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Continuous symmetry analysis of a dissipative constitutive law: application to the time-temperature superposition

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Abstract

The isothermal inelastic behaviour of the dry polyamid 66 (PA66) is considered. It is shown that the so called time-temperature equivalence principle can be recovered by a symmetry analysis of the differential equations governing the material rheology, which are written within a thermodynamical framework of relaxation. The symmetry analysis leads to the expression of a translation shift factor from a reference curve to another curve at a different temperature. This shift factor is compared to that given by the well-known Williams-Landel-Ferry empiric relation.

Key words: Thermodynamics of Relaxations, Lie Groups, DNLR Approach, Williams Landel Ferry Relation.

1 Introduction

The powerfullness of the Lie group symmetry analysis has been extensively used to support the finding of analytic solutions to partial differential equations (for a body of results, see Ibragimov (1995)). In the context of continuum solids mechanics, Lie groups have been applied to solve both the Navier and the Lamé equations (see Ozer (2003), Chirkunov (1973)), or in a similar spirit, to partially solve the ideal plasticity equation (Senashov (1980), Annin et al. (1985)).

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The point of view advocated in this contribution is the involvement of Lie groups as a predictive method to obtain invariance properties of materials: from the knowledge of the constitutive law of a specific material and its experimental response for a given set of control conditions, the ability of Lie symmetries to predict the material behaviour under various control conditions shall be assessed.

The focus of the present paper is on the time temperature equivalence principle (here abbreviated as TTEP), which was successfully confirmed by experimental data on several polymers, and fitted with empiric relations such as the Williams-Landel-Ferry (WLF) relation (e.g. Hotta and Terentjev (2001), Laot (2001), Ricco and Pegoretti (2000)) or the Kohlrausch relation (Meyer et al. (1999), O'Connell and McKenna (1997), Nicholson et al. (2001)). To briefly illustrate the TTEP, let us consider the data summarized in the Figure 1, representing the experimental and isothermal evolution of the secant modulus $E_s(t, T)$ (introduced here as a function of the time t and the temperature T) of a polymer (polyamid 66, abbreviated as PA66) versus time, at different constant temperatures and for a given strain rate. Each curve being parameterized by the temperature T' (taken in the set 413K, 433K, and 453K) can be translated along the time axis with a horizontal shift factor, $a_{T' \rightarrow T}$, to coincide with a master curve at a reference temperature T (here 393K, see Figure 2). This invariance property may be mathematically expressed as

$$E_s(t, T) = E_s(a_{T' \rightarrow T} t, T') \quad \Rightarrow \quad E_s(\log t, T) = E_s(\log t + \log a_{T' \rightarrow T}, T') \quad (1)$$

where $a_{T' \rightarrow T}$ is a shift factor that may be empirically formulated as a function of the reference temperature T and the temperature T' .

In a previous paper (Rahouadj et al. (2003a), Rahouadj et al. (2003b)), Rahouadj *et al* showed that a thermomechanical behaviour formalized within an approach of relaxation called DNLR (Distribution of Non Linear Relaxations) approach (Cunat (2001), Cunat (2000)) obeys the TTEP, and that the symmetry analysis proves a convenient method to predict this principle. Relying on the initial methodology presented in (Rahouadj et al. (2003a), Rahouadj et al. (2003b)) and on the work of Magnenet *et al* (Magnenet et al. (2005), Magnenet et al. (2007)), the purpose of the present work is then to theoretically express the shift factor $a_{T' \rightarrow T}$ of the TTEP and to compare it with the empiric form given by the WLF formulation. This theoretical formulation will be obtained from a Lie groups analysis of the DNLR constitutive equations.

The following conventions shall be used below: vectors and matrices are denoted by bold face letters, and the total derivative of an expression, e.g. $u(t, f(t))$, with respect to time t will be written $\dot{u} = \frac{\partial u}{\partial t} + \frac{\partial u}{\partial f} \dot{f}$. Accordingly, the total derivative \dot{u} accounts for both the explicit and the implicit dependence of the functional u upon time (u depends on f , which itself is a function of the time).

