Oscillatory shear rheology of polymers

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Outline

- elastic solids and viscous liquids (revision)
- viscoelastic materials (revision)
- the Maxwell model in time domain (revision)
- Small Amplitude Oscillatory Shear (SAOS)
- linear viscoelastic functions: $G'(\omega), G''(\omega), \tan\delta(\omega)$
- the Maxwell model in time domain
- some examples involving thermoplastic polymers and elastomers
- the time-temperature superposition principle (TTS)
- complex notation and Cox-Merz rule
- Medium and Large Amplitude Oscillatory Shear (MAOS and LAOS)


**Constitutive Equations**

**Robert Hooke (1678)**

\[
\sigma = G\gamma
\]

- **Elastic Body**
  - Stores elastic energy!

**Isaac Newton (1687)**

\[
\sigma = \eta \frac{d\gamma}{dt} = \eta \dot{\gamma}
\]

- **Viscous Liquid**
  - Dissipates energy!

**Creep and Creep Recovery**

- Time:
  - \( t_0 \) to \( t_1 \)

**Graphs**

- **Stress vs. Time**
  - \( t_0 \) to \( t_1 \)
  - \( \sigma \) vs. \( t \)
  - \( \sigma = G\gamma \)
  - \( \sigma = \eta \dot{\gamma} \)

- **Strain vs. Time**
  - \( t_0 \) to \( t_1 \)
  - \( \gamma \) vs. \( t \)
  - \( \gamma = G^{-1} \sigma \)
  - \( \gamma = \frac{1}{\eta} \dot{\sigma} \)
viscoelastic body

James Clerk Maxwell (1868)

Stores and wastes at the same time elastic energy of deformation!

Deborah number:

\[ De = \frac{\tau_{\text{mat}}}{\tau_{\text{exp}}} \]

“…even the mountains flowed before the Lord…”

(Prophetess Deborah, Judges, 5:5)
Maxwell model

stress relaxation

a constant strain \( \gamma_0 \) is imposed and the evolution of the stress is followed.

\[
G(t) = G_0 \cdot e^{-\left(\frac{t}{\tau}\right)}
\]

stress relaxation modulus:

\[
G(t) = \frac{\sigma(t)}{\gamma_0}
\]

time constant:

\[
\tau = \frac{\eta}{G}
\]
Rheological experiments in oscillatory regime

we need some basics in:

rheology

oscillatory shear

rheometry
Small Amplitude Oscillatory Shear

by applying a sinusoidal strain

or equivalently a cosinusoidal strain rate

how does the shear stress evolves with time?

elastic solid

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t)$$

viscous liquid

$$\sigma(t) = G \gamma_0 \sin(\omega t)$$

$$\sigma(t) = \eta \omega \gamma_0 \cos(\omega t)$$
Viscoelastic body in oscillatory regime

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]

\[ \sigma(t) = \sigma_0 \sin(\omega t + \delta) \]

\[ \sigma(t) = \sigma_0 \left[ \sin(\omega t) \cos \delta + \cos(\omega t) \sin \delta \right] \]

\[ G'(\omega) = \frac{\sigma_0}{\gamma_0} \cos \delta \]

\[ G''(\omega) = \frac{\sigma_0}{\gamma_0} \sin \delta \]

\[ \sigma(t) = \gamma_0 \left[ G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t) \right] \]
Physical meaning of the oscillatory viscoelastic functions

G’ is proportional to the elastic energy stored during a cycle:

\[ E = \int_{0}^{T} \gamma \sigma \, dt = \frac{\gamma_{0}^{2}}{2} G' \]

G” proportional to the energy dissipated during a cycle:

\[ E = \int_{0}^{T} \gamma \sigma \, dt = \pi \gamma_{0}^{2} G'' \]

The loss tangent is an indicator bearing information on which contribution prevails, in the rheological response: elastic (\( \tan \delta < 1 \)) or viscous (\( \tan \delta > 1 \))

\[ \tan \delta = \frac{G''}{G'} \]
A workflow to obtain oscillatory viscoelastic functions

**the experimentalist:**
- material
- geometry
- sample preparation
- choice setup of the method

**the instrument:**
- impose oscillatory stress or strain
- measure the response
- data elaboration
- viscoelastic functions
We need to do rheometry to study rheology!
The crucial step: cross correlation algorithm

Suppose the rheometer imposes a sinusoidal strain (deflection angle): 

\[ \theta(t) = \theta_0 \sin(\omega t + \varphi) \]

The output signal will be a torque \( M(t) \) out of phase (phase angle difference \( \varphi \)): 

\[ M(t) = M_0 \sin(\omega t + \varphi) + \text{noise} \]

After filtering the signal to avoid noise it will be digitalized (2048 points/cycle): 

\[ M(t) = M_0 \sin(\omega t + \varphi) \]
The crucial step: cross correlation algorithm

The rheometer calculates the cross correlation coefficient between the output function and the reference one evaluating the following integral:

$$\int_0^{2N\pi/\omega} M_0 \sin(\omega t + \delta) \varrho_0 \sin(\omega t) \, dt = \frac{N\pi}{\omega} M_0 \varrho_0 \cos \delta$$

And the cross correlation coefficient between the output function and that 90° out of phase with respect to the reference one evaluating the following integral:

$$\int_0^{2N\pi/\omega} M_0 \sin(\omega t + \delta) \varrho_0 \cos(\omega t) \, dt = \frac{N\pi}{\omega} M_0 \varrho_0 \sin \delta$$

From the ratio between the values of the two integrals we obtain $\tan \delta$ and the value of $M_0$. 

