Practical Linear Viscoelastic Models by Control Theory

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Contents

- Introduction: Short history and development branches of Control Theory
- Linear models for relaxation modulus $G(t)$, complex $\eta^*(\omega)$, shear viscosity $\eta(\dot{\gamma})$ and transition effects related to the MWD.
- Explanation to the Cox-Merz rules and Power Laws.
- Characterization of polymers in macro and micro sales.
- Molecular dynamics during high shear and relaxed state.
- Temperature dependence modelled using control theory

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Authors and References

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[1]T. Borg, E. J. Pääkkönen, Linear viscoelastic models: Part I. Relaxation modulus and melt calibration, J. Non-Newtonian Fluid Mech. 156 (2009) 121–128.

[2]T. Borg, E. J. Pääkkönen, Linear viscoelastic models: Part II. Recovery of the molecular weight distribution using viscosity data, J. Non-Newtonian Fluid Mech. 156 (2009) 129–138.

[3]T. Borg, E. J. Pääkkönen, Linear viscoelastic models: Part III. Start-up and transient flow effects from the molecular weight distribution, J. Non-Newtonian Fluid Mech. 159 (2009) 17–25.

[4]T. Borg, E. J. Pääkkönen, Linear viscoelastic models: Part IV. From molecular dynamics to temperature and viscoelastic relations using control theory, J. Non-Newtonian Fluid Mech. 165 (2010) 24-31.

[5]T. Borg, E. J. Pääkkönen, Linear viscoelastic models Part V. Elongation viscosity and chain branches, to be submitted to J. Non-Newtonian Fluid Mech.

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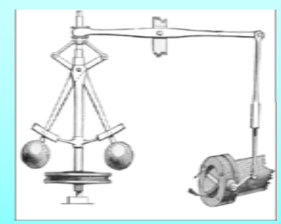
Control Theory; A Brief History

Some of the earliest control included before 1900:

- Time keeping with ancient water clocks
- Clocks with a conical pendulum
- Centrifugal governor of steam engines
- Windmills: facing sails into the wind

➔No theory for feedback. Control was empirical.



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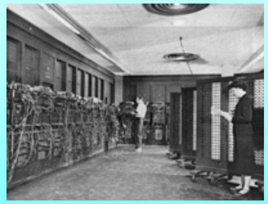
Classical Control

Covers approximately 1900-1955

– Applications drivers
– Electronics and telecommunications networks
– Defence
– General increasing industrialisation
– The Second World War
– Fluid dynamics



ENIAC computer

Most problems involved linear, single-input, single-output, time-invariant, finite-dimensional systems

➔Mathematical understanding

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Modern Control

The second wave (1960-)

– Demanding applications: Space, process industry
– New components: digital computers
– Aircrafts

Feedback plays a major role in the Internet and in cellular communication.

Also Complexity Management and Model Reduction

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Linear Time Invariant Systems (LTI)

$$\frac{d^n y}{dt^n} + \frac{d^{n-1} y}{dt^{n-1}} + \cdots + a_n y = \frac{d^{n-1} u}{dt^{n-1}} + \cdots + b_n u$$

Has the solution

$$y(t) = \sum_{k=1}^{n} C_{k-1}(t) e^{a_k t} + \int_0^t g(t-\tau) u(\tau) d\tau$$

➔LTI Systems can be manipulated by Laplace and similar transforms and further expansions …….

We will concentrate on **Linear Viscoelastic Models by Control Theory,** a branch of LTI Systems

Strategy: First accurate model on macroscale by ***molecular*** and ***control*** theories, then more nanoscale studies.

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Starting from Molecular Theories

Independent chain response (elastic dumbbell, Rouse, Zimm) or pseudo-independent chain response (unmodified Doi-Edwards) can be used for predicting of molecular weight distribution according to Graessley[1]

$$G(t) = \sum w_i \, G_i(t)$$

Relaxation modulus functional[2] by *rheologically effective distribution* RED *w*(log *t*)⟵➔ w(log *M*)

$$G(t) = \sum w_i(t) G_i(t)$$

$G_i(t)=P' G_0 h(t_i)$ ➔ $$G(t) = G_0 \, P' \int_{-\infty}^{t} w(\tau) h(t-\tau) d\tau$$

[1]Graessley W. W., Polymetric Liquids and Networks: Dynamics and Rheology. (Garland Science, London, 2008).
[2]Anderssen R. S. and Loy R. J., "On the scaling of molecular weight distribution functionals", J. Rheol. 45, (2001) 891-901.

