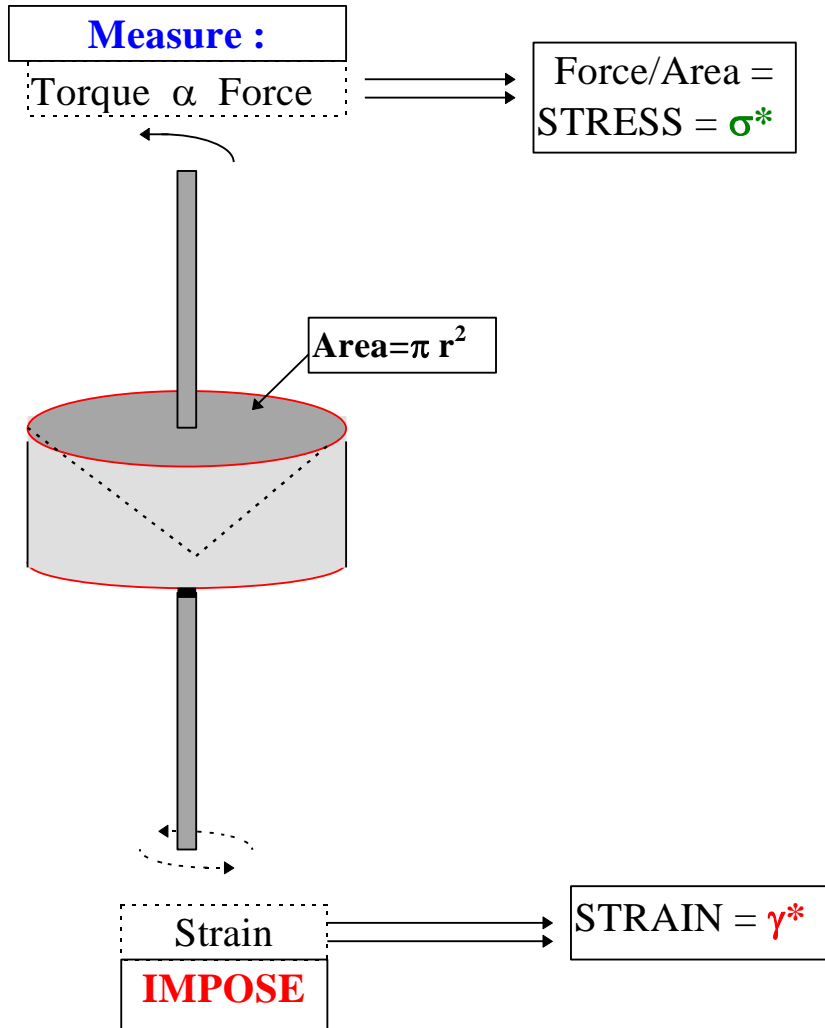
Typical Relaxation Moduli

Relaxation Moduli for HDPE resins after a sudden 100% strain at $T=210^{\circ}\text{C}$



OSCILLATORY RHEOMETRY

Oscillatory rheometry



$$\text{MODULUS} = \text{STRESS} / \text{STRAIN}$$

$$G^* = \sigma^* / \gamma^*$$

$$\gamma = \gamma_o \sin(\omega t)$$

$$\sigma = \sigma_o \sin(\omega t + \delta)$$

$$\sigma_o = \gamma_o G$$

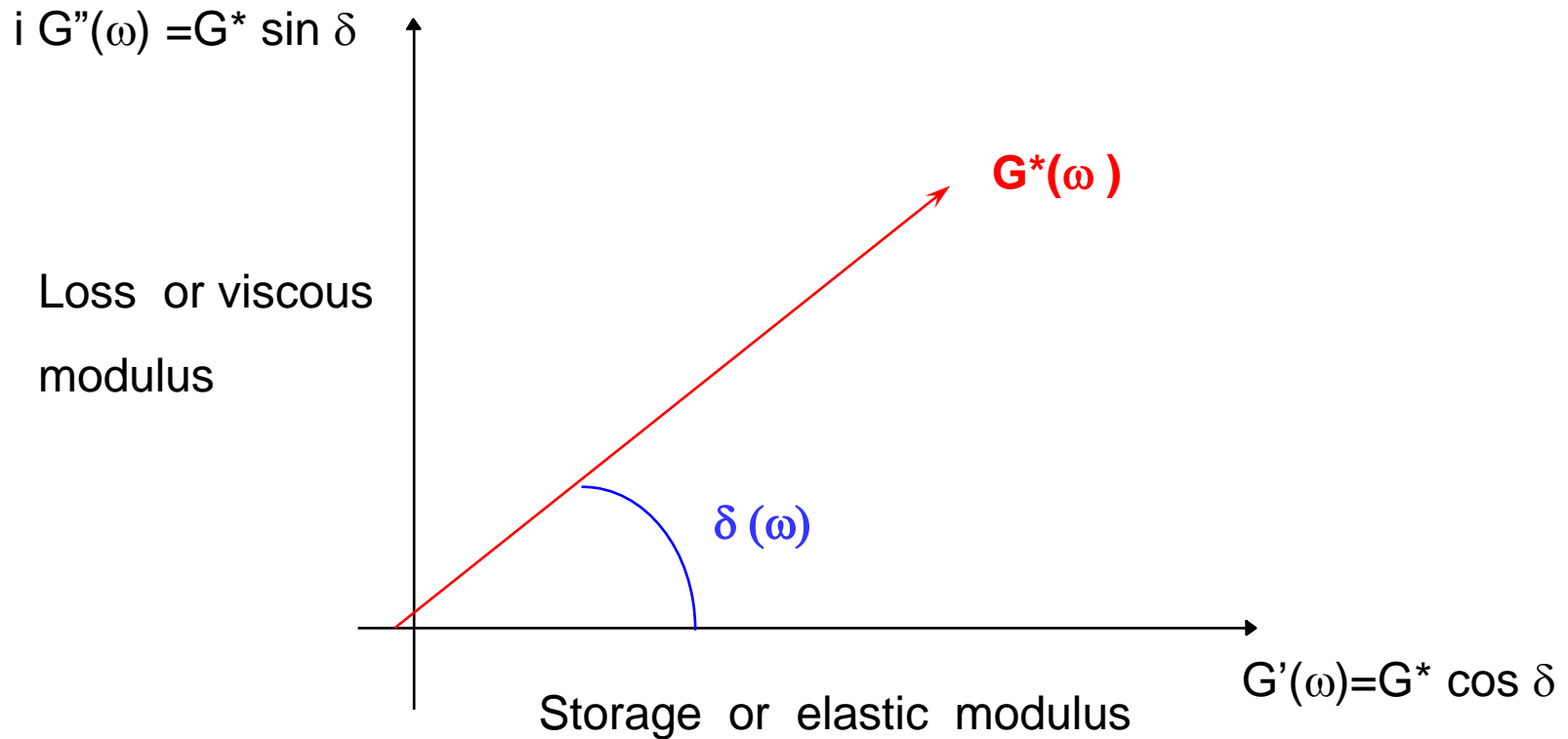
$$\sigma = \gamma_o (G \sin(\omega t) \cos(\delta) + G \cos(\omega t) \sin(\delta))$$

