

***ESTIMATION OF THE FIRST NORMAL  
STRESS DIFFERENCE ( $N_1$ ) AND CREEP  
COMPLIANCE( $J(t)$ ) OF POLYPROPYLENE (PP)  
RESINS  
USING A CONSTITUTIVE EQUATION***

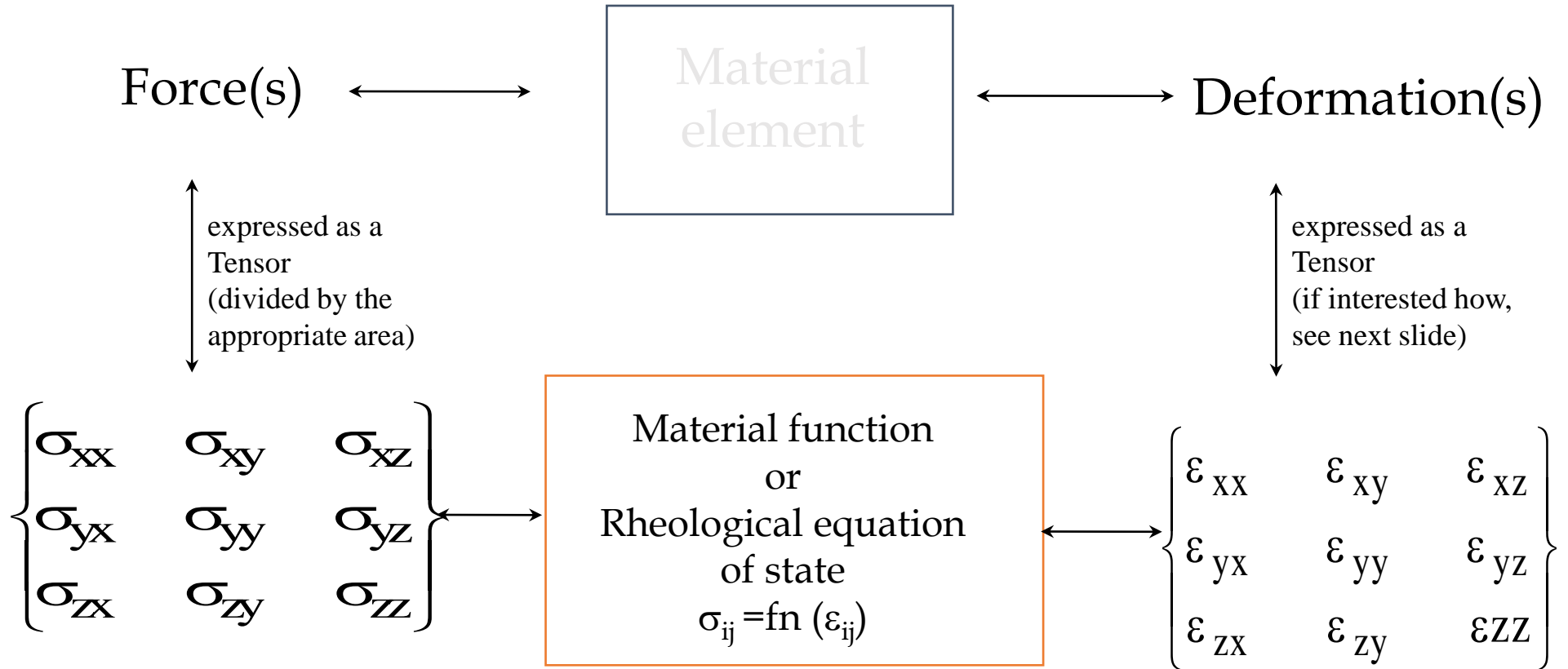
# RELEVANCE

- The constitutive equation can be used for estimation of  $N1$ ,  $J(t)$  and  $J_e(t)$  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



Examples:

- ✓ Wagner Model
- ✓ Phan Thien Tanner Model

# 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

# Lodge Model

# Model

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

## Wagner Model

**SEPARABILITY OF MEMORY FUNCTION IN:**

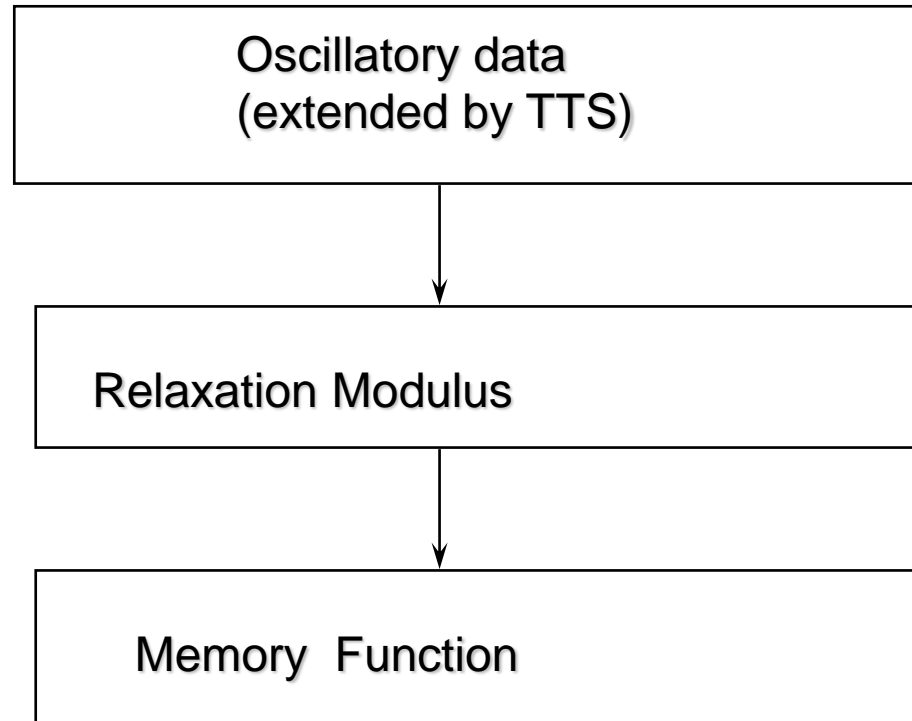
**Time Dependent Memory Function (  $\mu_{(t-t')}$  )**