Maxwell model in oscillatory regime

\[ G' = \frac{G\omega^2\tau}{1 + \omega^2\tau^2} \]
\[ G'' = \frac{G\omega}{1 + \omega^2\tau^2} \]
\[ \tan \delta = \frac{1}{\omega\tau} \]

Modello di Maxwell (\( \tau = 1 \text{ s} \))

at low \( \omega \):
\[ G' \sim \omega^2 \]
\[ G'' \sim \omega \]
Isochronal temperature sweep (τ will change)

Polystyrene

\[ M_w = 170,000 \]

- **G'**
- **G''**

Elastic

Viscous

Segmental relaxation (\( T_g \))

High De

Low De

Reptation

Moduli (Pa)

T (°C)

50 75 100 125 150 175 200 225 250

10^4 10^5 10^6 10^7 10^8 10^9 10^10
High Impact Polystyrene

TEM micrograph for a HIPS copolymer
Isochronal temperature sweep: a tool for comparisons and quantitative analysis

High Impact Polystyrene Moduli (Pa)

- $G'$ (5% PB)
- $G'$ (50% PB)
- $G''$ (5% PB)
- $G''$ (50% PB)
Thermoplastic elastomers: structure

- Diblock copolymers
- Triblock copolymers
- Trichain copolymers
- Tetrachain copolymers
Some common thermoplastic elastomers

- **Styrene Isoprene**
  - PS
  - PI
  - SI

- **Styrene Butadiene**
  - PS
  - PB
  - SB

- **Styrene Isoprene Styrene**
  - PS
  - PI
  - SIS

- **Styrene Butadiene Styrene**
  - PS
  - PB
  - PS
  - SBS

- **Styrene Ethylene-co-Butylene Styrene**
  - PS
  - EB
  - SEBS
Thermoplastic elastomers: applications

- automotive
- personal care
- sports and toys
Isochronal temperature sweep:

tool to detect morphological transitions

SIS copolymer (styrene-isoprene-styrene)

Moduli (Pa)

Loss tangent

T (°C)

G'

G''

tanδ

T_{OOG}

T_{ODT}

PS  PI  PS

10^3  10^4  10^5  10^6
Isochronal temperature sweep: \( T_g, ODT \) and crosslinking of a tetrachain SBS copolymer (S=38%, B=62%)
Isochronal temperature sweep: $T_g$ and ODT of linear SEBS copolymers

Increasing $M_w$

PS  EB  PS

crankshaft of -(CH$_2$)$_n$- units

$T_g$ of PS

$T_g$ of EB

OOT

$M_w=62K$

$M_w=80K$

$M_w=213K$
Acrylonitrile-butadiene-styrene copolymers

TEM micrograph for an ABS copolymer
Isothermal and isochronal strain sweep ($\gamma_0$ is allowed to change): linear viscoelastic region of SAN and ABS copolymer melts

The linear viscoelastic region for melts is wide and its amplitude depends on structural parameters!
Isothermal and isochronal strain sweep ($\gamma_0$ is allowed to change): the linear viscoelastic region of HIPS in the solid state.
Isothermal frequency sweep ($\omega$ is allowed to change)

Polystyrene
$M_w = 170.000$

G' (Pa)

$\omega$ (rad/s)

Low De

high De

T=160°C
T=170°C
T=180°C
T=190°C
T=200°C
T=210°C
T=220°C
T=230°C
T=240°C
T=250°C
T=260°C
Time-temperature superposition principle (TTS)

If the material exhibits several relaxation times at $T_0$:

$$\tau_i(T_0) \quad i = 1, \ldots, n$$

which are all multiplied at a new $T$ by the same shift factor $a_T$:

$$\tau_i(T) = \tau_i(T_0) \cdot a_T \quad i = 1, \ldots, n$$

The curves perfectly overlap when shifted along the frequency axis to form a MASTER CURVE.

Polystyrene
$M_w = 170,000$

- $T = 160°C$
- $T = 170°C$
- $T = 180°C$
- $T = 190°C$
- $T = 200°C$
- $T = 210°C$
- $T = 220°C$
- $T = 230°C$
- $T = 240°C$
- $T = 250°C$
- $T = 260°C$
Williams-Landel-Ferry (WLF) equation

\[
\log a_T = - \frac{C_{1,0}(T - T_0)}{C_{2,0} + (T - T_0)}
\]

Polystyrene
\[ M_w = 170,000 \]
To describe real cases more than one relaxation time has to be taken into account!