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Analytical Model by Control Theory

$$y(t) = \int_{-\infty}^{t} w(\tau)h(t-\tau)d\tau \qquad \text{(convolution of } w*h\text{)}$$

As *system input* MWD is normally *w*(log *M*), here *w*(log *t*)

➔*Pulse response* y(*t*) and *impulse response h*(*t*) are in log form

$$\log\frac{G(t)}{G_0} = -P'\int_{-\infty}^{\log t} w(\log\tau)(\log t - \log\tau)d\log\tau$$

the logarithmic or scale convolution with the *rheologically effective distribution* RED *w'*(log *t*)=*w*(log *M*) and $\log t - \log\tau = \log\frac{t}{\tau}$

➔Relation solely between MWD and G(*t*).

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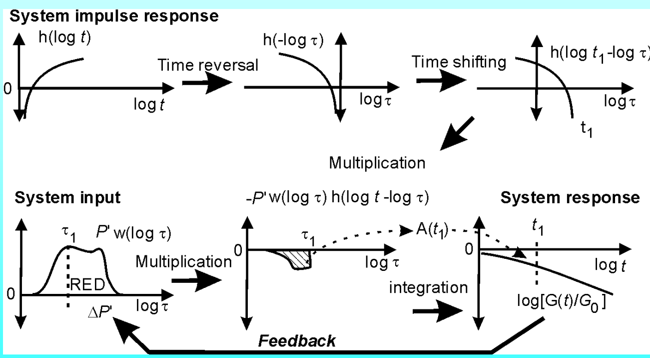
Control System and Polymer Melt



For normalized relaxation function log [$G(t)/G_0$]

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Comparison of the Principles

Maxwell model, where $g(t)=G(t)/G_0$

$$g(t) = \int_0^{\infty} F(\tau)\, e^{-\frac{t}{\tau}}\, d\tau \qquad ;F(\tau) \text{ is spectrum function}$$

Mixing rule

$$g(t) = \int_{M_e}^{\infty} w(M)\, k(t,M)\, dM$$

;*k*(*t*,*M*) is kernel
w(*M*) is MWD

Control theory

$$g(t) = \int_{-\infty}^{t} w(\tau)\, h(t-\tau)\, d\tau$$

; system input *w'*(*t*) = *w*(*M*) by melt calibration,
h(*t*) is impulse response

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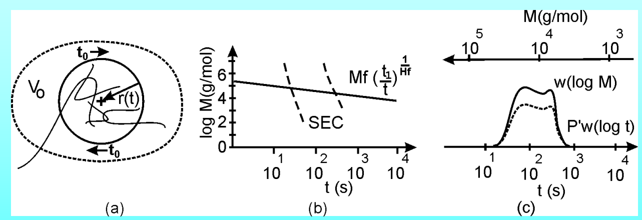
Melt Calibration Sets Relations

Between time t, frequency ω and molecular weight M scales

Similarities with Universal Calibration used with SEC/GPC



$$dM = Mf\,\frac{4}{3}\pi\frac{dr^3}{V_0} \qquad Hf\frac{dM}{dt} + \frac{M}{t} = 0 \qquad M = Mf\left(\frac{t}{t_1}\right)^{-\frac{1}{Hf}}$$

Mf Structural factor; Hf Conversion factor (~4.19)

RED←→MWD w(t)←→w(M)

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Model for Shear Viscosity $\eta(\dot\gamma)$

Characteristic Model

$$\log\frac{\eta(\dot\gamma)}{\eta_0} = -\log\frac{\dot\gamma}{\dot\gamma_c}\int_{-\infty}^{\log\dot\gamma}\left(P' w(\log\psi) + P'' w(\log\frac{\psi}{R})\right) d\log\psi$$

