ESTIMATION OF THE FIRST NORMAL STRESS DIFFERENCE (N1) AND CREEP COMPLIANCE(J(t)) OF POLYPROPYLENE (PP) RESINS USING A CONSTITUTIVE EQUATION

RELEVANCE

- The constitutive equation can be used for estimation of N1, J(t) and Je(t) and can save time and money in the characterization of polymers

- The constitutive equation can be substituted into the momentum and energy equations to model a polymer process (examples: injection molding, fiber spinning, blown film, etc.)

What is a Constitutive Equation ?

- The motion and the energy equations used in explaining the flow of polymers require the **stress tensor** to be expressed **as a function of various kinematic tensors** (i.e.: strain tensor, rate of strain tensor, etc.).

- The equation used to express such functionality is called a **constitutive equation**.

Physical and mathematical relations

Force(s) ⟷ Material element ⟷ Deformation(s)

expressed as a Tensor (divided by the appropriate area)

expressed as a Tensor (if interested how, see next slide)

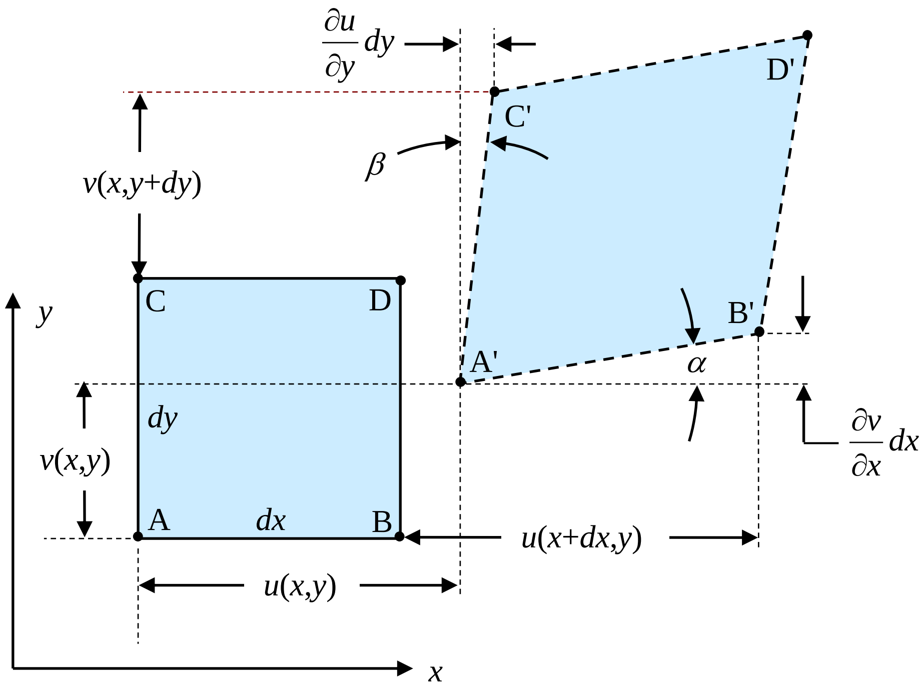
$$\begin{Bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{Bmatrix} \longleftrightarrow \boxed{\begin{array}{c}\text{Material function} \\ \text{or} \\ \text{Rheological equation} \\ \text{of state} \\ \sigma_{ij} = fn\ (\varepsilon_{ij})\end{array}} \longleftrightarrow \begin{Bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{Bmatrix}$$

Examples:

- ✓ Wagner Model
- ✓ Phan Thien Tanner Model

Deformation and Strain

Two-Dimensional Theory



Strain Displacement Relations

$$e_x = \frac{\partial u}{\partial x}$$

$$e_y = \frac{\partial v}{\partial y}$$

$$e_{xy} = \frac{1}{2}\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right) = \frac{1}{2}\gamma_{xy}$$

Three-Dimensional Theory ➡

$$\mathbf{e} = [\mathbf{e}] = \begin{bmatrix} e_x & e_{xy} & e_{xz} \\ e_{yx} & e_y & e_{yz} \\ e_{zx} & e_{zy} & e_z \end{bmatrix}$$

The Wagner Model

Why the Wagner model ?

- ⇨ It uses rheological data easy to obtain
- ⇨ It has been tested with other polyolefins
- ⇨ It is a modification of the Lodge model
- ⇨ Numerical method can be implemented

Model

Lodge Model

$$\sigma = \int_{-\infty}^{t} \mu(t - t', I_1, I_2)\, C_t^{-1}\, dt'$$

Wagner Model

SEPARABILITY OF MEMORY FUNCTION IN:

Time Dependent Memory Function ($\mu_{(t-t')}$)

and

Strain Dependent Damping Function: h(γ (t-t'))

$$\sigma = \int_{-\infty}^{t} \overbrace{\mu(t - t')}^{1}\, \overbrace{h(I_1, I_2)}^{3}\, \overbrace{C_t^{-1}}^{2}\, dt'$$

1. Memory function

Oscillatory data
(extended by TTS)