Polystyrene
$M_w = 170,000$

- $\omega a_T$ (rad/s)
- $\log G'$ (Pa)

- slope=2
- experimental data
- single relaxation time
- 5 relaxation times
But nowadays we are able to predict LVE of linear polymers!
Tan δ is not affected by geometry uncertainties:

it is suited to highlight “fine details”

D. Ferri, L. Castellani, Macromolecules, 34, 3973-3981 (2001)
Frequency sweep; a tool to estimate the molecular weight between entanglements

\[ G_0 = \frac{\rho RT}{M_c} \]
Master curves to determine the molecular weight between entanglements of polystyrene

\[ M_e = 18350 \text{ g/mol} \]

Master curves to determine the molecular weight between entanglements of polyisoprene

\[ T_{\text{red}} = 60^\circ \text{C} \]

\[ 0.384 \text{ MPa} \]

\[ G', G'' \]

\[ \tan \delta \]

Monodisperse polyisoprene

\[ M_w = 148000 \]

\[ M_e = 6350 \text{ g/mol} \]

Low frequency moduli for LLDPE/LDPE blends

The positive deviation is a signature of immiscibility!

\[ \log(G') = \sum \phi_i \log(G_i') \]

\[ \log(G'') = \sum \phi_i \log(G_i'') \]

T = 190°C
\( \omega = 0.1 \text{ rad/s} \)

0 10 20 30 40 50 60 70 80 90 100

0 500 1000 1500 2000

Moduli (Pa)

LDPE %
Isothermal frequency sweep test:
PP/carbon nanofibers composites (L \sim 100 \mu m, d \sim 100 \text{nm})

\[ \begin{align*}
G' (\text{Pa}) \quad & \quad T=210^\circ C \\
\log_{10} \omega (\text{rad/s}) \quad & \quad \log_{10} G' (\text{Pa})
\end{align*} \]
Isothermal and isochronal time sweep test: PE rigidization

\[ \dot{G}_{\text{normalized}} (\text{Pa}) \]

\[ \text{time (min)} \]

\[ \rho = 0.92 \pm 0.03 \text{ g/cm}^3 \]
Complex numbers notation

\[ z^* = \rho e^{i\vartheta} = \rho (\cos \vartheta + i \sin \vartheta) \]

if

\[ \gamma^* = \gamma_0 e^{i\omega t} \]

then

\[ \sigma^* = \sigma_0 e^{i(\omega t + \delta)} \]

we can define a “complex modulus”:

\[ G^*(\omega) \equiv G'(\omega) + i G''(\omega) \]

and write:

\[ \sigma^* = G^* \gamma^* \]

a “complex viscosity” can be defined:

\[ \eta^*(\omega) \equiv \frac{G^*(\omega)}{\omega} \]
The Cox-Merz rule

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

Polystyrene
\[ M_w = 170,000 \]

We can use data from an oscillatory experiment to predict non linear properties!

Viscosity (Pa·s)

- 10^4
- 10^3
- 10^2
- 10^1

\[ \omega a_T \text{ (rad/s) or shear rate}^{-1} \text{/s} \]

- time domain (cone-plate)
- time domain (capillary rheometer)
- master curve in oscillatory regime (parallel plates)

Some suggestions and problems!

Isochronal temperature sweeps:
ensure the linearity with respect to the relaxation at study
choose dT/dt for a certain $\omega$ to allow thermal pseudo-equilibrium

Isothermal frequency sweeps:
ensure the linearity with respect to the different $\omega$ values
decide if the sweep has to begin at low or high frequencies
allow the sample to equilibrante
pay attention to flow instabilities: edge fracture
pay attention to inertia effects due to the geometry
pay attention to inertia effects due to the transducers
Large Amplitude Oscillatory Shear (LAOS)

Allows changes of $\omega$ and $\gamma_0$ independently!

In the linear viscoelastic regime the Boltzmann superposition principle holds:

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t') dt'$$

which allows the moduli to be calculated:

$$G'(\omega) = \omega \int_{0}^{\infty} G(s) \text{sen}(\omega s) ds$$
$$G''(\omega) = \omega \int_{0}^{\infty} G(s) \cos(\omega s) ds$$

In the case of large strain amplitudes ($\gamma_0 >> 1$):

$$\sigma(t) = \sum_{n=\text{odds}} \sigma_n \text{sen}(n\omega t + \delta_n)$$
$$\sigma_n = \sigma_n(\omega, \gamma_0)$$
$$\delta_n = \delta_n(\omega, \gamma_0)$$
Non linearity is evident only at high strain values!
Lissajous plot

Experimental warnings: fluid inertia, viscous heating, wall slip

PS $M_w = 180$ KDa

stress (Pa) vs strain (%) diagram
LAOS and MAOS of Polystyrene

It is particularly useful to test the validity of constitutive models!
Non linear behavior is the rule in polymer processing industry!

But we cannot escape the reality that most real world phenomena are highly non linear.

The division of viscoelastic behavior into two categories, linear and non-linear, suggests that non-linear behavior is somehow exceptional, but this point of view does not reflect reality.

The late mathematician Stanislav Ulam noted that this is like classifying all animals that are not elephants as “nonelephants”.

`non-linearity`
References