$$\sigma = \gamma_o (G' \sin(\omega t) + G'' \cos(\omega t))$$

$$\sigma / \gamma_o = (G' \sin(\omega t) + G'' \cos(\omega t))$$

$$G^*(\omega) = G'(\omega) + i G''(\omega)$$

Vector representation of the moduli in the complex domain



Parameters derived from $G'(\omega)$ and $G''(\omega)$

□ Complex moduli □ $|G^*(\omega)| = [G'(\omega)]^2 + [G''(\omega)]^2$

□ Tan delta □ $\tan \delta = G''(\omega) / G'(\omega)$

□ Complex viscosity □ $\eta^*(\omega) = \frac{\sqrt{|G^*(\omega)|}}{\omega}$

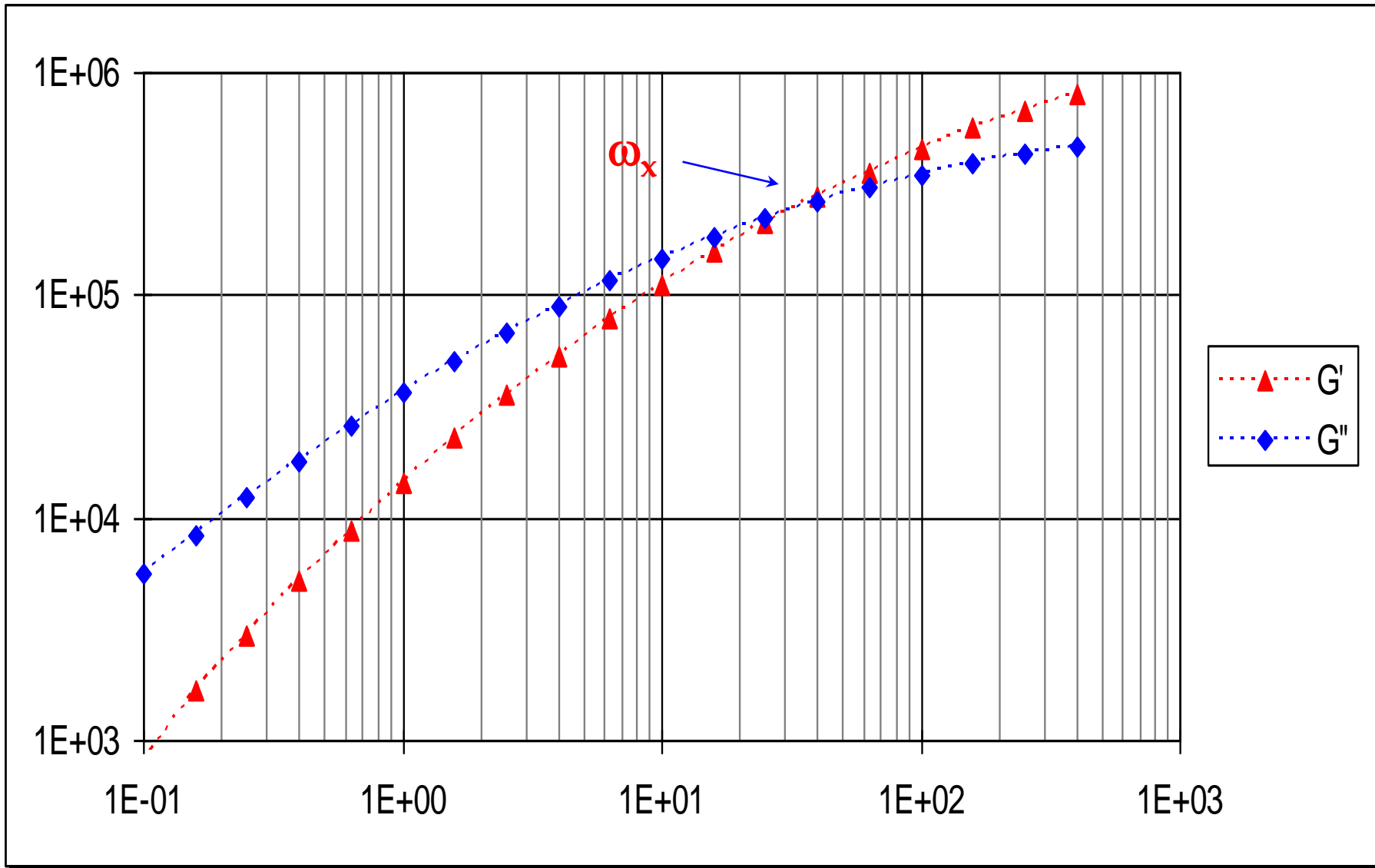
by Cox Mertz Rule □ $\eta^*(\omega) = \eta(\dot{\gamma})$

where $(\dot{\gamma}) \equiv (\omega)$

Frequency Sweeps

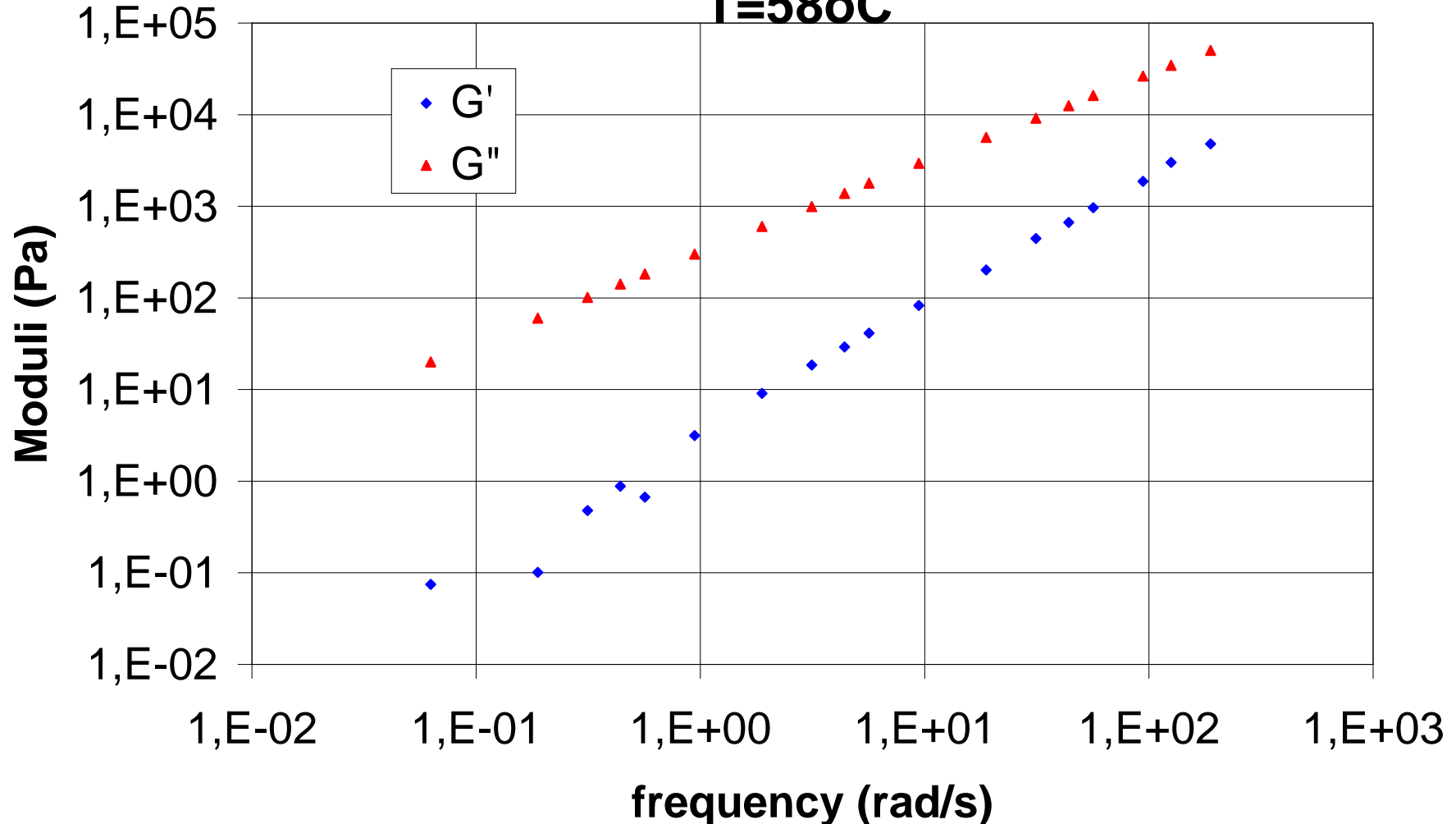
- The material is subjected to a series of oscillatory deformations ($\gamma_i = \gamma_o \sin(\omega t)$) each of them at different frequencies (ω_i) and an oscillatory stress is registered $\sigma_i = \sigma_o \sin(\omega_i t + \delta_i)$
- A series of **complex** moduli are calculated at each frequency (it can be done automatically by the software inside the computer which is connected to the rheometer and the data is then plotted)