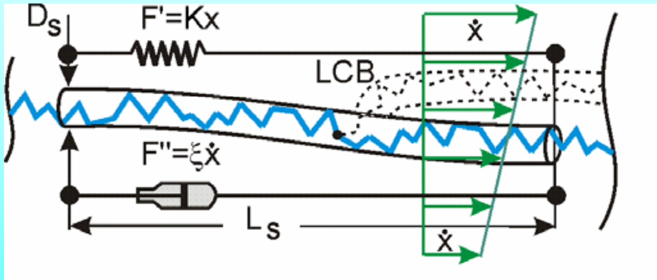
No visible differences in results compared to the *analytical model*

Melt calibration

Mf Structural factor; ***Hf*** Conversion factor (~4.19)

$$M = Mf\left(\frac{\dot\gamma_1}{\dot\gamma}\right)^{\frac{1}{Hf}}$$

Relations to Molecular Dynamics



Dimensions of an oriented unit segment in a tube related to Elasticity P' and Viscosity P'' values as shown later.

Complex Viscosity: All Formulas

Analytical: $$\log\frac{\eta^*(\omega)}{\eta^*_0} = -\int_{\log\omega/T}^{\log\omega}\left(P' w(\log\psi) + P'' w(\log\frac{\psi}{R})\right)\log\frac{\omega}{\psi}\, d\log\psi$$

Melt Calibration: $$M = Mf\left(\frac{\omega_1}{\omega}\right)^{\frac{1}{Hf}}$$

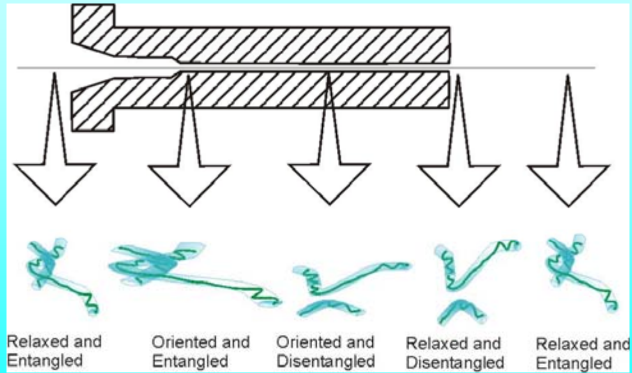
Characteristic: $$\log\frac{\eta_c^*(\omega)}{\eta^*_0} = -\log\frac{\omega}{\omega_c}\int_{-\infty}^{\log\omega}\left(P' w(\log\psi) + P'' w(\log\frac{\psi}{R})\right) d\log\psi$$

Differentiation: $$w_c(\log\omega) = -\frac{d}{d\log\omega}\frac{1}{P'}\left(\frac{\ln\frac{\eta^*}{\eta^*_0}}{\ln\frac{\omega}{\omega_c}} + P''\int_{-\infty}^{\log\omega} w(\log\frac{\psi}{R})\, d\log\psi\right)$$

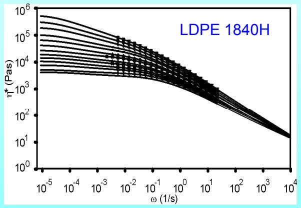
Similar sets for other viscoelastic properties

Molecular Model during Capillary Flow

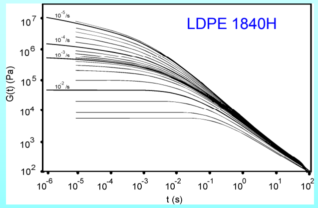
In every steady shear rate polymer has own orientation and entangling state, which defines viscoelastic properties.