↓

Relaxation Modulus

↓

Memory Function

$$\mu(t) = a_i \exp(-t/\lambda_i)$$

3. The Finger strain tensor for shear

$$C_t^{-1}(t') = \begin{vmatrix} 1+\gamma^2(t,t') & \gamma(t,t') & 0 \\ \gamma(t,t') & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

where: $\gamma(t,t') = \gamma(t) - \gamma(t')$ is the relative shear strain between any two times t and t'

$I_1 = I_2 = 3 + \gamma^2(t,t')$ and

$I_3 = 1$ (incompressibility assumed)

2. The damping function for shear

$$h\,(I_1, I_2) = h\,(\gamma^2(t,t')) = h\,(|\gamma\,(t,t')|) \leq 1$$

Laun (1978):

$$h(t, t') = f_1 \exp[-n_1 |\gamma\,(t,t')|] + f_2 \exp[-n_2 |\gamma\,(t,t')|]$$

What type of data is needed ?

The model requires:

- ⇨ Oscillatory data in the widest range of frequencies possible. Some high shear rate viscosity data might be needed

- ⇨ Numerical method for the solution of the constitutive equation

What type of data can be obtained ?

The model can be used to estimate:

⇨ Creep compliance

⇨ Recovery compliance

⇨ Stress growth (transient shear viscosity)

⇨ First normal stress difference under shear: at constant shear rate and constant shear stress

⇨ Elongational viscosity (transient and steady state) [experimental data might be needed to adjust the parameters of the model

⇨ The estimation can then be compared to measured data (own and published by other authors)

Stress response to a step shear rate

(the relation of these two gives viscosity)

G(t)

μ(t)

h(γ)

WAGNER MODEL

$$\sigma(t) = \int_0^t \mu(t-t')\, h(t,t')\, \gamma(t,t')\,dt' \; + \; \gamma(t)\, h(t) \int_{-\infty}^0 \mu(t-t')\, dt'$$

Compare to measured steady shear viscosity to obtain damping function

h(γ)

transient state shear viscosity

Shear viscosity as function of a given shear rate ($\dot{\gamma}_o$), time (t), a_i (the i^th elastic value of the Maxwell element), λ_i (the i^th characteristic time of the Maxwell element), n_1 and n_2 (from fitting the shear viscosity curve at steady state)

$$\eta\,(t,\dot{\gamma}_o) = \sum_{i=1}^{8} f_1\ (a_i / \alpha_i^{\,2})\ \{1-\exp[-\alpha_i\, t\,]*[1-n_1\,\lambda_i\,\dot{\gamma}_o\,\alpha_i\, t\,]\,\}$$

$$+$$

$$(1-f_1) \sum_{i=1}^{8} (a_i /\beta_i^{\,2})\ \{1-\exp[-\beta_i\, t\,]*[1-n_2\,\lambda_i\,\dot{\gamma}_o\,\beta_i\, t]\,\}$$

Where

$\alpha_i = (1+ \mathbf{n}_1\,\lambda_i\,\dot{\gamma}_o\,) / \lambda_i\,)$; $\beta_i = (1+ \mathbf{n}_2\,\lambda_i\,\dot{\gamma}_o\,) / \lambda_i\,)$