Example of frequency sweep (1)



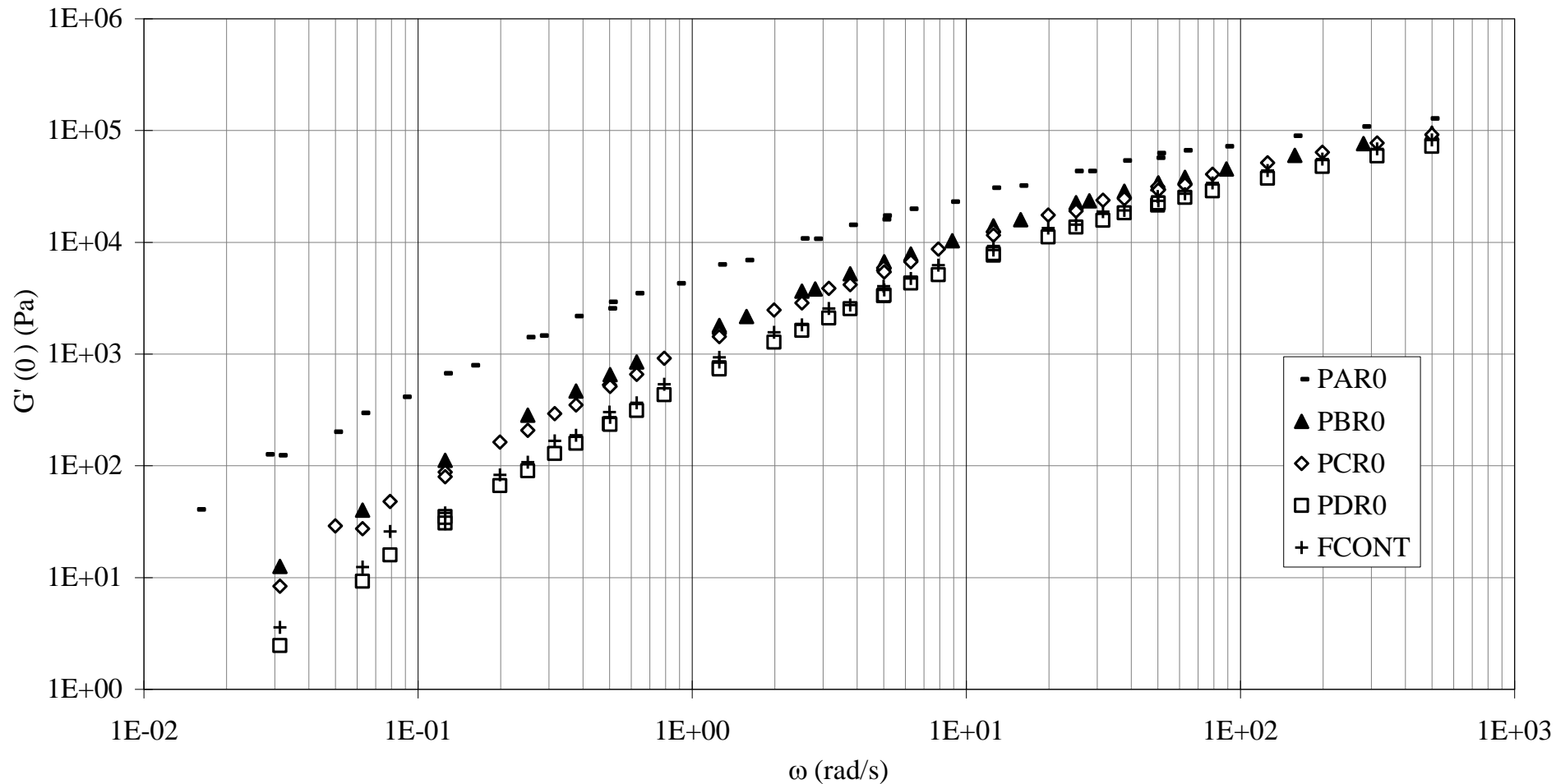
Example of frequency sweep (2)