**and**

**Strain Dependent Damping Function:  $h(\gamma(t-t'))$**

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

# 1. 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  $t'$

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

$$I_3 = 1 \quad (\text{incompressibility assumed})$$

## 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

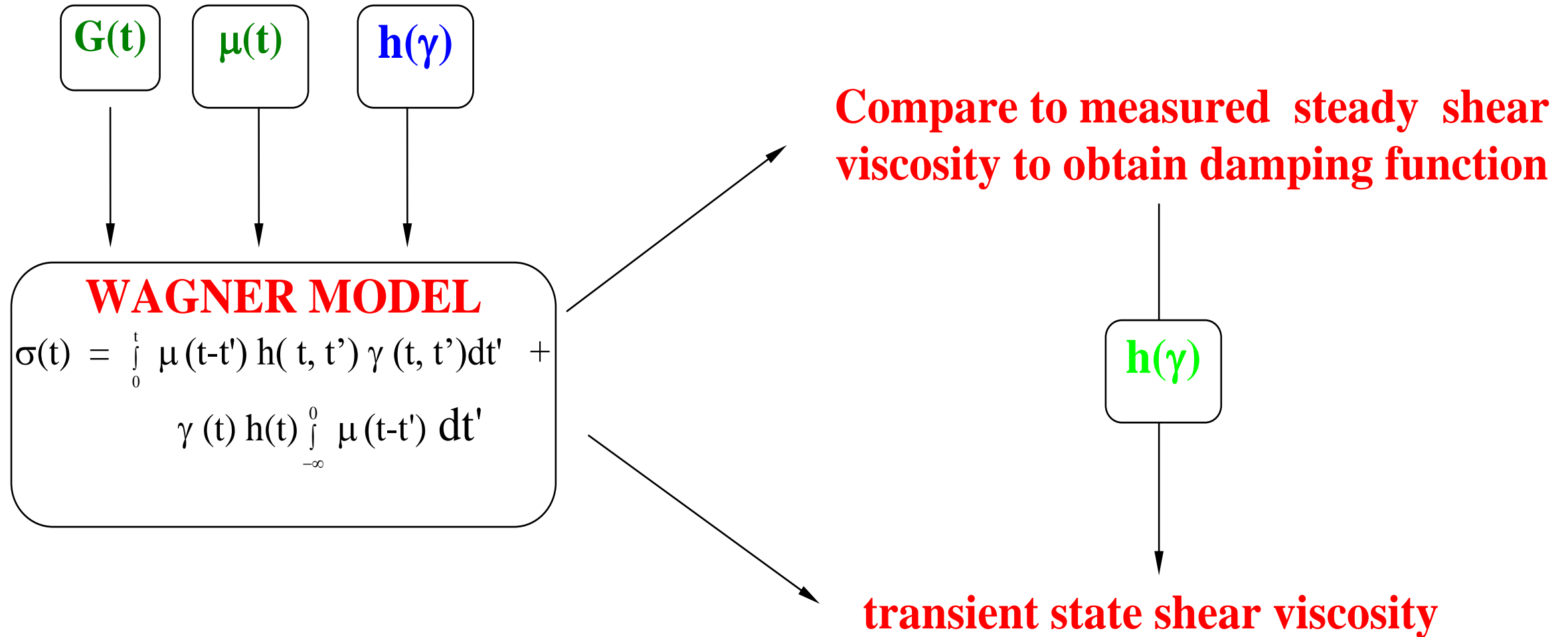
# What type of data can be obtained ?

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)



Shear viscosity as function of a given

shear rate ( $\dot{\gamma}$ ), time ( $t$ ),  $a_i$  (the  $i^{\text{th}}$  elastic value of the Maxwell element),  $\lambda_i$  (the  $i^{\text{th}}$  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

$$\alpha_i = (1 + n_1 \lambda_i \dot{\gamma}_o) / \lambda_i ; \quad \beta_i = (1 + n_2 \lambda_i \dot{\gamma}_o) / \lambda_i$$

Fitting steady state viscosity ( $\eta(t, \dot{\gamma}_o) \rightarrow \infty$ )  
 curve to get  $n_1$  and  $n_2$