Fitting steady state viscosity (t $\rightarrow \infty$) curve to get n_1 and n_2

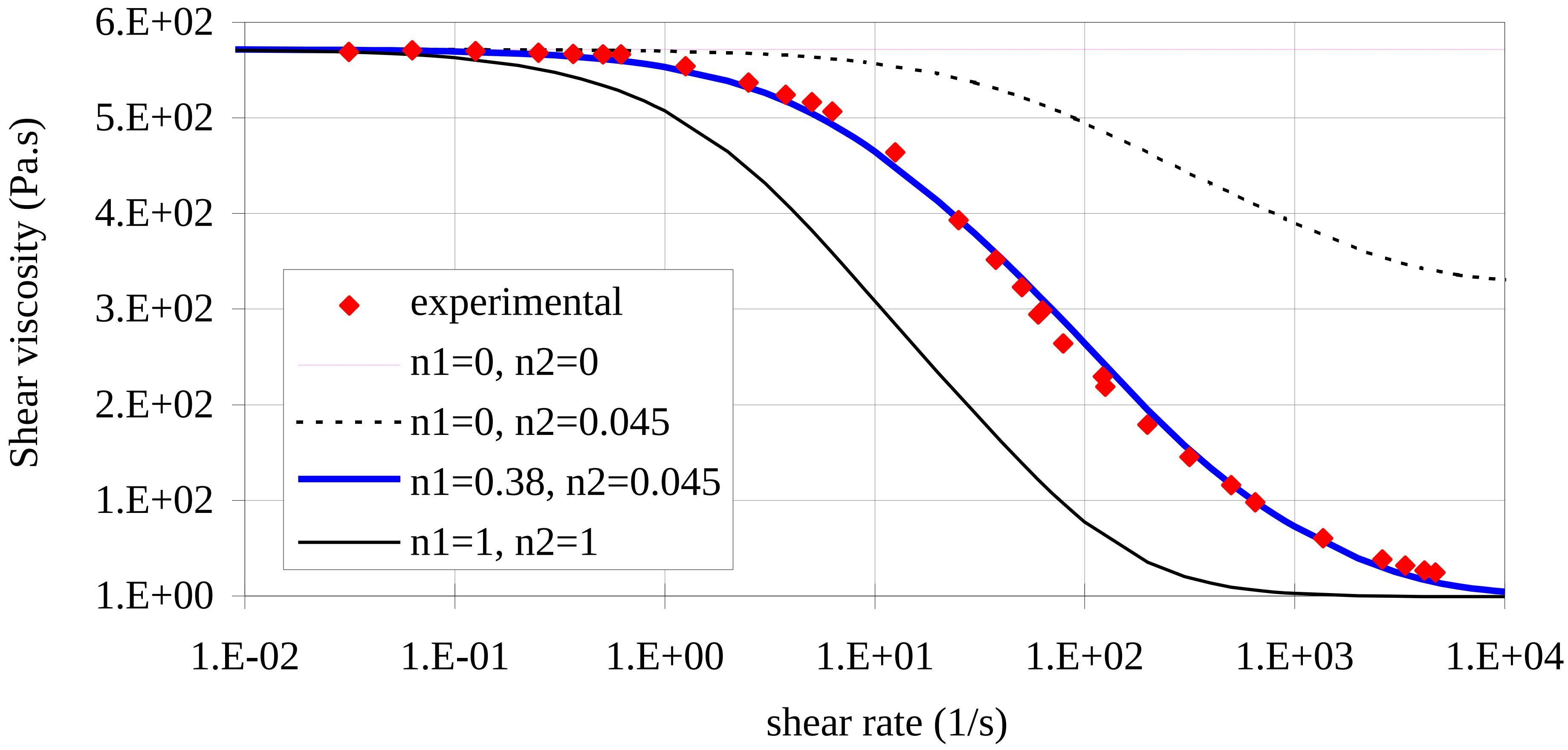
$$\eta\,(t,\dot{\gamma}_o) =$$

$$f_1 \sum_{i=1}^{8} (a_i / \alpha_i^{\,2})\,\{1\} \quad + \quad (1-f_1) \sum_{i=1}^{8} (a_i / \beta_i^{\,2})\,\{1\}$$

Where

$$\alpha_i = (1 + \mathbf{n}_1 \lambda_i \dot{\gamma}_o) / \lambda_i) \; ; \qquad \beta_i = (1 + \mathbf{n}_2 \lambda_i \dot{\gamma}_o) / \lambda_i)$$

Adjustment of n1 and n2 to fit shear viscosity



n1 and n2 values from viscosity fittings

Resins	f_1	n_1	n_2
A_0	0.57	0.22	0.07
A_1	0.57	0.60	0.08
B_0	0.57	1	0.12
B_1	0.57	0.56	0.10

Once we have the n1 y n2 values,

then we can use them to estimate other material functions such as $N1(\gamma)$, $N1(t)$, Je(t); Jr(t), $\eta_e(\varepsilon)$ or $\dot{\eta}_e(t)$

N1 response to a step shear rate

$G(t)$ $\mu(t)$ $h(\gamma)$

WAGNER MODEL

$$\sigma(t) = \int_0^t \mu(t-t')\, h(t, t')\, \gamma(t, t')\,dt' + \gamma(t)\, h(t) \int_{-\infty}^{0} \mu(t-t')\, dt'$$

steady shear

first normal stress difference (N1)

$$N1(t, \dot{\gamma}_o) = \dot{\gamma}_o^{\,2} \left\{ f_1 \sum_{i=1}^{n} a_i \alpha_i^{\,3} + (1-f_1) \sum_{i=1}^{n} a_i \beta_i^{\,3} \right\}$$

transient state shear viscosity

transient state N1

Calculation of N1

$$N1\,(t, \dot{\gamma}_o) = \dot{\gamma}_o^{\,2}\{f_1 \sum_{i=1}^{8} a_i\,\alpha_i^{\,3}\,\{1-\exp[-\alpha_i\,t]*$$

$$[1+\alpha_i\,t-\alpha_{i\,1}^{\;2}\,(\,n_1\,\lambda_i\,\dot{\gamma}_o/\,2\,)\,t^2]\,\}+$$

$$(1-f_1)\sum_{i=1}^{8} a_i\,\beta_i^{\,3}\,\{1-\exp[-\beta_i\,t]*$$

$$[1+\beta_i\,t-\beta_i^{\,2}\,(\,n_2\,\lambda_i\,\dot{\gamma}_o/\,2\,)\,t^2]\,\}$$

