

Today's Plan

# Linear viscoelasticity

- I. DMA
- II. Time-temperature superposition
- **III. Mathematical representation**
- **IV. Rheological models**
- V. Summary

### **Recall : Usual mechanical tests**

Viscoelastic deformation is time and temperature dependant. Hence, we characterise the influence of strain rate, frequency, or temperature. We do :

1 Loading tests at various strain rate

<sup>2</sup> Creep : apply a stress and then follow strain vs. time

3 Stress relaxation : apply a sudden length change and then watch the stress decay

④ Dynamic measurements : apply an oscillating strain at a fixed frequency and measure the amplitude and phase of the response

# I. DMA (Dynamic Mechanical Analysis )

• Dynamic modulus

$$E_{*}(i\,\overline{\omega}) = \frac{\sigma^{*}(i\,\omega)}{\varepsilon^{*}(i\,\overline{\omega})} = E'(\,\overline{\omega}) + iE''(\,\overline{\omega})$$

• Conservation modulus (stored elastic energy)

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$

• Lost modulus (dissipated energy)

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$

- Internal friction (damping factor, loss tangent)
  - $\tan \delta = \frac{E''}{E'}$

> Input  $\sigma = \sigma_0 \sin(\omega t)$ > Response  $\mathcal{E} = \mathcal{E}_0 \sin(\omega t - \delta)$ 



## **Application : Damping in car tyres**



- The damping factor tan¢ represents the ratio between the dissipated energy in one cycle and the maximum of free energy in one cycle
- Most of the time, the lost factor largely depends on temperature



Why using rubber ?

For their high strain elasticity and energy absorbing qualities

## Molecular motions and peaks



Peaks in G" and in  $tan\delta$  occur when the frequency of some molecular motion matches the imposed frequency.

# Typical dynamic mechanical response



Recall : Tg may differ substantially from T $\alpha$  6

• Effect of chemical composition



All polymers have secondary relaxations; but the shift between  $\beta$  relaxation and  $\alpha$  varies

• Effect of crystallinity



• Effect of plasticizer



#### • Blend of polymers



Blends of polymers  $A_{50}B_{50}$   $\alpha$  relaxation depends on morphology, while  $\Delta Cp$  doesn't change

### **II.** Time-Temperature Equivalency

Rheological properties are highly temperature dependent: Experiments must be carried out at several temperatures in order to obtain a complete picture of the material response.

It is often found that data, for example  $G'(\omega)$  and  $G''(\omega)$ , taken at several temperatures can be brought together on a single master curve by means of "time-temperature superposition".

This makes possible the display on a single curve of material behavior covering a much broader range of time or frequency that can ever be measured at a single temperature. Materials whose behavior can be displayed in this way are said to be "thermorheologically simple".

# **Time-temperature equivalency**

Construction of master curves (for amorphous polymers)

### Hypothesis of thermorheological simplicity

We can observe the same behaviour by varying time (frequency) or temperature.



 $a_T$  is the shift factor

#### Master curve : example



Figure 7.11. Storage compliance of poly-n-octyl methacrylate in the glass transition region plotted against frequency at 24 temperatures as indicated (after Ferry).

# Shift factors: WLF equation

WLF equation (Williams, Landel, Ferry)

$$\log \alpha T = \log \frac{\tau(T)}{\tau(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

where  $C_1 = 17.44$  and  $C_2 = 51.6$ so called « universal constants » but need in reality to be determined for each polymer.

For amorphous polymers with simple structures, within [Tg , Tg+50K ]

*Example:* You have a bucket of bricks and the bottom falls out after 30 min at  $T_g$ +50°C. At  $T_g$ +20°C, the bottom will drop out in 128 days.



Figure 7.14. Temperature dependence of the shift factor  $a_T$  used in plotting Figure 7.13. Points, chosen empirically; curve is WLF equations with a suitable choice of  $T_g$  (or  $T_s$ ) (after Ferry).

Polymère	<i>T</i> <sub>g</sub> [K]	$c_1^{\rm g}$	$c_2^{g}[K]$
polyisobutylène	205	16,6	104,4
polystyrène	373	13,7	50
polydiméthyl siloxane	150	6,1	69
polyméthacrylate de méthyle	381	34	80
poly(n-octyl méthacrylate)	253	16,1	107,3

after [Ferry]

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**II.** Mathematical representation

# **Recall : framework**

- Small Perturbation Hypothesis (SPH) small deformations  $_{sup}|\varepsilon| << 1$ infinitesimal strain tensor :  $\varepsilon_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right]$
- Linear viscoelasticity

if  $\epsilon = f(\sigma)$ then f(m $\sigma$ 1+n $\sigma$ 2)=mf( $\sigma$ 1)+nf( $\sigma$ 2)

(it means that viscoelastic functions are independent of level of loading)

- isothermal
- isotropic and non-ageing materials
- uniaxial frame

## **Recall : Hereditary constitutive relationships**

• Creep integral form :

$$\mathcal{E}(t) = J_{u}\sigma + \int_{-\infty}^{t} J(t-\tau) \frac{d\sigma(\tau)}{d\tau} d\tau$$

 $\mathcal{E}=J\otimes \frac{D\sigma}{Dt}$ 

• Relaxation integral form :

$$\sigma(t) = E_r \mathcal{E} + \int_{-\infty}^{t} E(t - \tau) \frac{d\mathcal{E}(\tau)}{d\tau} dt$$
$$\sigma = E \otimes \frac{D\mathcal{E}}{Dt}$$

*J(t): creep function Ju : unrelaxed compliance* 

 $\otimes$ : convolution product

*E(t): relaxation function Er : relaxed modulus* 

Viscoelastic functions rule entirely the material's response.