**Frequency sweeps for an AC-10 asphalt at
 $T=58^{\circ}\text{C}$**

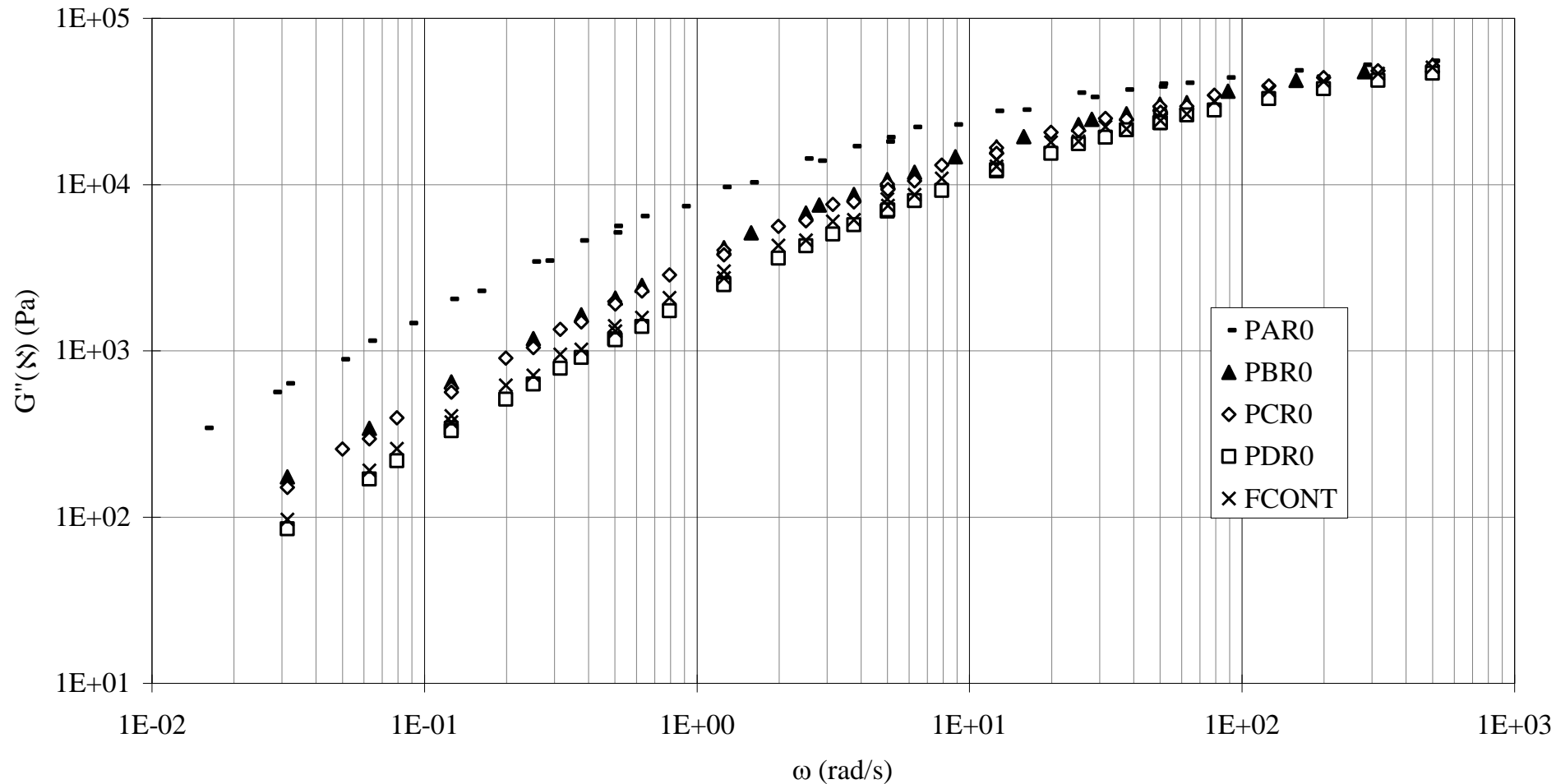


Storage modulus vs. frequency

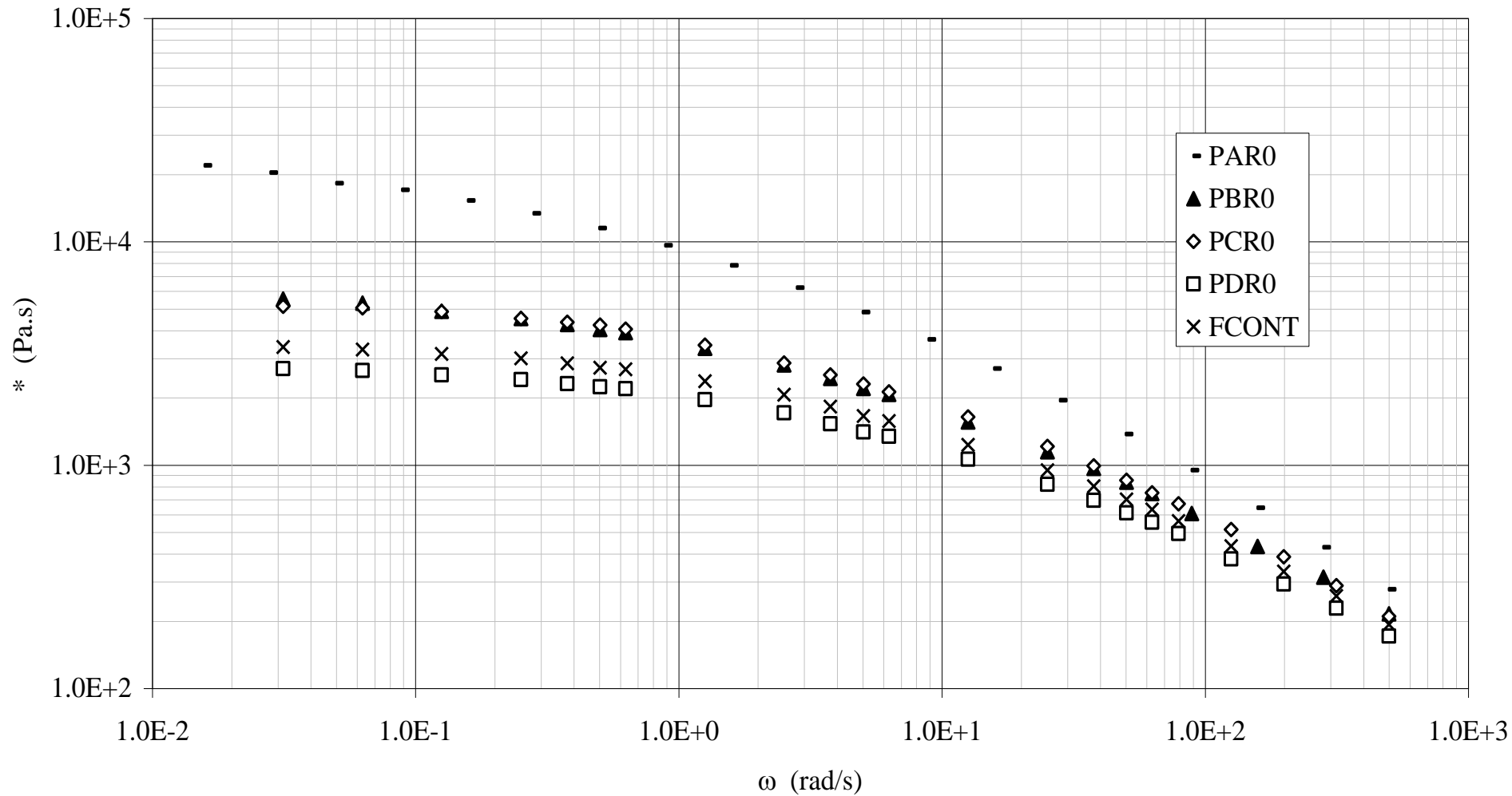
for a set of reactor grade polypropylene resins



Loss modulus vs. frequency for a set of reactor grade polypropylene resins



Complex viscosity vs. frequency for a set of reactor grade polypropylene resins



Expected results from rheological measurements

- To determine material constants:

η_0 , J_e^0 , λ_{at} which Non-Newtonian behavior starts.