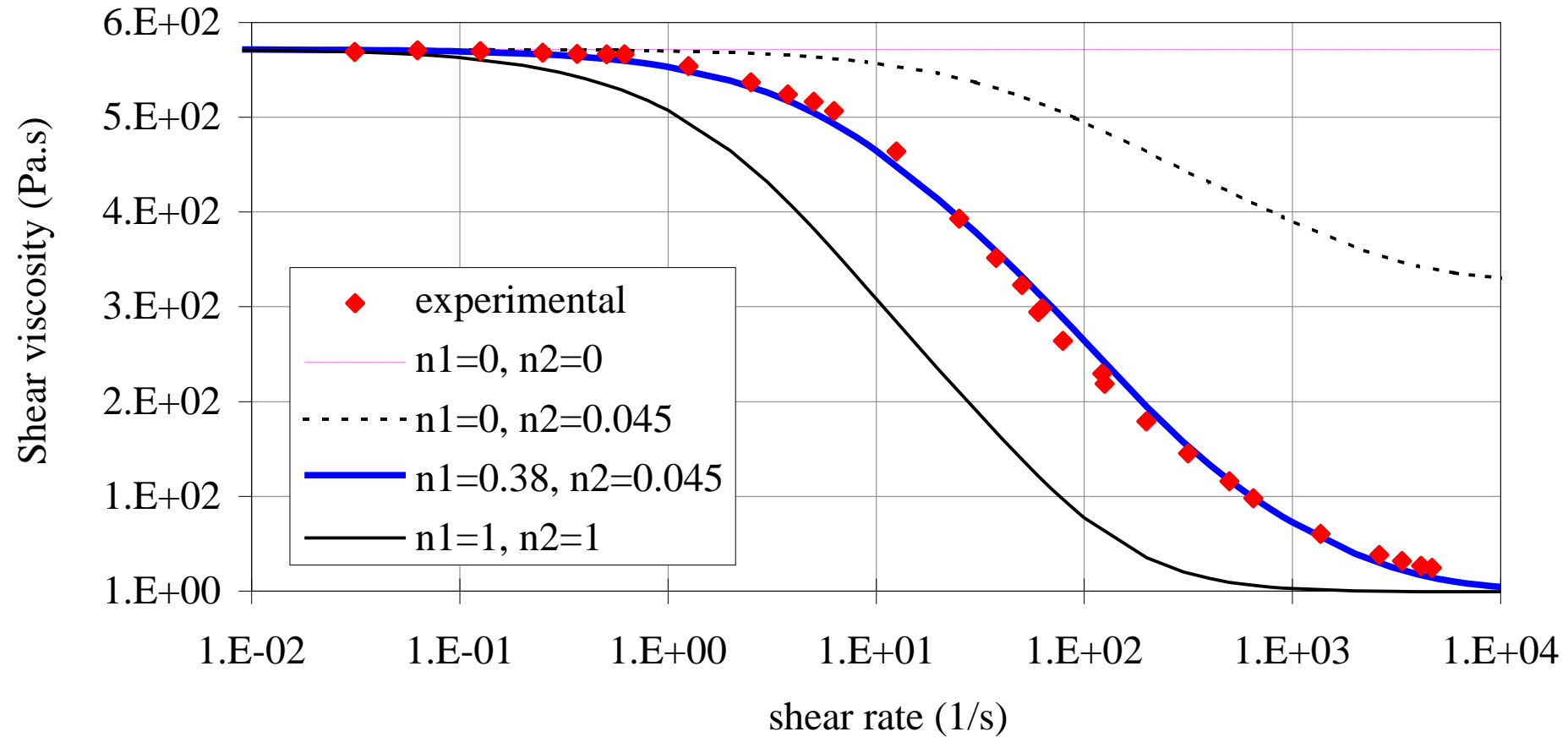
$$\eta(t, \dot{\gamma}_o) =$$

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

Where

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

# 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  $n_1$  y  $n_2$  values,  
then we can use them to estimate  
other material functions such as  
 $N_1(\gamma)$ ,  $N_1(t)$ ,  $J_e(t)$ ;  $J_r(t)$ ,  
 $\eta_e(\varepsilon)$  or  $\dot{\eta}_e(t)$  .

# N1 response to a step shear rate

**G(t)**      **μ(t)**      **h(γ)**

## WAGNER MODEL

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

**steady shear**

**first normal stress difference (N1)**

$$N1(t, \dot{\gamma}_0) = \dot{\gamma}_0^2 \left\{ f_1 \sum_{i=1}^n a_i \alpha_i^3 + (1-f_1) \sum_{i=1}^n a_i \beta_i^3 \right\}$$

**transient state shear viscosity**

**transient state N1**

# Calculation of N1

$$\begin{aligned} N1(t, \dot{\gamma}_o) = & \dot{\gamma}_o^2 \left\{ f_1 \sum_{i=1}^8 a_i \alpha_i^3 \{1 - \exp[-\alpha_i t]\}^* \right. \\ & \left. [1 + \alpha_i t - \alpha_i^2 (n_1 \lambda_i \dot{\gamma}_o / 2) t^2] \right\} + \\ & (1 - f_1) \sum_{i=1}^8 a_i \beta_i^3 \{1 - \exp[-\beta_i t]\}^* \\ & [1 + \beta_i t - \beta_i^2 (n_2 \lambda_i \dot{\gamma}_o / 2) t^2] \} \end{aligned}$$