Calculation of N1 as t $\rightarrow \infty$

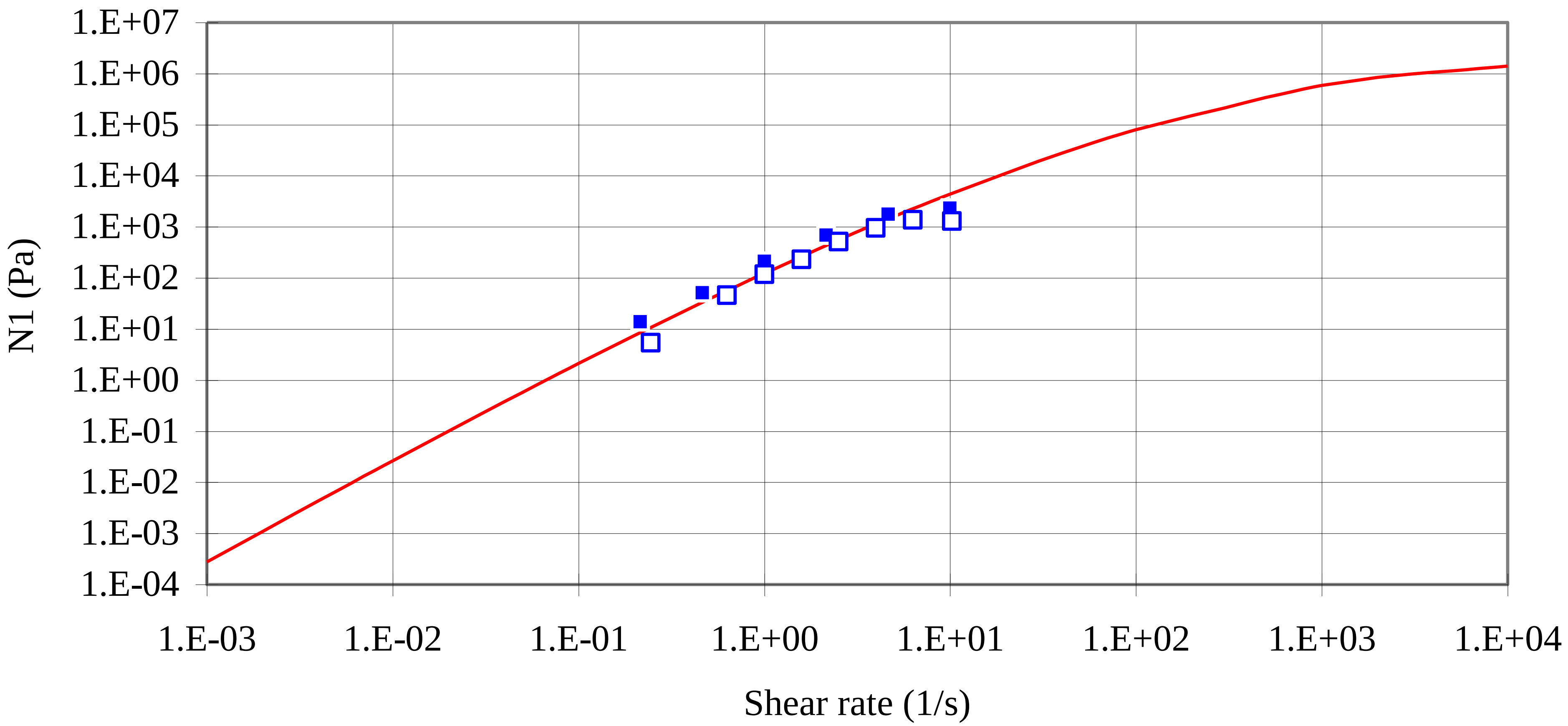
$$N1\,(t, \dot{\gamma}_o) = \dot{\gamma}_o^{\,2} \{ f_1 \sum_{i=1}^{8} a_i \alpha_i^{\,3} \{1\} +$$

$$(1-f_1) \sum_{i=1}^{8} a_i \beta_i^{\,3} \{1\}$$

Where

$\alpha_i = (1 + \mathbf{n}_1 \lambda_i \dot{\gamma}_o) / \lambda_i)$; $\beta_i = (1 + \mathbf{n}_2 \lambda_i \dot{\gamma}_o) / \lambda_i)$