# Laplace-Carson transform

- Laplace Carson transform :  $f^*(p) = p \int_0^\infty f(t) e^{-pt} dt$  Properties  $\left(\frac{df}{dt}\right)^* = p f^*(p)$

hence 
$$\left(A \otimes \frac{DB}{Dt}\right)^* = \left[\int_{-\infty}^t A(t-\tau) dB(\tau)\right]^* = A^*(p)B^*(p)$$

hence 
$$\sigma^*(p) = E^*(p)\varepsilon^*(p)$$
  $\varepsilon^*(p) = J^*(p)\sigma^*(p)$   
with  $E^*(p) = 1/J^*(p)$ 

by inverse transform : E(t) and J(t)

the complexe modulus is obtained by:  $\tilde{E}(\omega) = E^*(p = i\omega)$ 

Conclusion : Classical laws of linear elasticity can be applied in ٠ linear viscoelasticity as soon as quantities are remplaced by their Laplace transform counterparts.

# Laplace-Carson transform properties

Function	Transformed	Function	Transformed
f(t)	$f^+(p)$		1/p
C.f(t)	$C.f^+(p)$	t <sup>n</sup>	$\frac{n!}{p^n}$
$\frac{d}{dt}$	p	exp(-at)	$\frac{p}{p+a}$
H(t)		$1 - \exp(-at)$	$\frac{a}{p+a}$
$H(t-\tau)$	$\exp(-\tau p)$	$\cos \omega t$	$\frac{p^2}{p^2 + \omega^2}$
$f(t-\tau)$	$\exp(-\tau p) f^+(p)^*$	sin $\omega t$	$\frac{p\omega}{p^2 + \omega^2}$
$ \begin{aligned} & \text{if } f(t) = 0 \\ & f'(t) \\ & \frac{\mathrm{d}f}{\mathrm{d}t}(t) \otimes q(t) \end{aligned} $	for $t \leq 0$ $pf^+(p)$ $f^+(p)g^+(p)$	$f(t) \exp(-at)$ $(-t)^{m} f(t)$	$\frac{p}{p+a}f^{+}(a+p)$ $p\frac{d^{m}}{da^{m}}\left(\frac{f^{+}(p)}{p}\right)$

### Relationship between creep and stress relaxation

Consider a stress program in which

$$\frac{d\sigma(\tau)}{d\tau} = \frac{dG(\tau)}{d\tau}$$

 $\mathcal{E}(t) = \int_{0}^{t} J(t-\tau) \frac{d \mathcal{O}(\tau)}{d \tau} d\tau$   $\mathcal{E}(t) = \int_{0}^{t} J(t-\tau) \frac{d G(\tau)}{d \tau} d\tau = cst$ normalize :  $\int_{0}^{t} J(t-\tau) \frac{d G(\tau)}{d \tau} d\tau = 1$ hence :  $\int_{0}^{t} G(\tau) J(t-\tau) d\tau = t. \longrightarrow G(t) \neq \frac{1}{J(t)}$ However, for dynamic responses:  $G^{*}(i\omega) = \frac{1}{J^{*}(i\omega)}$ 

### **Differential representation of linear viscoelasticity**

General linear differential equation

$$a_n \frac{\partial^n \sigma}{\partial t^n} + a_{n-1} \frac{\partial^{n-1} \sigma}{\partial t^{n-1}} + \ldots + a_0 \sigma = b_n \frac{\partial^n \varepsilon}{\partial t^n} + b_{n-1} \frac{\partial^{n-1} \varepsilon}{\partial t^{n-1}} + \ldots + b_0 \varepsilon$$

where a<sub>i</sub>, b<sub>i</sub> are material parameters

This is equivalent to describing the viscoelastic behaviour by rheological models constructed of elastic springs and viscous dashpots.

### **Elementary rheological models**

Viscoelastic materials display the characteristics of both elastic solids and viscous fluids. These 2 ideal behaviours are modeled by the spring and the dashpot.



- Spring:  $\sigma = E\mathcal{E}$ 
  - Hooke's law

Viscous Fluid



Dashpot  $\sigma = \eta \dot{\mathcal{E}}$ 

Newton's law

### Maxwell model



dynamic response

$$\widetilde{E}(\omega) = E^*(p = i\omega) = E \frac{i\omega}{i\omega + E/\eta}$$

### Voigt model

![](_page_23_Figure_1.jpeg)

creep response

![](_page_23_Figure_3.jpeg)

dynamic response 
$$\widetilde{J}(w) = J^*(iw)$$
  
 $J(w) = \frac{1}{E} \left(\frac{1}{1+iw\tau}\right)$ 

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### Standard linear solid (Zener model)

 $a_0\sigma + a_1\frac{d\sigma}{dt} = b_0\varepsilon + b_1\frac{d\varepsilon}{dt}$ 

![](_page_24_Figure_2.jpeg)

Homework : plot creep and relaxation responses

## Linear viscoelasticity #2 : Summary

- Viscoelastic behavior of polymers is time (frequency) and temperaturedependant.

- DMA is an efficient tool for investigating linear viscoelastic properties (relaxations, molecular mobility, morphology..)

- *Time temperature superposition* holds if all relevant molecular motions speed up by the same ratio with an increased temperature.

- Two mathematical descriptions of linear viscoelasticity :

- Hereditary integrals, deriving from Boltzmann superposition pple.
- Linear differential representation

This leads to combinations of elastic springs and viscous dashpots.

- Relationships between viscoelastic functions have been established and efficiency of Laplace Carson transform has been shown.

Thank you for your attention

Lecture# 8 will be given on June 12<sup>th</sup>