2 Constitutive law within the thermodynamics of relaxation

A short reminder of the constitutive thermomechanics framework of relaxation is first given. For a homogeneous continuous medium, Cunat (Cunat (2001), Cunat (2000)) showed that the evolution of the intensive variables \mathbf{Y} (e.g. stress tensor σ , temperature T) and intensive generalized forces \mathbf{A} may be associated with the dual extensive variables \mathbf{y} (e.g. volume weighted strain tensor $V\varepsilon$, entropy s) and extensive internal variables \mathbf{z} (describing the microstructure) by the rate form of the constitutive equations

$$\begin{cases} \mathbf{Y} = \frac{\partial e}{\partial \mathbf{y}} \\ -\mathbf{A} = \frac{\partial e}{\partial \mathbf{z}} \end{cases} \Rightarrow \begin{pmatrix} \dot{\mathbf{Y}} \\ -\dot{\mathbf{A}} \end{pmatrix} = \begin{pmatrix} \mathbf{a}^u & \mathbf{b} \\ \mathbf{b}^T & \mathbf{g} \end{pmatrix} \begin{pmatrix} \dot{\mathbf{y}} \\ \dot{\mathbf{z}} \end{pmatrix} \quad (2)$$

where $\mathbf{a}^u = \frac{\partial^2 e}{\partial \mathbf{y}^2}$ is the Tisza matrix (the superscript “u” means “unrelaxed”), $\mathbf{b} = \frac{\partial^2 e}{\partial \mathbf{y} \partial \mathbf{z}}$ is the coupling matrix, and $\mathbf{g} = \frac{\partial^2 e}{\partial \mathbf{z}^2}$ the matrix of dissipation, defined as the matrices of second order derivatives of the generalized internal energy potential $e(\mathbf{y}, \mathbf{z})$. These matrices are, for the sake of simplicity, assumed to be constant in the vicinity of the thermodynamical equilibrium. Eqs. (2) may be reasonably completed (Cunat (2001), Cunat (2000)) by a linear kinetic evolution of the internal variables

$$\dot{\mathbf{z}} = \mathbf{L}\mathbf{A} \quad (3)$$

where \mathbf{L} is the matrix of kinetic coefficients satisfying Onsager’s properties (see Onsager (1931)). To obtain the corresponding constitutive equations, Cunat proposed to introduce a state of reference, called “the relaxed state” (or eventually the steady state in non equilibrium situations), defined by the condition $-\dot{\mathbf{A}}^r = 0$ (the superscript “r” refers to this state). Using (2) and (3), one can show (Cunat (2001), Cunat (2000)) that the kinetic evolution equation of the microstructural reaction advancement is given by

$$\dot{z}_k = -\frac{z_k - z_k^r}{\tau_k} \quad | \quad k = 1..N \quad (4)$$

where z_k^r is the value of the k^{th} reaction advancement at the relaxed state, N the number of modes (or chemical processes), and τ_k the corresponding relaxation time.

Actually, in an experimental context, it can be easier to control a subset of the extensive variables \mathbf{y} completed by another subset of intensive variables \mathbf{Y} . Thus, let be $\boldsymbol{\gamma} \subset \{\mathbf{y}, \mathbf{Y}\}$ the vector of experimentally controled variables, and $\boldsymbol{\beta}$ the set of the dual thermodynamic variables. By using a Legendre transformation of the internal energy $e(\mathbf{y}, \mathbf{z})$, the thermodynamic potential $\psi(\boldsymbol{\gamma}, \mathbf{z})$ may be expressed as a function of $\boldsymbol{\gamma}$ and \mathbf{z} . In this case, it has been

shown that the DNLR equations take the general form (Cunat (2001),Cunat (2000))

$$\begin{pmatrix} \dot{\boldsymbol{\beta}} \\ -\dot{\mathbf{A}} \end{pmatrix} = \begin{pmatrix} \mathbf{a}^u & \mathbf{b} \\ \mathbf{b}^T & \mathbf{g} \end{pmatrix} \begin{pmatrix} \dot{\boldsymbol{\gamma}} \\ \dot{\mathbf{z}} \end{pmatrix} \quad (5)$$

where $\mathbf{a}^u = \frac{\partial^2 \psi}{\partial \boldsymbol{\gamma}^2}$, $\mathbf{b} = \frac{\partial^2 \psi}{\partial \boldsymbol{\gamma} \partial \mathbf{z}}$, and $\mathbf{g} = \frac{\partial^2 \psi}{\partial \mathbf{z}^2}$ are the “new” formulations of the Tisza, coupling and dissipation matrices. Note that dissipative reorganizations are modelled by a spectral analysis based on fluctuating modes, relatively to the new relaxed state associated with the new value of $\boldsymbol{\gamma}$.