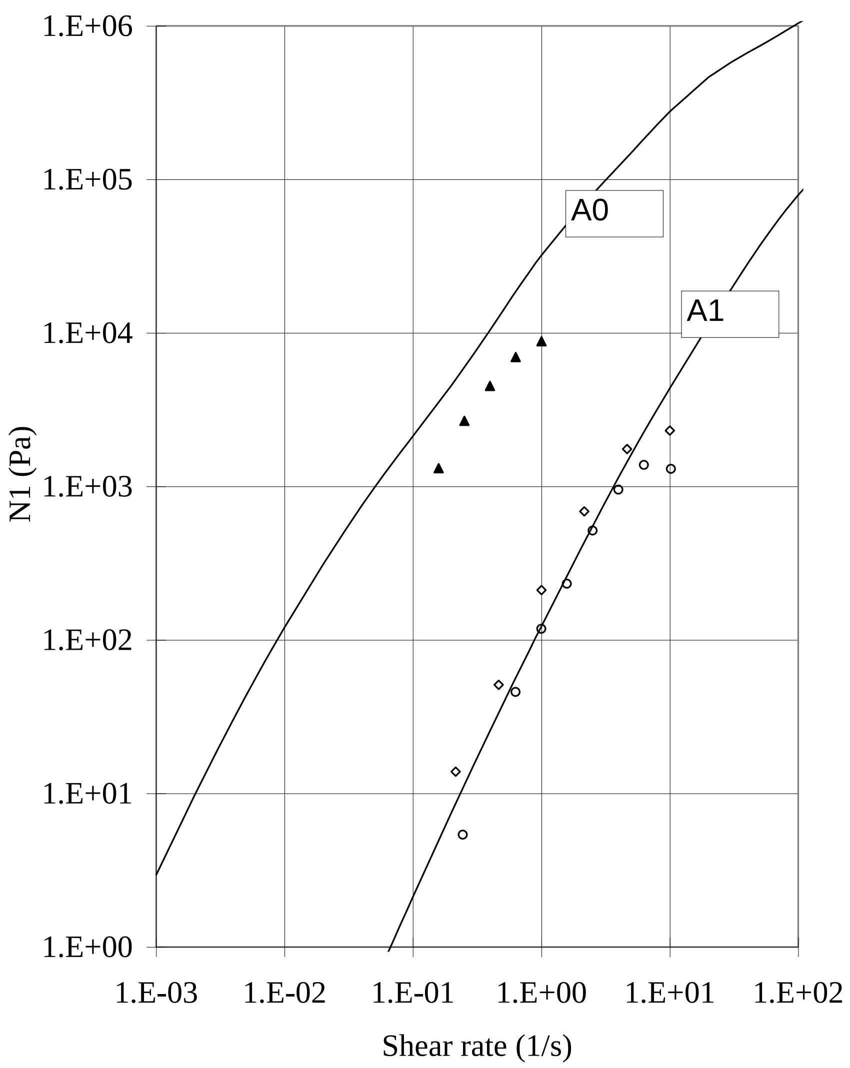
Measured and predicted N1 versus shear rate

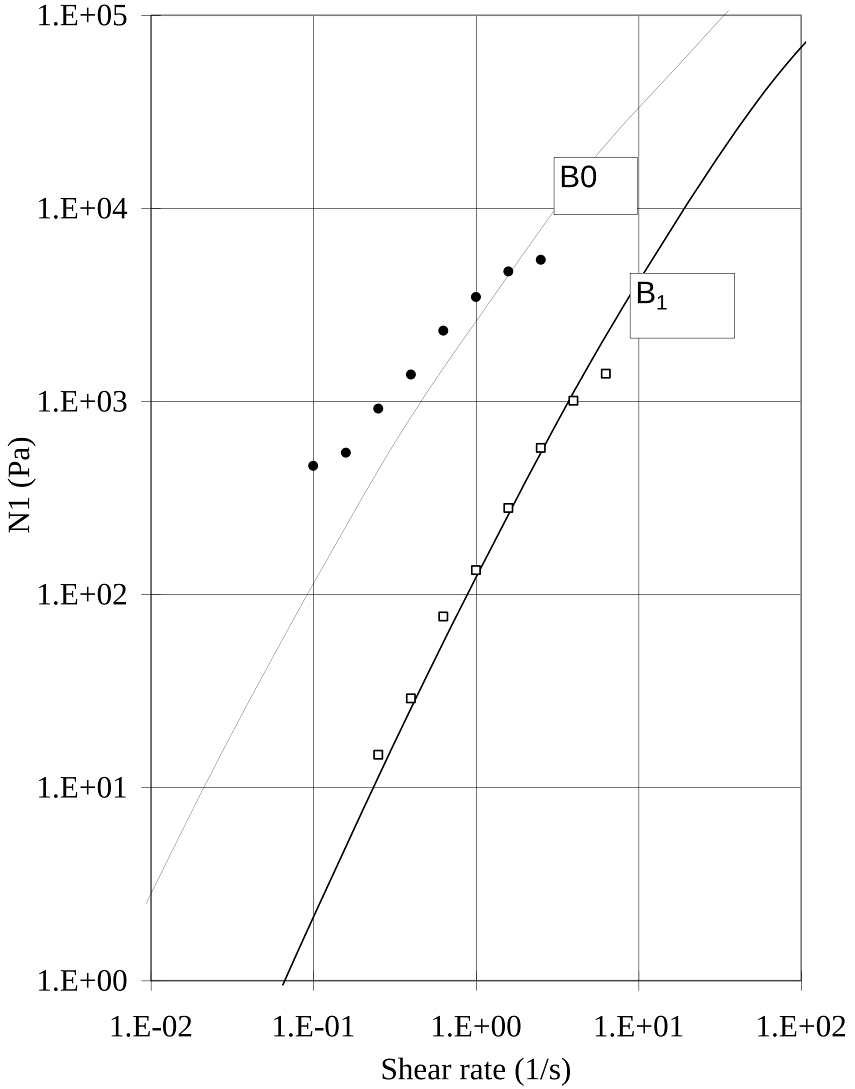


CRPP resin A1

different symbols correspond to independent measurements

Measured and predicted N1





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Strain and N1 response to a step stress