Such material constants can be related to average molecular weight, polydispersity index

- To determine material functions:

$H(\lambda)$, $G(t)$, $\mu(t)$ which can be used to

identify changes in the molecular weight distribution and predict modulus difficult to measure otherwise

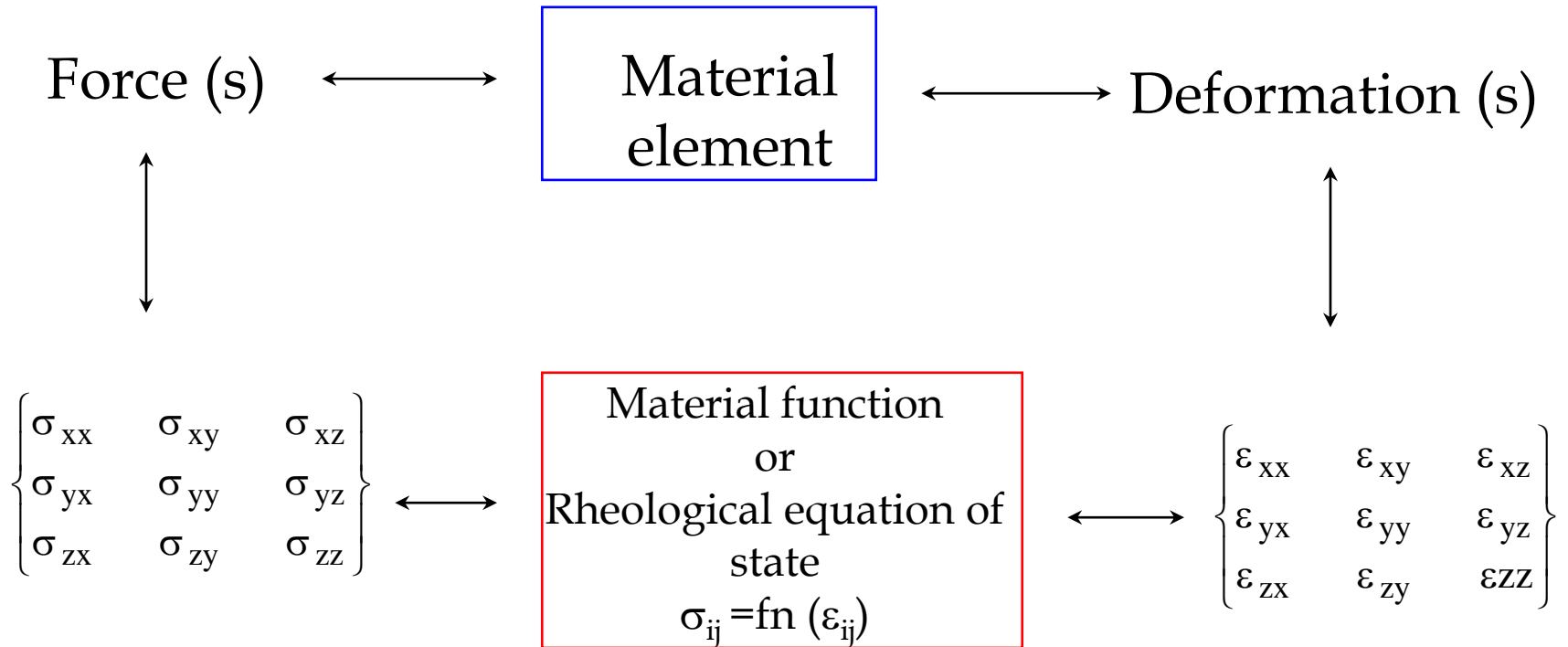
But...

*Do we have to measure every
property, every time?*

Go to

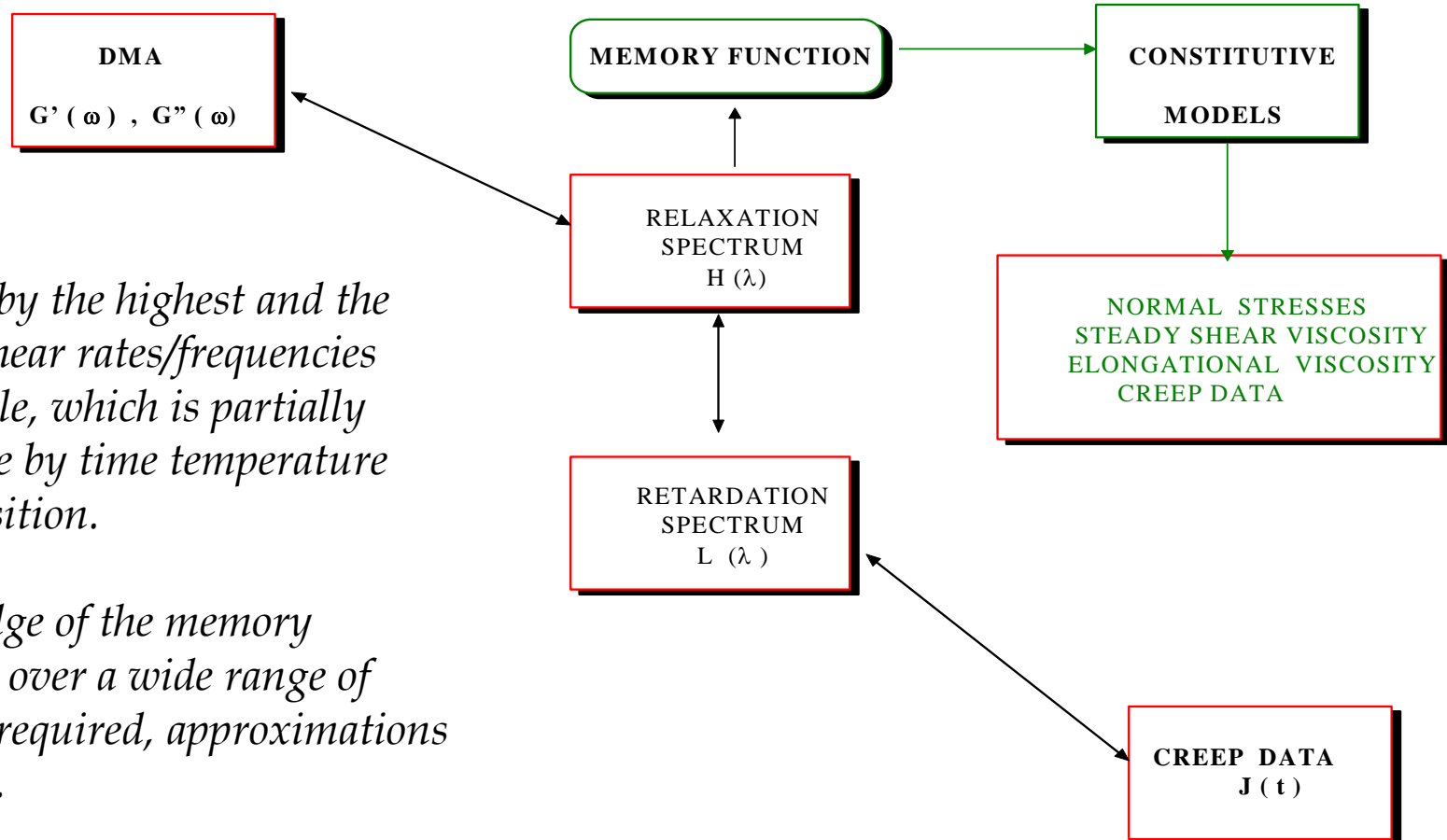
*Microsoft document “clase 5b”,
Microsoft excel “clase5b”*