Calculation of N1 as t

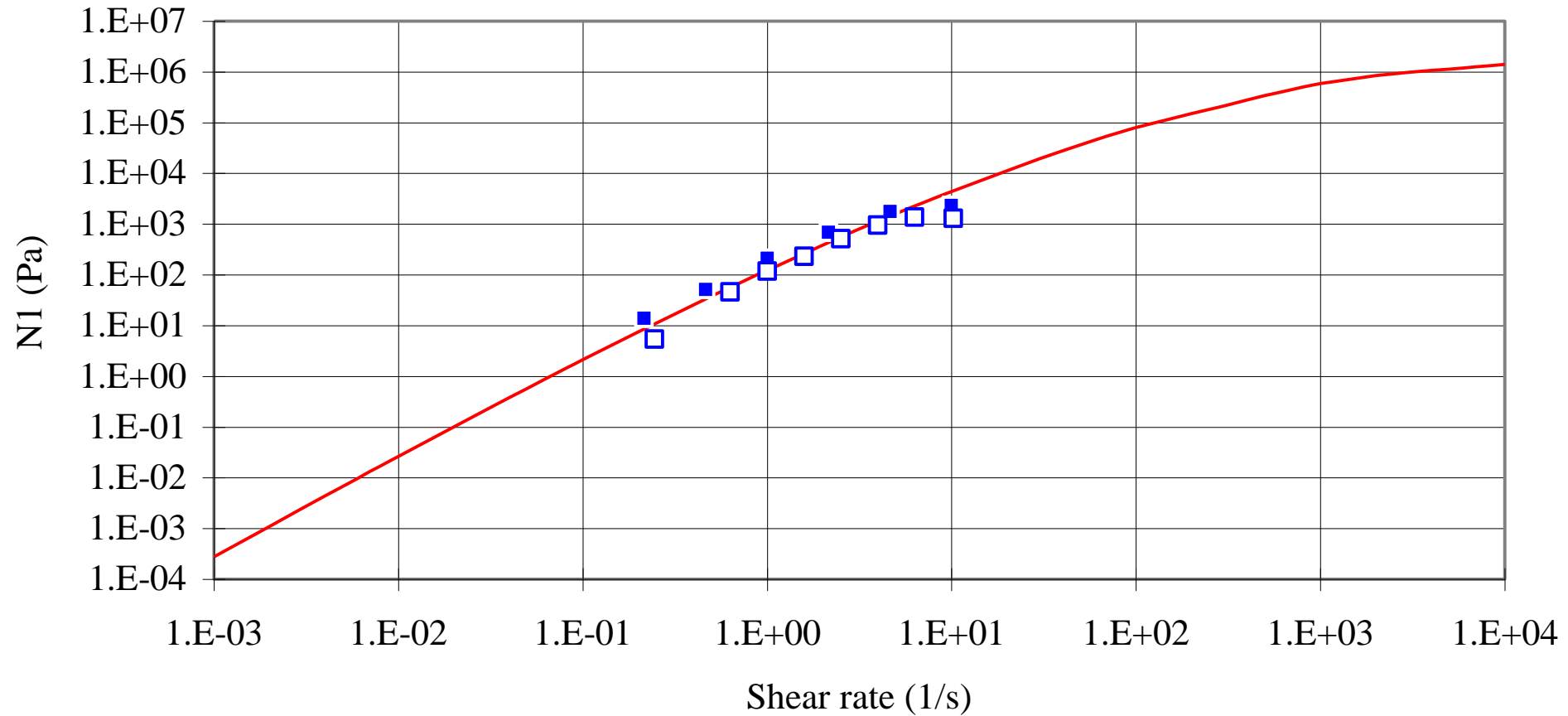
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$$N1(t, \dot{\gamma}_o) = \dot{\gamma}_o^2 \left\{ f_1 \sum_{i=1}^8 a_i \alpha_i^3 \{1\} + \right. \\ \left. (1-f_1) \sum_{i=1}^8 a_i \beta_i^3 \{1\} \right.$$