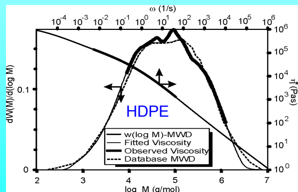
Viscoelasticity and MWD



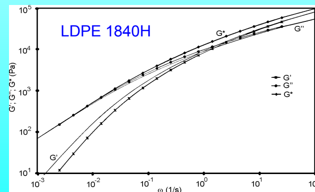
Measured and modelled complex viscosity



Relaxation modulus at different oriented states



MWD from viscosity and GPC results



Measured and computed dynamic moduli

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Revised Boltzmann

Revised Boltzmann superposition principle for **shear viscosity** and **molecular orientation**: the total effect of applying several shear deformations and changes in molecular orientations is simply the sum of their individual effects. ➔From $\eta(t,\dot{\gamma})$ we get

$$\eta(t) = \hat{\eta} + \sum_{i=1}^{N} (1 - g(t - t_i))^D \; \delta\,\eta(t_i)$$

For continuous changes in viscosity and orientation, this sum is generalized to an integral as follows:

$$\eta(t) = \hat{\eta} + \int_{-\infty}^{t} (1 - g(t - \tau))^D \, \frac{d\eta(\tau)}{d\tau} \, d\tau$$

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Power law and orientation level

Polymer structure function $P(\dot{\gamma})$

$$P(\dot{\gamma}) = \int_{-\infty}^{\log\dot{\gamma}} \left(P' w(\log\dot{\gamma}) + P'' w(\log\frac{\dot{\gamma}}{R}) \right) d\log\dot{\gamma}$$

And characteristic model solved for viscosity

$$\eta(\dot{\gamma}) = \eta_0 e^{-P(\dot{\gamma})\log\frac{\dot{\gamma}}{\dot{\gamma}_c}}$$

After algebraic simple conversions if $\dot{\gamma}_c$ = 1/s

$$\eta = \eta_0 \left|\dot{\gamma}\right|^{-P(\dot{\gamma})}$$

In power law P=1-n

➔P is important in flow simulations

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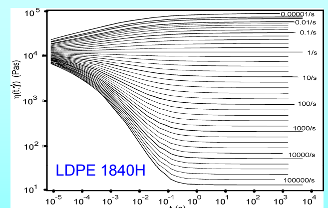
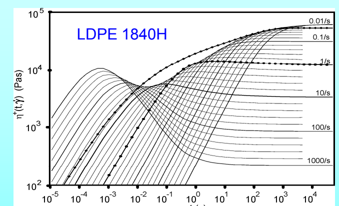
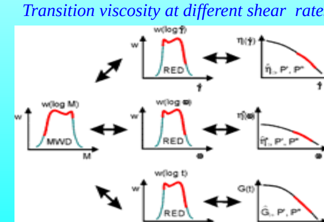
Transition Effects and Power Law



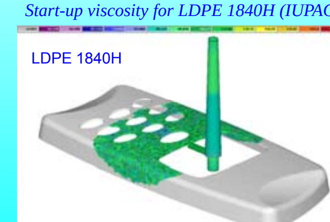
Transition viscosity at different shear rates



Start-up viscosity for LDPE 1840H (IUPAC)



Cox-Merz rule from rigid platform, MWD



Orientation simulation for cellular cover

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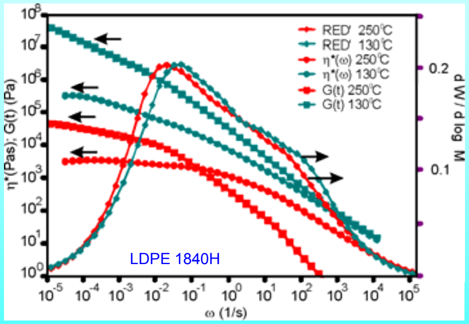
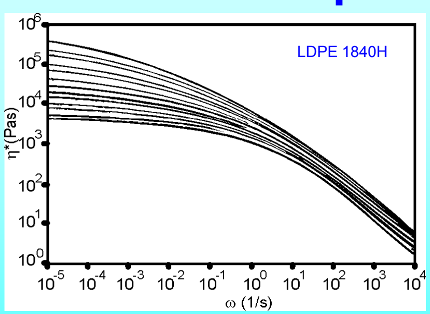
TTS Puzzle: Computed MWD (and RED) are not temperature sensitive



The above puzzle conflicts with many previous studies on rheology and time–temperature superposition.