3 Application to the inelastic behaviour for uniaxial loading paths

Let identify the components of the controlled variables $\boldsymbol{\gamma}$ to the uniaxial strain tensor ε and the temperature T , associated with the Cauchy stress tensor σ and the entropy s (components of $\boldsymbol{\beta}$), respectively. The suitable thermodynamical potential $\psi(\boldsymbol{\gamma}, \mathbf{z})$ is then the Helmholtz free energy $f(\varepsilon, T, \mathbf{z})$, and the relation (5) incorporating (4) gives (Cunat (2001),Cunat (2000))

$$\Delta = \begin{cases} \Delta_1 = \dot{\sigma} - E_u \dot{\varepsilon} + \alpha_u E_u \dot{T} + \sum_{k=1}^N b_k^1 \frac{z_k - z_k^r}{\tau_k} = 0 \\ \Delta_2 = -\dot{s} + \alpha_u E_u \dot{\varepsilon} - \frac{C_u}{T} \dot{T} + \sum_{k=1}^N b_k^2 \frac{z_k - z_k^r}{\tau_k} = 0 \\ \Delta_{2+i} = -\dot{A}_i - b_i^1 \dot{\varepsilon} - b_i^2 \dot{T} + \sum_{k=1}^N g_{ik} \frac{z_k - z_k^r}{\tau_k} = 0 \quad | \quad i = 1..N \end{cases} \quad (6)$$

where the constants E_u , b_k^1 , α_u , b_k^2 , $\frac{C_u}{T}$, and g_{ik} are defined as the following second order derivatives of f

$$E_u = \frac{\partial^2 f}{\partial \varepsilon^2}; \quad b_k^1 = \frac{\partial^2 f}{\partial \varepsilon \partial z_k} \quad | \quad k = 1..N; \quad -\alpha_u E_u = \frac{\partial^2 f}{\partial \varepsilon \partial T} \quad (7)$$

$$\frac{C_u}{T} = \frac{\partial^2 f}{\partial T^2}; \quad b_k^2 = \frac{\partial^2 f}{\partial T \partial z_k} \quad | \quad k = 1..N; \quad g_{ik} = \frac{\partial^2 f}{\partial z_i \partial z_k} \quad | \quad i, k = 1..N \quad (8)$$

among which we recognize the instantaneous Young modulus E_u , the dilatation coefficient α_u , and the specific heat C_u . The value of the internal variables at the relaxed state, denoted z_k^r , is given by the condition $-\dot{A}_k = 0$, i.e. $A_k = A_k^r = \text{constant}$. Under the assumption of an isothermal condition, $\dot{T} = 0$, the second equation of (5) leads to

$$-\dot{A}_i^r = 0 = b_i^1 \dot{\varepsilon} + \sum_{k=1}^N g_{ik} \dot{z}_k^r \quad \Rightarrow \quad \dot{z}_k^r = - \sum_{i=1}^N (g^{-1})_{ki} b_i^1 \dot{\varepsilon} \quad | \quad k = 1..N \quad (9)$$

In a first approach, the constants of integration appearing in (9) are assumed to be equal to zero, leading to a value of z_k^r that only depends on the applied strain ε , via

$$z_k^r = - \sum_{i=1}^N (g^{-1})_{ki} b_i^1 \varepsilon = c_k \varepsilon \quad | \quad k = 1..N \quad (10)$$

Considering a linear “thermo-visco-elastic” behaviour corresponding to a simplified DNLr version (more exactly called DLR version), Cunat showed that the relaxation times τ_j may be modeled as functions of the temperature T only, according to

$$\tau_j(T) = \frac{h}{kT} \exp\left(\frac{\Delta H_j - T \Delta S_j}{RT}\right) \quad | \quad j = 1..N \quad (11)$$

where h is the Planck constant, k the Boltzmann constant, and R the ideal gas constant. The physical parameters ΔH_j and ΔS_j correspond to the apparent activation enthalpy and entropy of the j^{th} dissipative mode respectively. The activation enthalpies are supposed to be the same for each mode, $\Delta H_j = \Delta H$, indicating that the material is considered as “thermorheologically simple”. The chosen deformation path is such that ε linearly increases as a function of the time ($\varepsilon = \dot{\varepsilon}t$). Summarizing Eqs. (6-11) then gives the final form of the constitutive equations