$G(t)$

$\mu(t)$

$h(\gamma)$

WAGNER MODEL

$$\sigma(t) = \int_0^t \mu(t-t')\, h(t, t')\, \gamma(t, t')\,dt' + \gamma(t)\, h(t) \int_{-\infty}^0 \mu(t-t')\, dt'$$

creep strain (γ)

$$\gamma(t) = (\sigma + A_1(t)) / (A_0(t) + h(\gamma(t))\, G(t))$$

compare to experimental data

N1 during creep

$$N_1(t) = \gamma^2(t)\, [A_0(t) + h(t)\, G(t)] - 2\,\gamma(t)\, A_1(t) + A_2(t)$$

recoverable strain (γ_r)

$$\gamma(t_r) = \gamma(t_n) - [A_1(t_r) / (A_0(t_r) + h(\gamma(t_r))\, G(t_r))]$$

compare to experimental data

N1 during recovery

$$N_1(t_r) = \gamma^2(t_r)\, [A_0(t_r) + h(t_r)\, G(t_r)] - 2\,\gamma(t_r)\, A_1(t_r)$$

Calculation of J(t)

$$\gamma(t) = (\ \sigma\ + A_1(t)\ )\ /\ (\ A_0(t) + h(\gamma(t))\ G(t)\ )$$

where:

σ is the stress, $h(\gamma(t))$ is the damping function at time t,

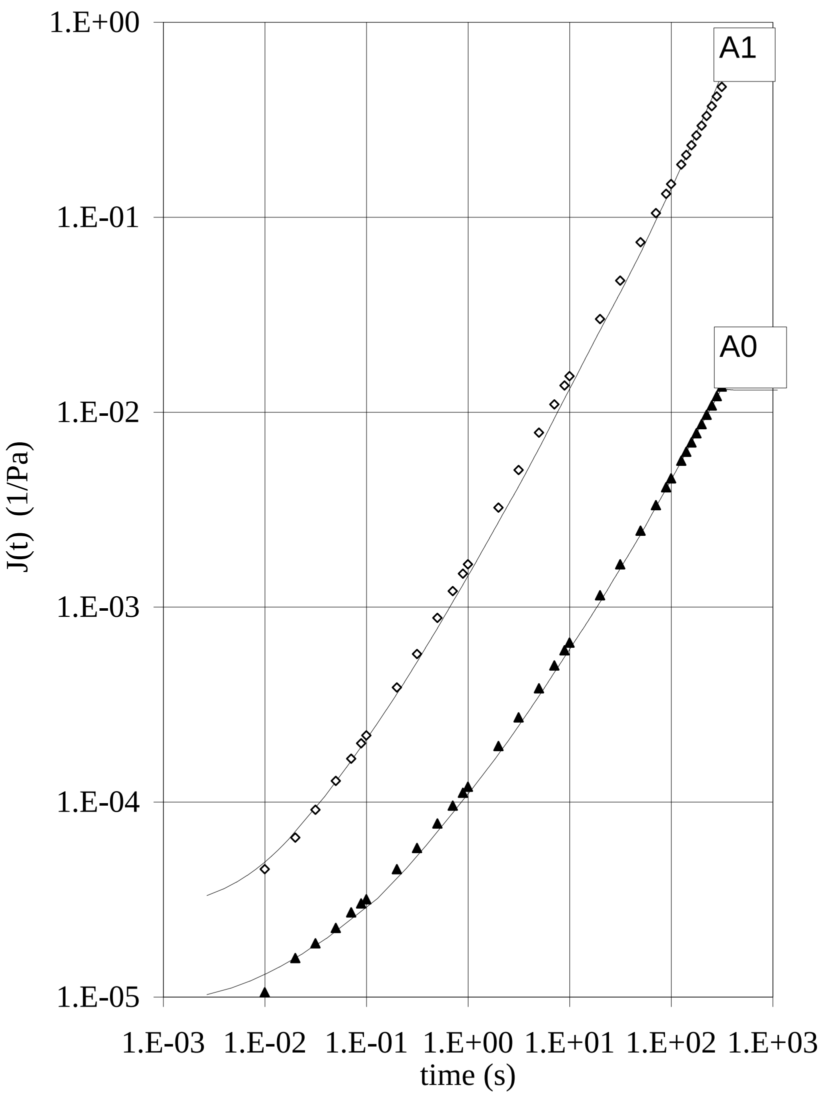
σ $h(t\ ) = f_1 \exp(-n_1|\gamma(t,t')|) + (1-f_1)\exp(-n_2|\gamma(t,t')|)$ and