At Different Temperatures

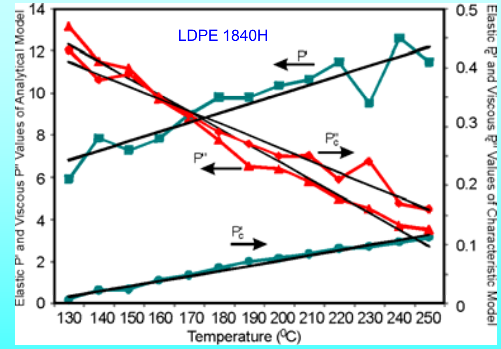


Complex viscosity by analytical model at different temperatures.

$$\log\frac{\eta^*(\omega)}{\eta^*_0} = -\int_{\log\omega/T}^{\log\omega}\left(P' w'(\log\psi) + P'' w''(\log\frac{\psi}{R})\right)\log\frac{\omega}{\psi}\, d\log\psi$$

➔New molecular model by P' and P''

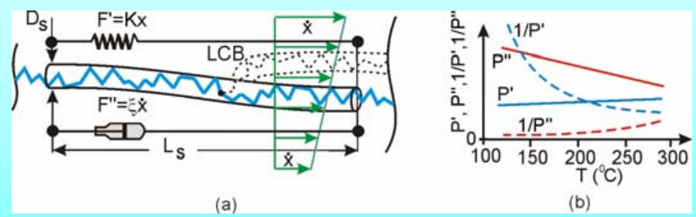
Elasticity P' and Viscosity P'' values



Characteristic model for complex viscosity with P'_c and P''_c:

$$\log\frac{\eta_c^*(\omega)}{\eta^*_0} = -\log\frac{\omega}{\omega_c}\int_{-\infty}^{\log\omega}\left(P'_c w'(\log\psi) + P''_c w''(\log\frac{\psi}{R})\right) d\log\psi$$

Relations to Molecular Dynamics



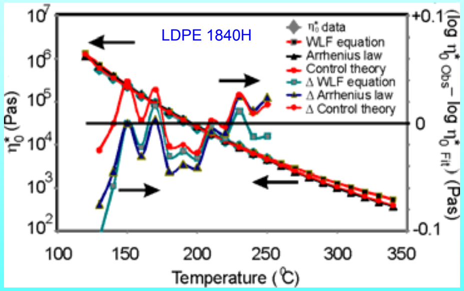
Dimensions of an oriented unit segment in a tube and graph of P' and P'' values at different temperatures.

$$P' = k'\frac{D_s}{L_s} + a'_T(T - T_0)$$

$$P'' = k''\frac{D_s}{L_s} + a''_T(T - T_0)$$

$$\eta^*_{R} = \frac{L_s^2 \xi \rho N_A}{36 M_0}$$ (Modified Rouse-Bueche)

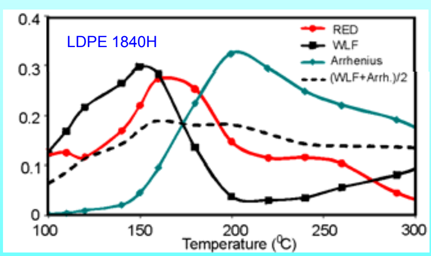
Temperature Dependence Modelled using Control Theory



Elasticity *P*' and viscosity *P*'' values and error obtained by modelling zero viscosity $\eta^*_0(T)$ with a characteristic model:

$$\log\frac{\eta_0^*(T)}{\eta_0^*} = -P^T \int_{-\infty}^{\log T} w(\log\theta)\left(\log\frac{T}{\theta}\right)\mathrm{d}\log\theta$$

RED^{T}s as Functions of Temperatures at Constant Frequency

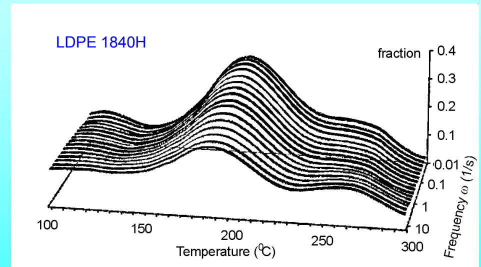


Modelled RED^{T}s for $\eta^*(\omega,T)$ at the frequency ω = 1/s obtained using the characteristic model.