Where

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

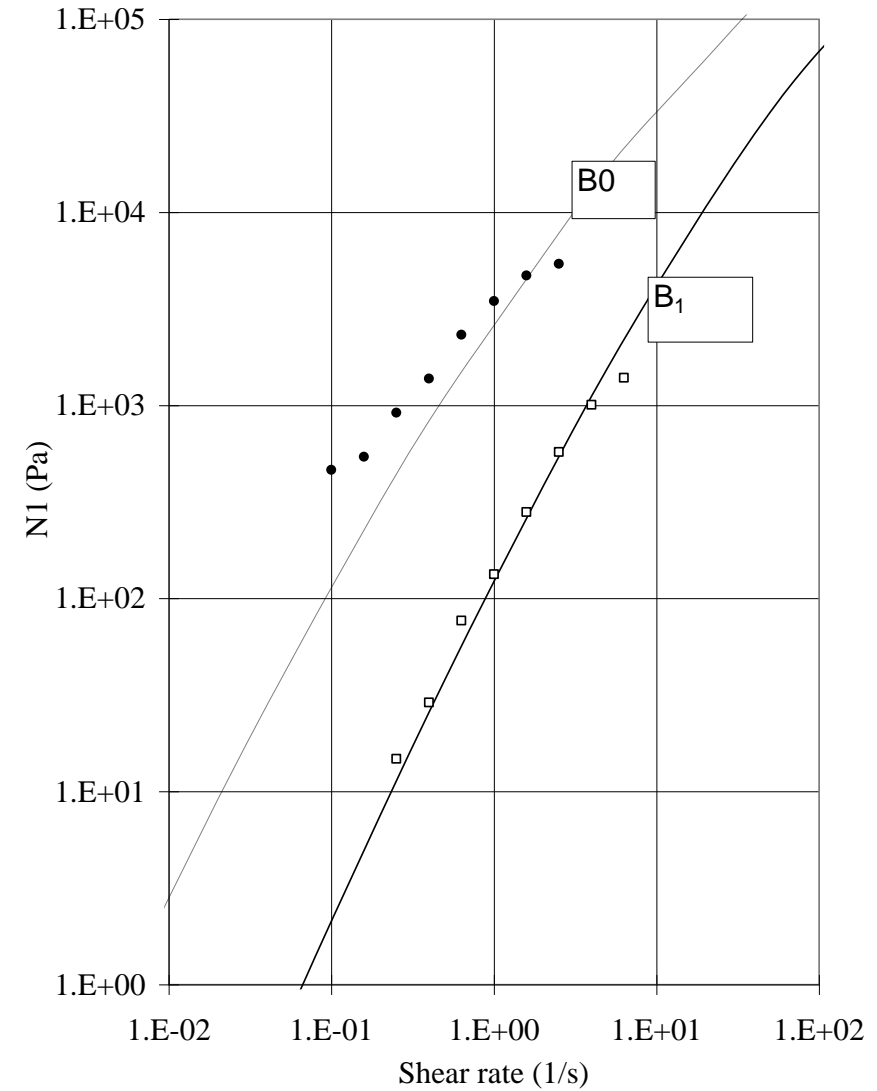
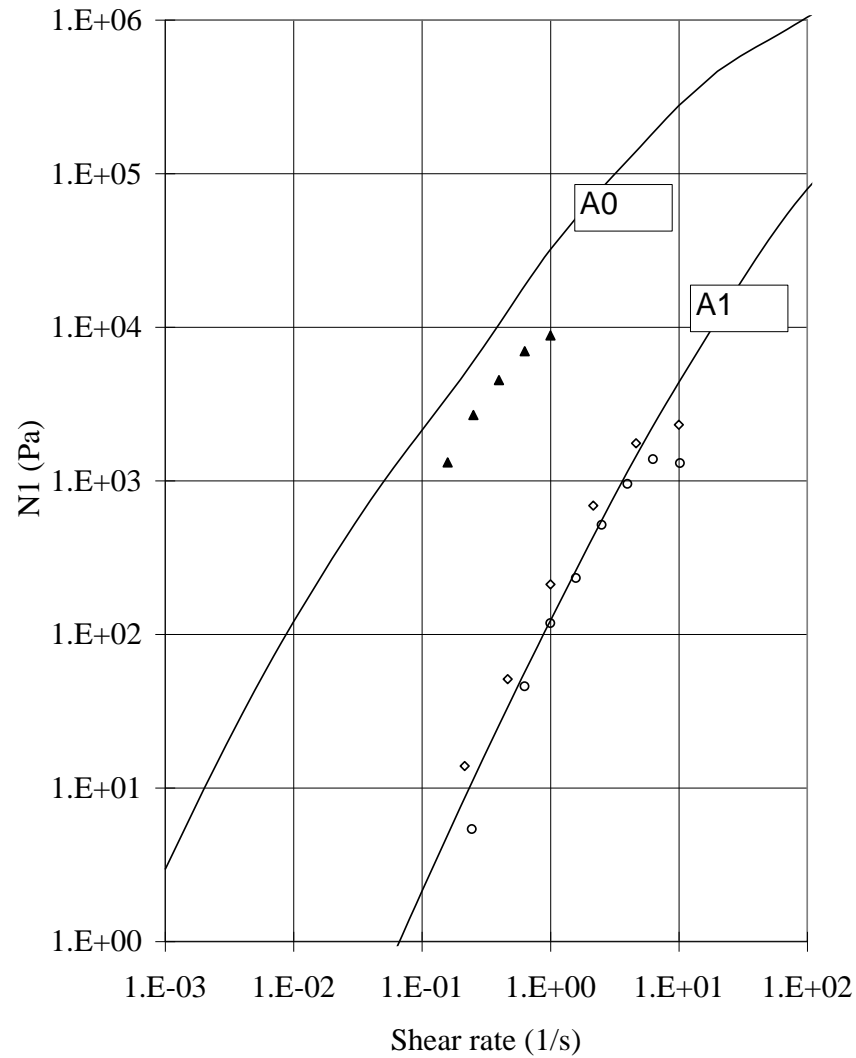
# Measured and predicted N1 versus shear rate