Physical and mathematical relations



very important for selecting surrogate tests

INTERCONVERSION OF RHEOLOGICAL DATA

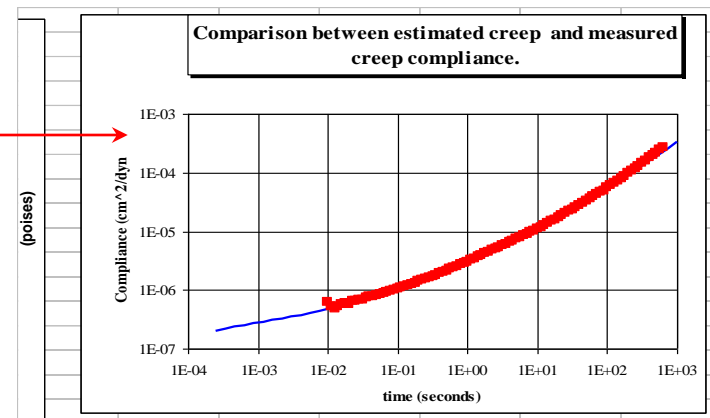
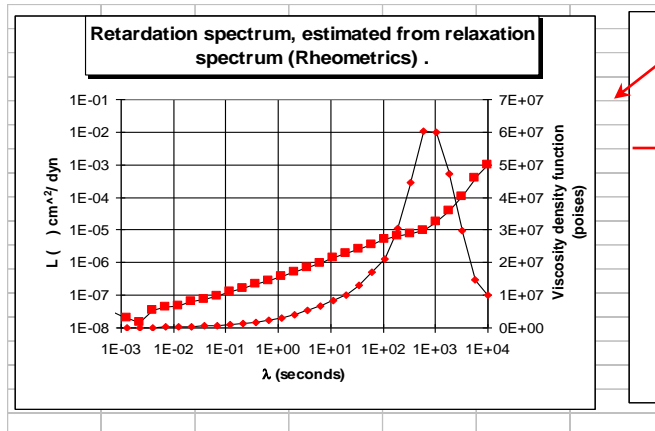
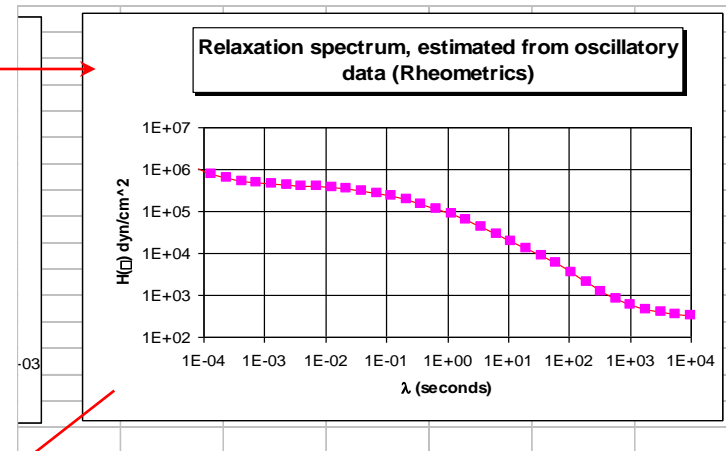
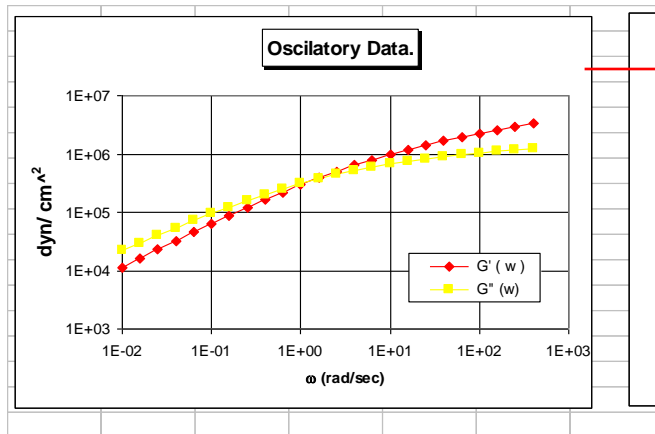


Limited by the highest and the lowest shear rates/frequencies achievable, which is partially overcome by time temperature superposition.

Knowledge of the memory function over a wide range of times is required, approximations required.

Interconversion

All the creep data estimated this way overlapped the measured creep data.



But...

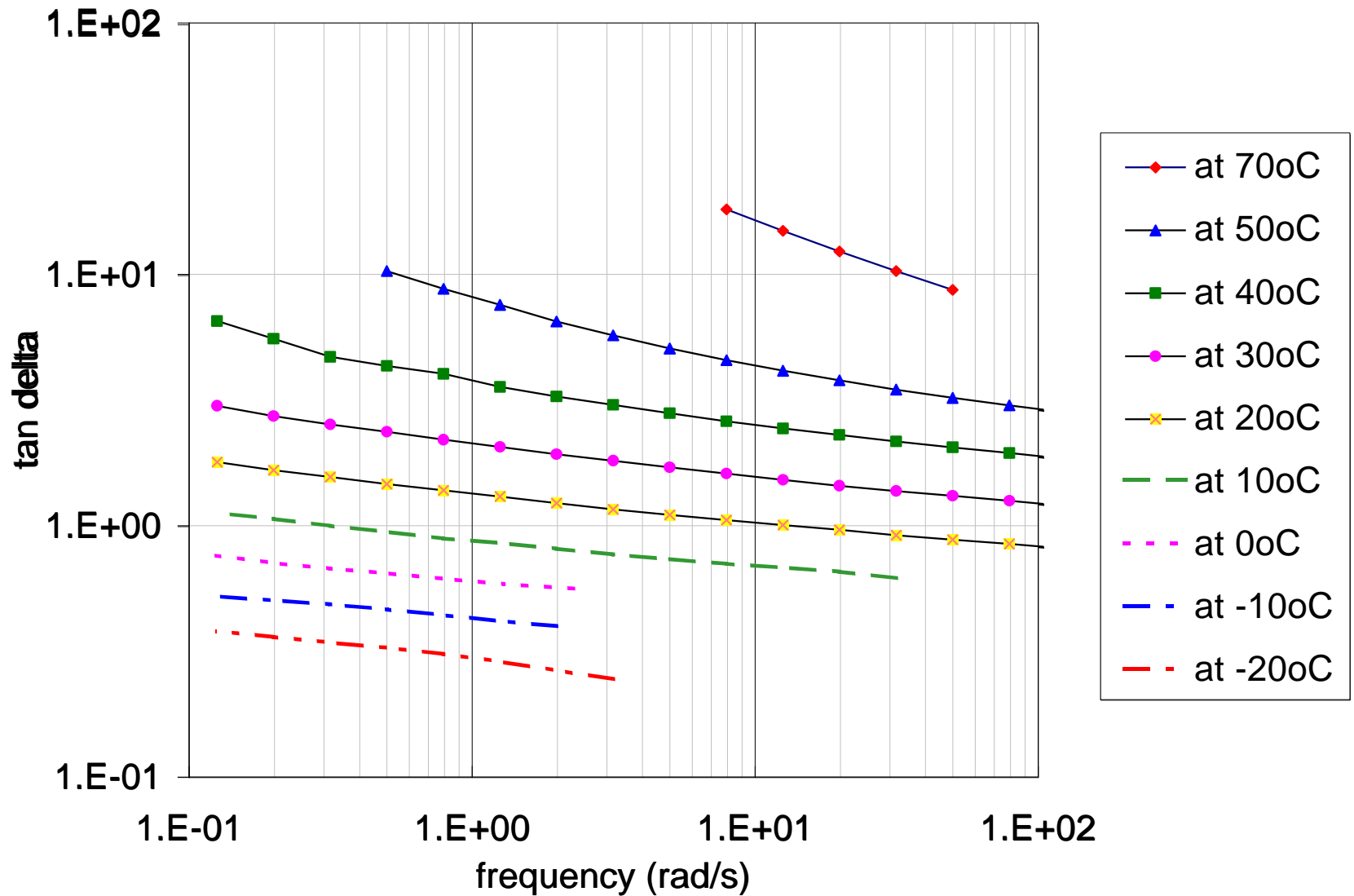
The interconversion might require to have a given modulus in a wider range of frequencies and times ... So the question is: how can we increase that range since the rheological instruments are limited in that respect?