$$w(\log T) = -\frac{\mathrm{d}}{\mathrm{d}\log T}\frac{1}{P_c^T}\frac{\log\frac{\eta_0^*(T)}{\eta_0^*}}{\log\frac{T}{T_c}}$$

At Different Temperatures and Frequencies

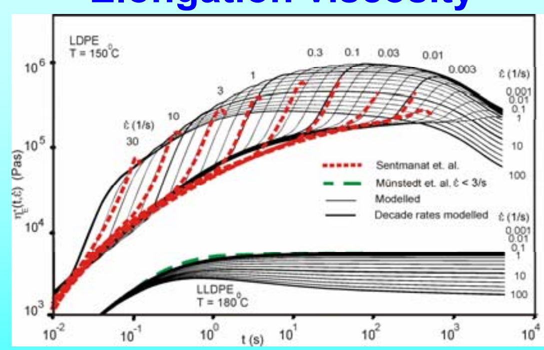
$$\eta*(\omega,T) = \eta_0^* e^{-P(\omega)-P^T(T)}$$



Hyphenated techniques at various temperatures and frequencies by characteristic model:

$$\log\frac{\eta_0^*(T)}{\eta_0^*} = -P_c^T\log\frac{T}{T_c}\int_{-\infty}^{\log T} w(\log\theta)\mathrm{d}\log\theta - P_c^{\prime\prime T}\log\frac{T}{T_c}\int_{-\infty}^{\log T} w(\log\theta/_R)\mathrm{d}\log\theta$$

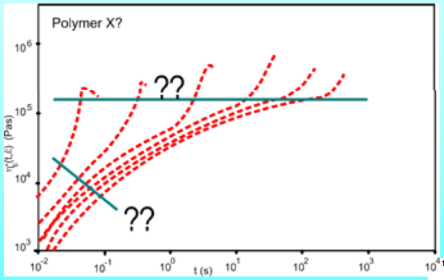
Elongation viscosity[5]

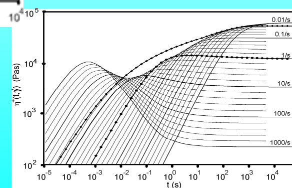


Time-dependent uniaxial elongation viscosity measured and modelled for LDPE and LLDPE.

[5]T. Borg, E. J. Pääkkönen, Linear viscoelastic models Part V. Elongation viscosity and chain branches, to be submitted to J. Non-Newtonian Fluid Mech.

Measured data for Polymer X???

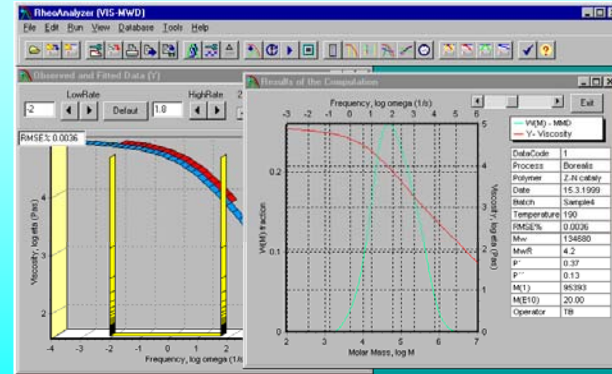




Important for the checking generated model and chain structures.

Windowed Interface

RheoPower programs have several windows, wizards and helps, visit at: **www.tomcoat.com**



Summarized

Control theory is applied to model the relationship between the relaxation modulus, dynamic and shear viscosity, transient flow effects, power law, Cox-Merz rule, revised Boltzmann, CAD simulations and temperature dependence related to the molecular weight distribution (MWD) and micro-level structures.

Micro-level stochastic processes are converted to the statistical micro-macro scale distributions of elasticity $P'(\omega)$ and viscosity $P''(\omega)$ functions and components in a linear manner.

All above presented forms linear relationship between viscoelastic flows linked by MWD and nanoscale structures.

➔New practical standpoint and tools for science and industry.

Commercial software packages are available

DataPower Server

Thank You