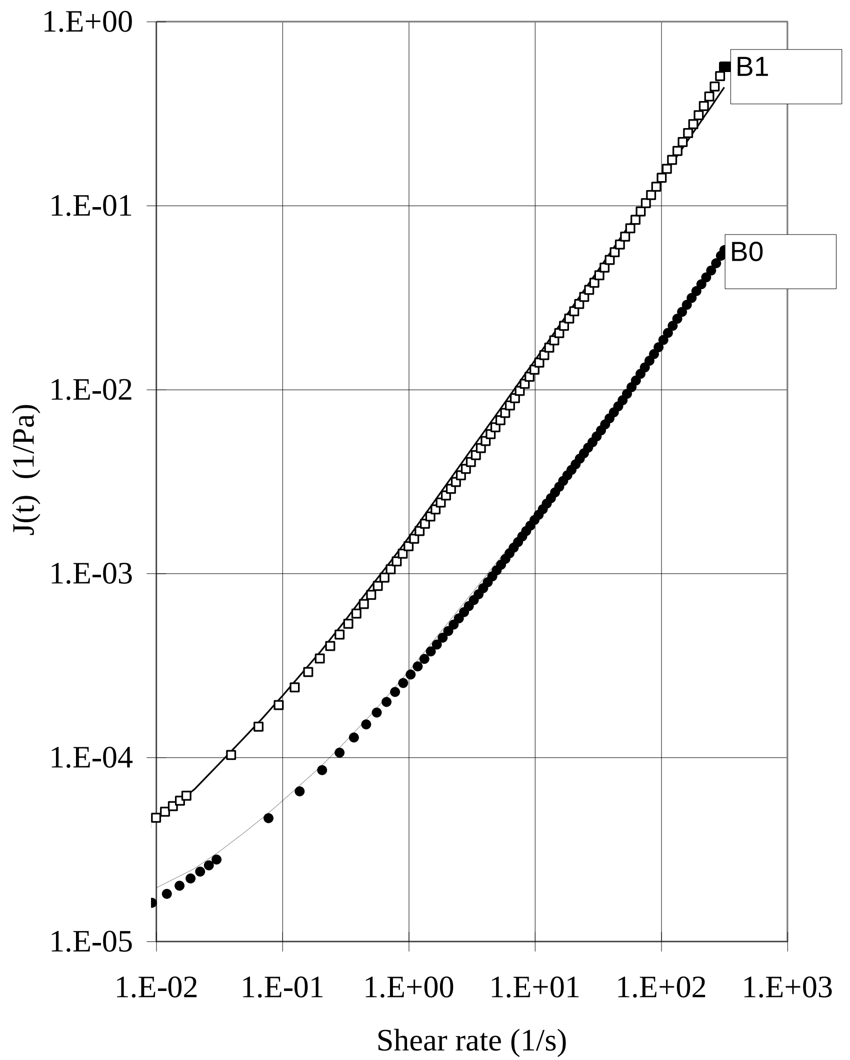
$$A_0(t)\ =\ \ \mu(t-t')\ \gamma(t,t')\ dt'$$

$$A_1(t) =\ \ \mu(t-t')\ \gamma(t,t')h(t,t')\ dt'$$

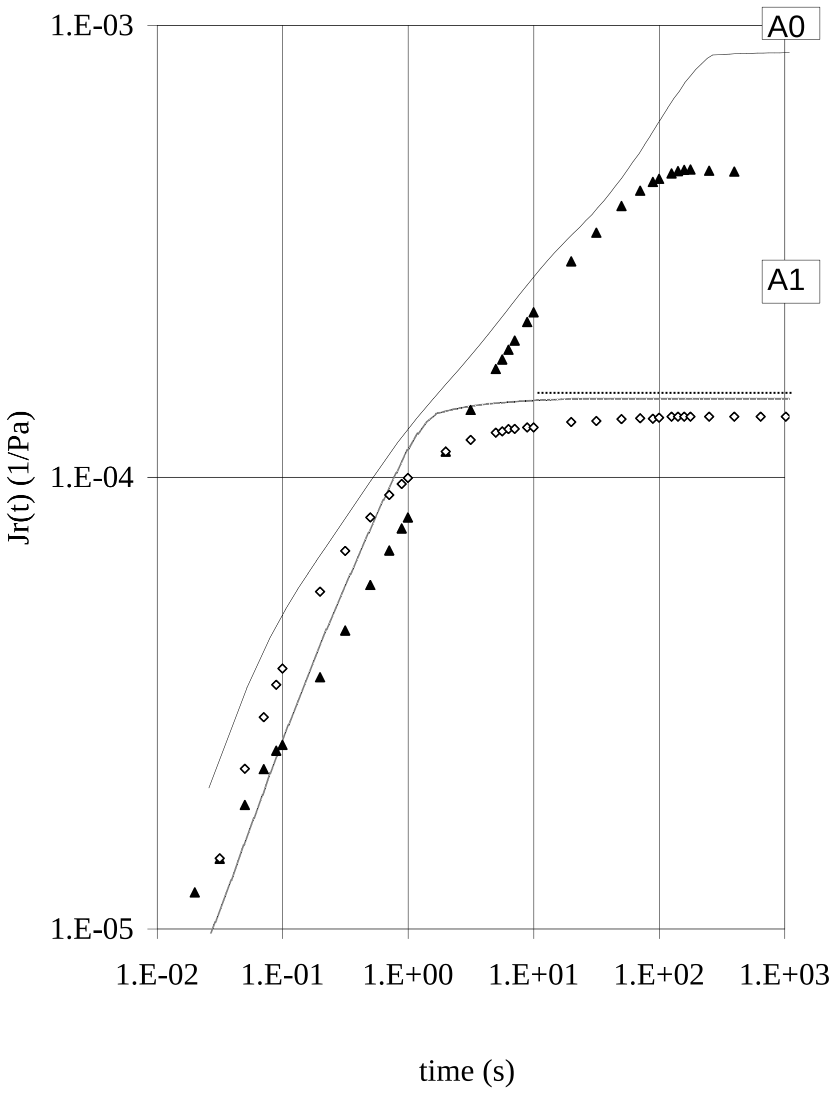
$$\gamma\ (t,t')\ =\ \gamma(t) - \gamma(t')$$