Time Temperature Superposition (TTS)

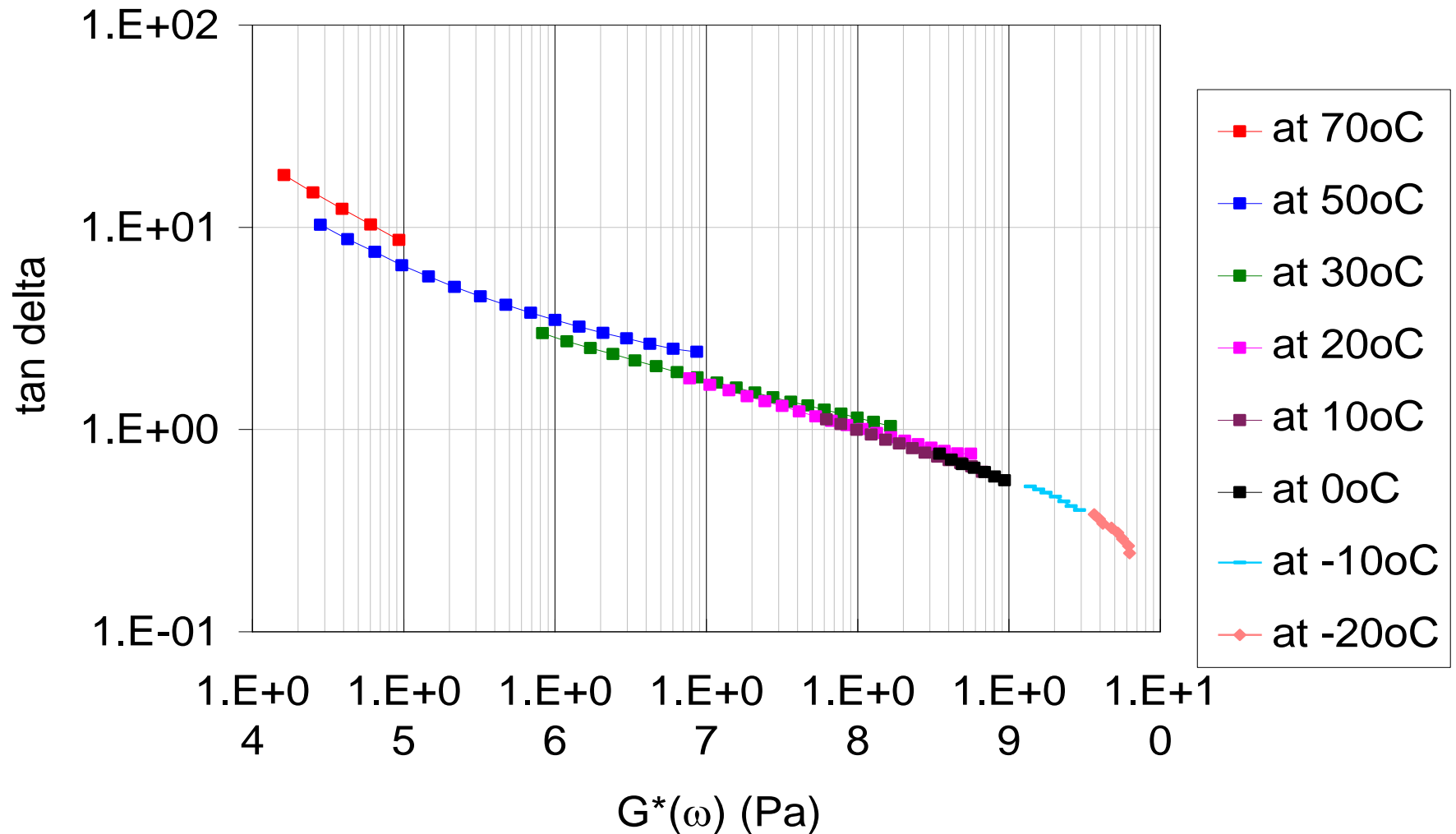
TTS... what for?

- To extend the frequency range of the parameter (*i.e.*: $G'(\omega)$) at the temperature T_0 (otherwise the range can be just from 0.01-500 rad/s),
- The extended curve, called **Master Curve** can be used to estimate other visco-elastic parameters