CRPP resin A1

different symbols correspond to independent measurements

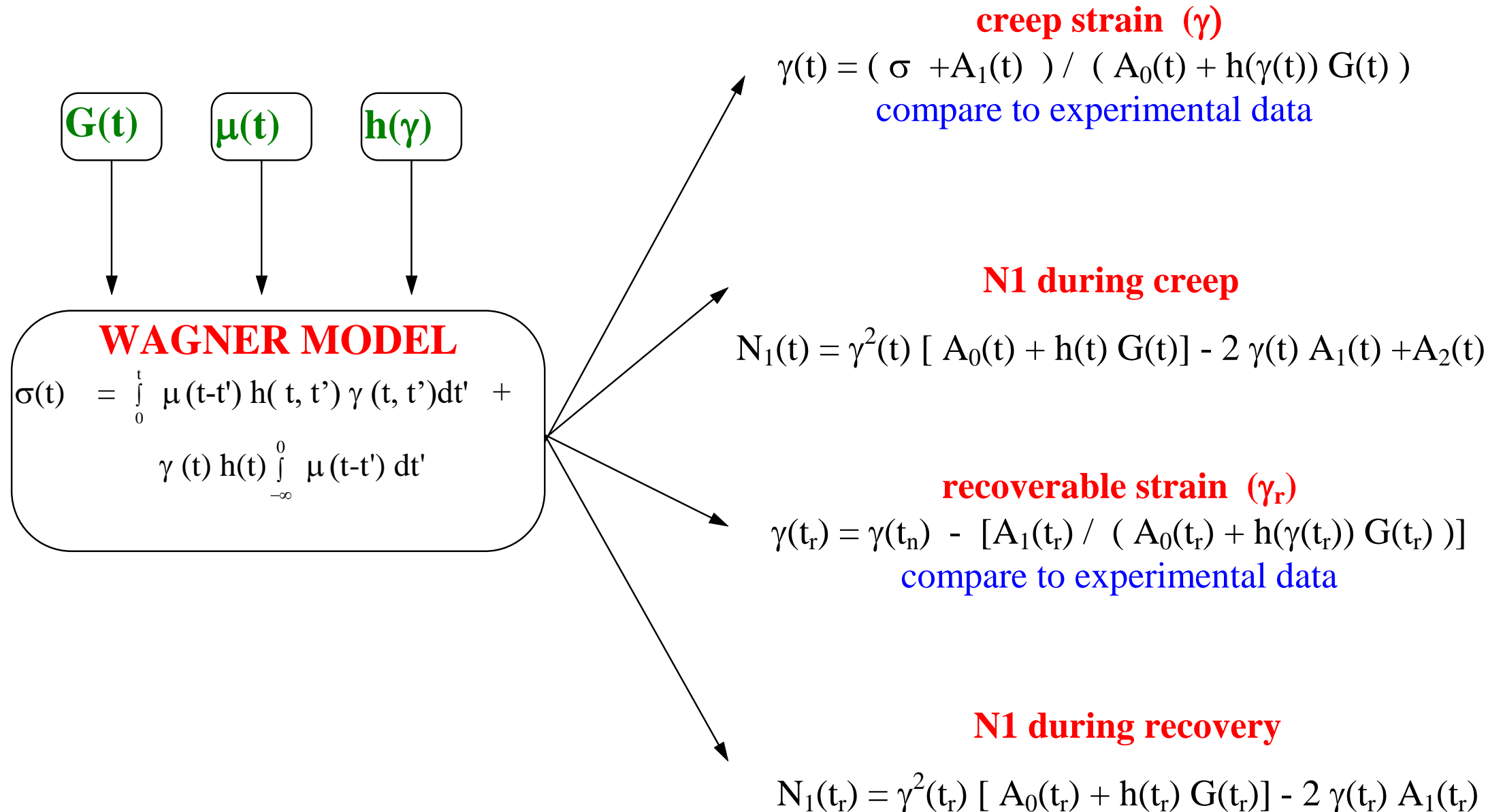
# Measured and predicted N1



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# Strain and N1 response to a step stress



# Calculation of $J(t)$

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

where:

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

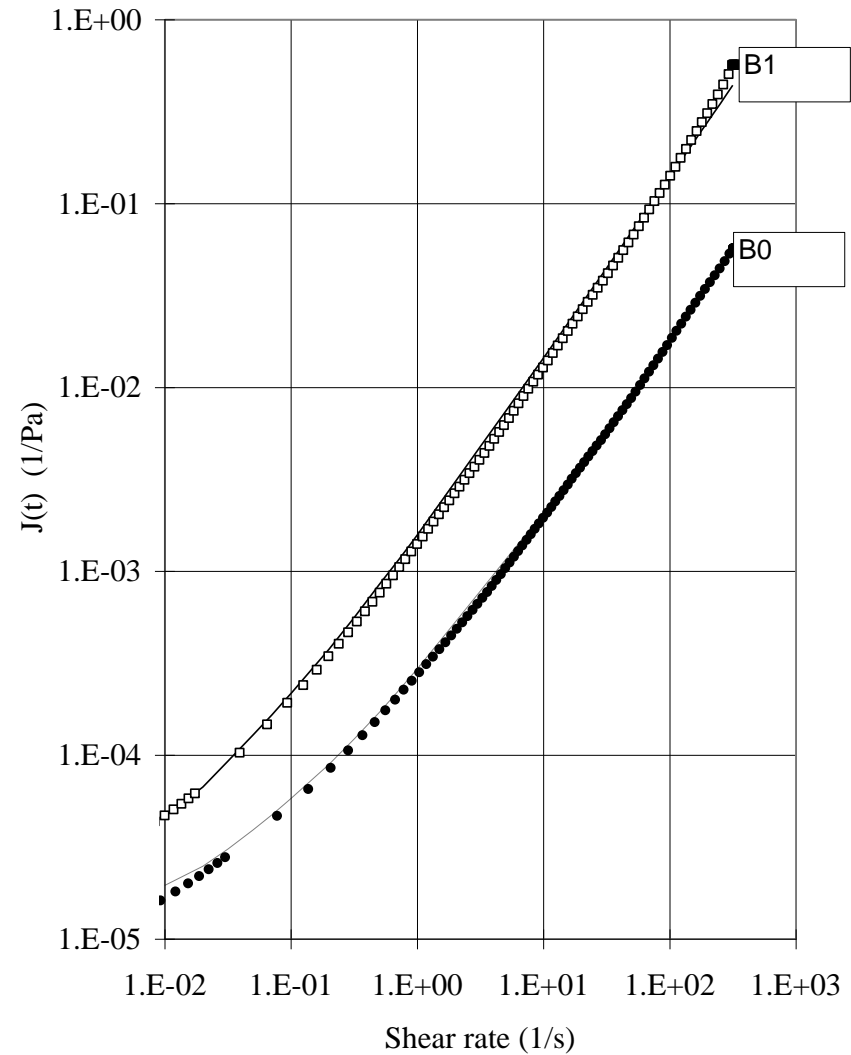
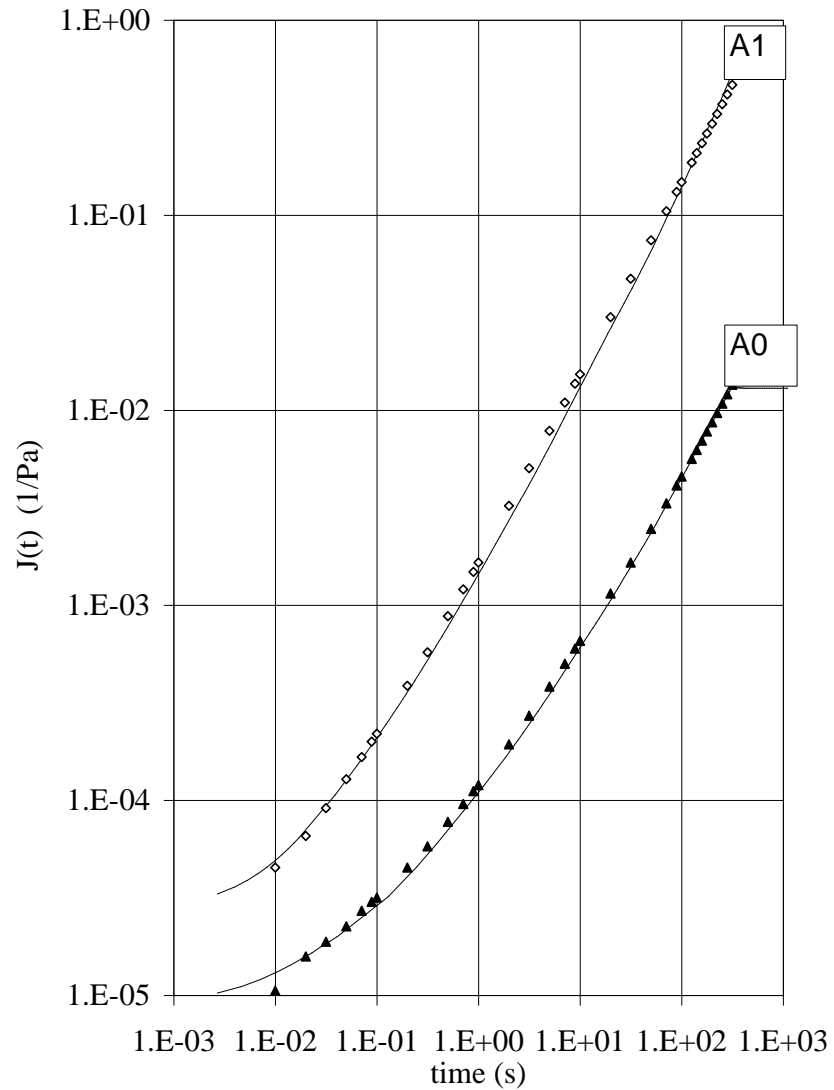
$$\sigma h(t) = f_1 \exp(-n_1 |\gamma(t, t')|) + (1-f_1) \exp(-n_2 |\gamma(t, t')|) \text{ and}$$