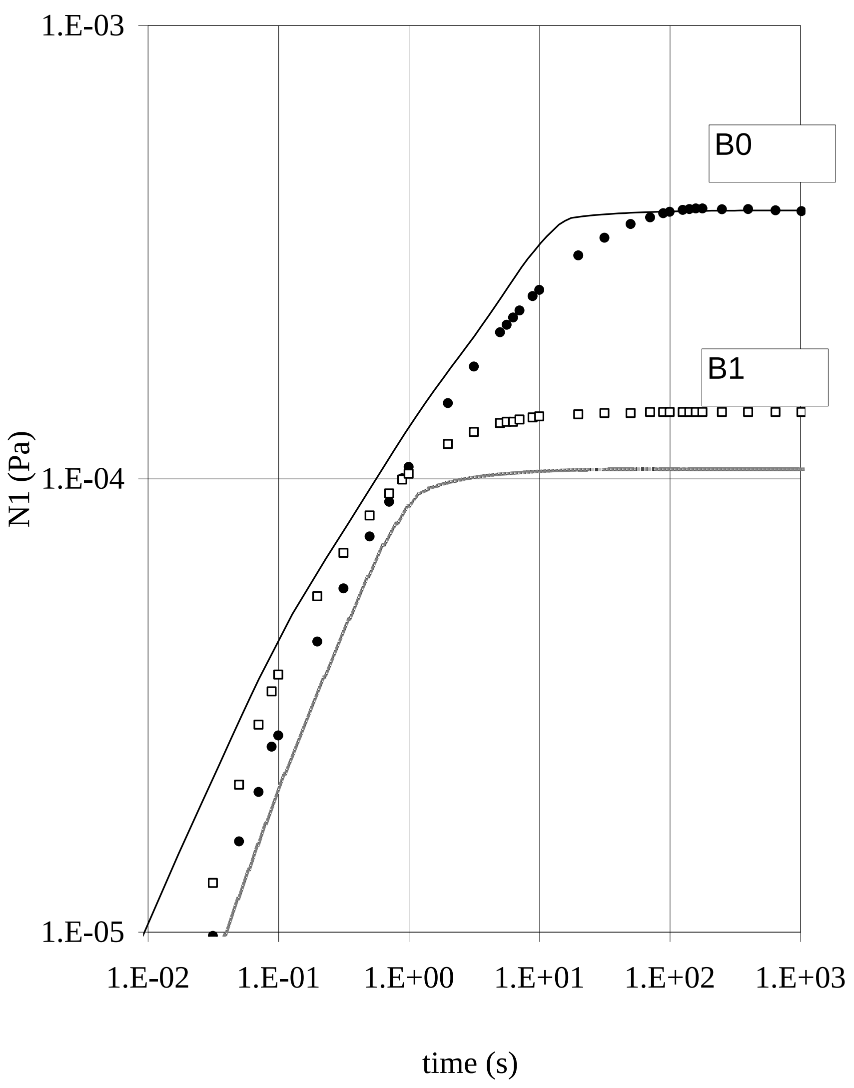
Measured and predicted J(t)





Measured and predicted Jr(t)





Conclusions (1)

- The prediction of N1 using the Wagner model (with the proposed damping function) is in good agreement for the CRPP resins and needs some improvement for the RGPP resins

- The predictions of J(t) is in good agreement with the actual data for all the resins

Conclusions (2)

- The predictions of Je(t) is in good agreement with the actual data for some of the resins. However, in this case the damping function was set equal to 1.

  (some authors have already pointed out that the recovery should have a distinct damping function)

General Conclusions

- The Wagner model seems to be an appropriate constitutive model in the prediction of N1 and J(t) as well as Je(t).

- The ability to predict N1 and creep and recovery compliance solely based on oscillatory data can be a very useful, specially for research facilities lacking constant stress rheometers and transducers to properly measure N1.

- The results presented in this study are in good agreement with those presented by Tzoganakis et al. (11) for PP resins.

Recommendations

- More research is required to refine the technique in order to make better predictions of N1 for materials with high molecular weight content (high Mz) such as A0 and B0 resins.

- It will be worthwhile to study the differences between the damping function in one direction (like in J(t)) and the one in the reverse direction (like in Jr(t)) and relate that to the features of the MWD.