Typical data to determine horizontal shift

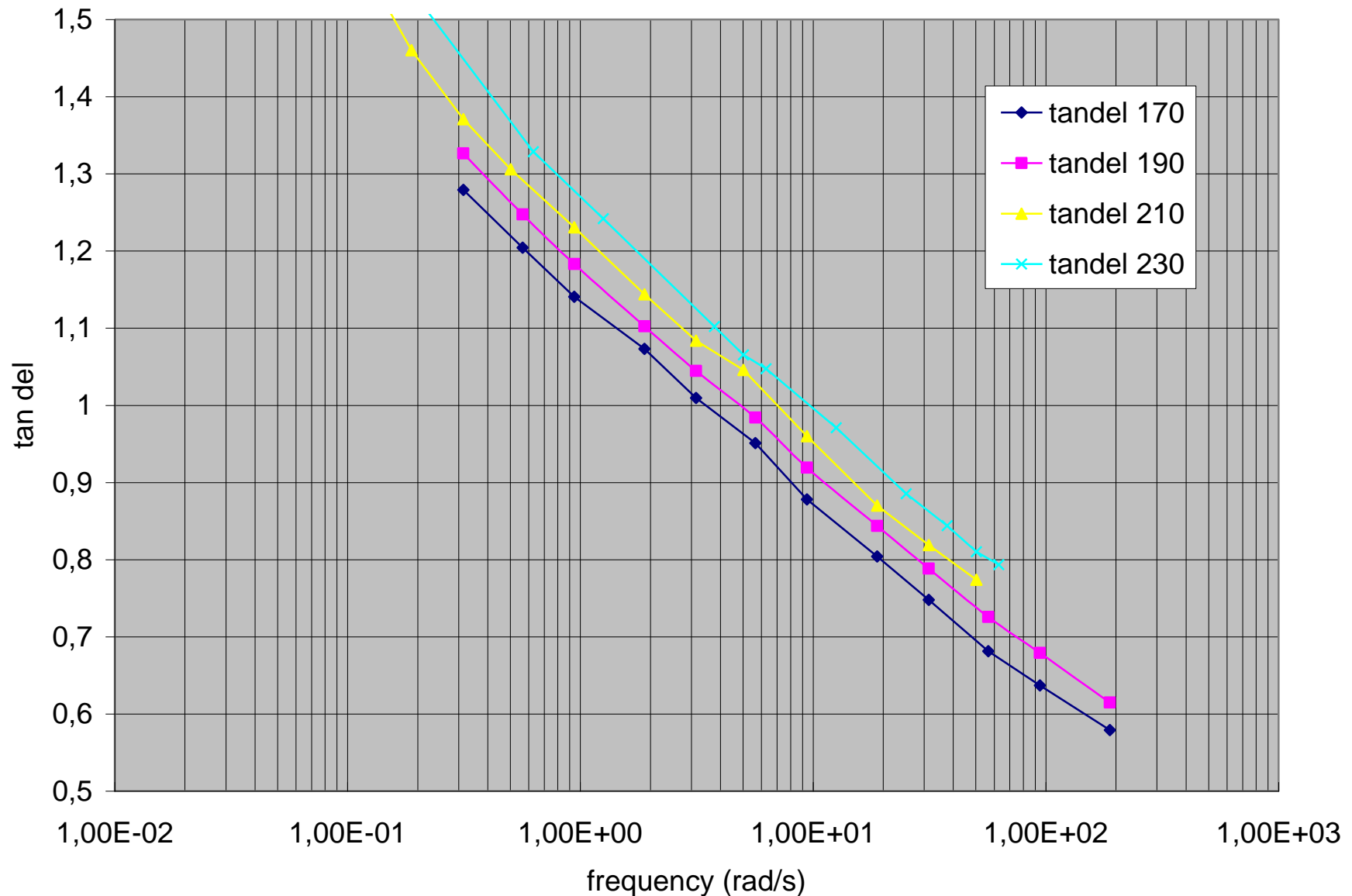


Typical data to determine vertical shift

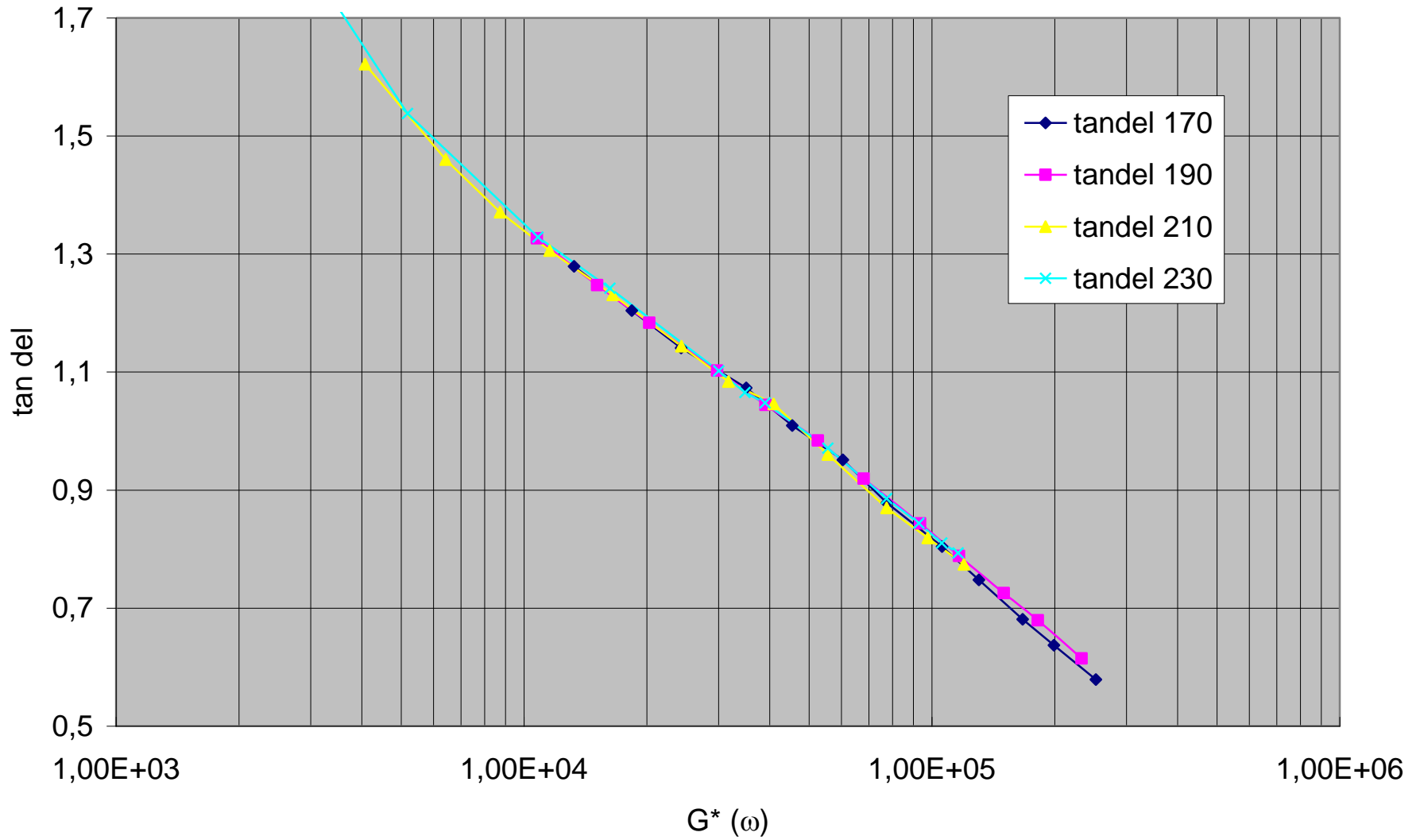


Tan del vs. complex modulus for the PAV residue of the polymer modified AC-5 asphalt

An HDPE resin at different temperatures



Tan del versus G^* for HDPE resins



TTS ...

- Obtaining a good master curve requires a careful selection of the parameter from which the shift factor is attained since the data might require a horizontal and a vertical shift.
- The shift factor a_T is better determined by plotting $\tan \delta$ versus frequency,
- The vertical shift is better determined by plotting $\tan \delta$ versus complex modulus

Time-Temperature Superposition

- $G'(\omega)$ and $G''(\omega)$ obtained at several temperatures can be brought together into a single master curve, mathematically can be expressed as:

$$G'(\omega)|_{T_0} = G'(a_T \omega)|_T$$

where $\ln a_T = \frac{Ea}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$ Arrhenius type

$$\log a_T = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \quad \text{WLF equation}$$

Examples of temperature sweeps

Loss moduli versus temperature for three HDPE resins
at 1 Hz