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

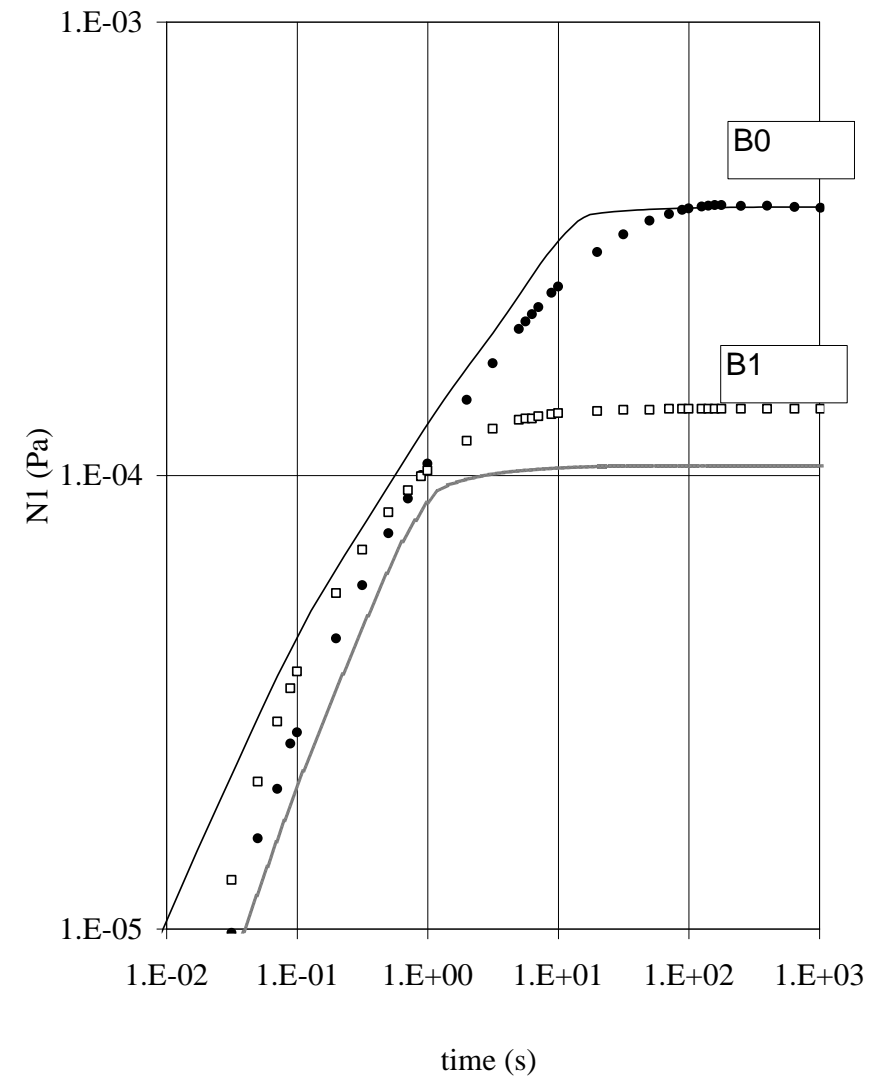
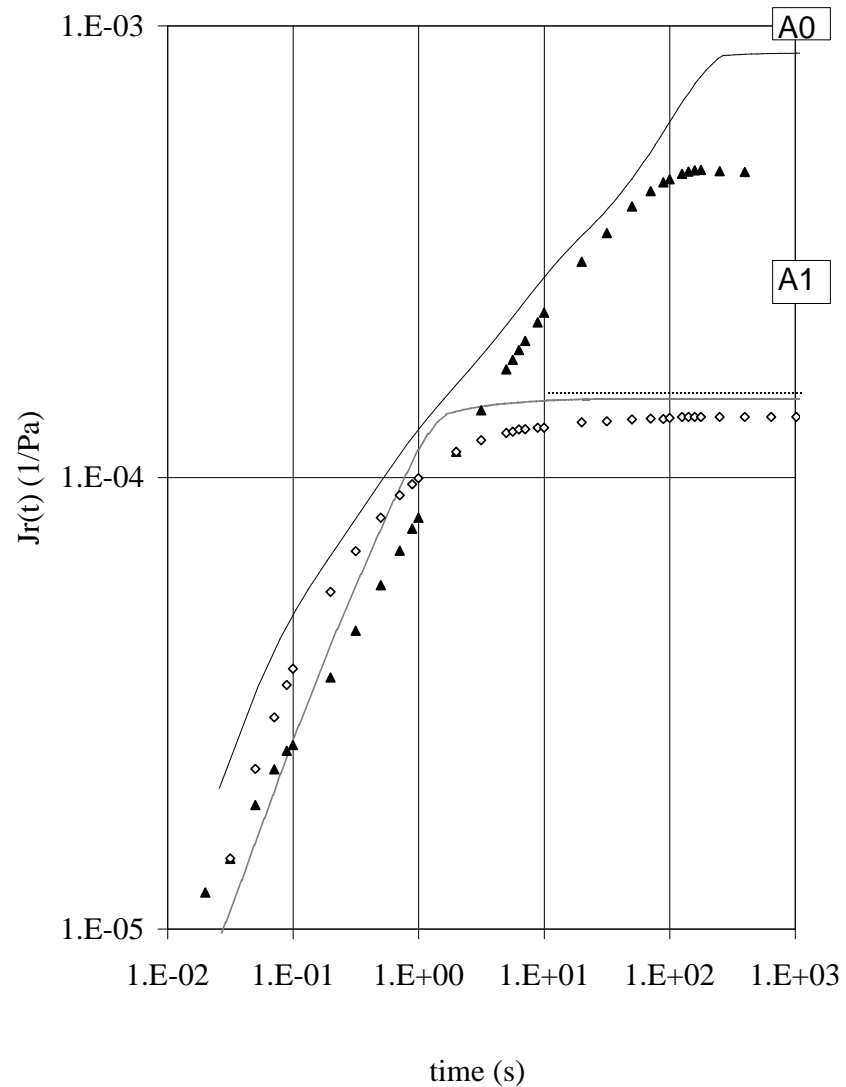
$$A_1(t) = \int \mu(t-t') \gamma(t, t') h(t, t') dt'$$

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

# Measured and predicted $J(t)$



# Measured and predicted $J_r(t)$



# 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  $J_e(t)$  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  $J_e(t)$ .
- 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  $N_1$  for materials with high molecular weight content (high  $M_z$ ) 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  $J_r(t)$ ) and relate that to the features of the MWD.