$$\Delta = \begin{cases} \Delta_1 = \dot{\sigma} - E_u \dot{\varepsilon} + \sum_{j=1}^N b_j^1 \frac{z_j - c_j \dot{\varepsilon}t}{\frac{h}{kT} \exp\left(\frac{\Delta H - T \Delta S_j}{RT}\right)} = 0 \\ \Delta_2 = -\dot{s} + \alpha_u E_u \dot{\varepsilon} + \sum_{j=1}^N b_j^2 \frac{z_j - c_j \dot{\varepsilon}t}{\frac{h}{kT} \exp\left(\frac{\Delta H - T \Delta S_j}{RT}\right)} = 0 \\ \Delta_{2+i} = -\dot{A}_i - b_i^1 \dot{\varepsilon} + \sum_{j=1}^N g_{ij} \frac{z_j - c_j \dot{\varepsilon}t}{\frac{h}{kT} \exp\left(\frac{\Delta H - T \Delta S_j}{RT}\right)} = 0 \quad | \quad i = 1..N \end{cases} \quad (12)$$

The parameters of the present DLR model are summarized into the following set

$$\{E_u, b_j^1, c_j, \Delta H, \Delta S_j, \alpha_u, b_j^2, g_{ij}\} \quad | \quad j = 1..N \quad (13)$$

For continuous thermal loadings, such a simple model can be used to reproduce inelastic behaviours, as we shall see in the following section.

4 Lie groups computational method

Let us now formulate the Lie groups computational method for the constitutive equations (12). Using Olver notations (Olver (1989)), one considers the smooth manifold $\mathbb{M} = X \times U$, where X is the set of independent variables (in our case, t) and U is the set of dependent variables

$$U = \{\varepsilon(t), T(t), z_k(t), \sigma(t), s(t), A_k(t)\} \quad | \quad k = 1..N \quad (14)$$

Let \mathbf{v} be a vector field on \mathbb{M} , expressed as an infinitesimal operator

$$\mathbf{v} = \xi \frac{\partial}{\partial t} + \phi_\varepsilon \frac{\partial}{\partial \varepsilon} + \phi_T \frac{\partial}{\partial T} + \sum_{k=1}^N \phi_{z_k} \frac{\partial}{\partial z_k} + \phi_\sigma \frac{\partial}{\partial \sigma} + \phi_s \frac{\partial}{\partial s} + \sum_{k=1}^N \phi_{A_k} \frac{\partial}{\partial A_k} \quad (15)$$

where the components $\xi, \phi_\varepsilon, \phi_T, \phi_{z_k}, \phi_\sigma, \phi_s, \phi_{A_k}$ ($k = 1..N$) depend *a priori* on all the variables $t, \varepsilon, T, z_k, \sigma, s, A_k$. The vector field \mathbf{v} generates a symmetry group for equations (12) if and only if it transforms a solution of (12) into another one. It is well-established (Olver (1989)) that a necessary and sufficient condition for this property is given by

$$pr^{(1)}\mathbf{v}\Delta = 0 \quad \text{whenever } \Delta = 0 \quad (16)$$

where $pr^{(1)}\mathbf{v}$ is the first prolongation of \mathbf{v} given in the present case (accounting for $\dot{T} = 0$) by the more specific expression

$$\begin{aligned} pr^{(1)}\mathbf{v} = & \mathbf{v} + (\dot{\phi}_\varepsilon - \dot{\xi}\dot{\varepsilon}) \frac{\partial}{\partial \dot{\varepsilon}} + \dot{\phi}_T \frac{\partial}{\partial \dot{T}} + \sum_{k=1}^N (\dot{\phi}_{z_k} - \dot{\xi}\dot{z}_k) \frac{\partial}{\partial \dot{z}_k} \\ & + (\dot{\phi}_\sigma - \dot{\xi}\dot{\sigma}) \frac{\partial}{\partial \dot{\sigma}} + (\dot{\phi}_s - \dot{\xi}\dot{s}) \frac{\partial}{\partial \dot{s}} + \sum_{k=1}^N (\dot{\phi}_{A_k} - \dot{\xi}\dot{A}_k) \frac{\partial}{\partial \dot{A}_k} \end{aligned} \quad (17)$$

The search of the symmetry groups of (12) amounts to find all generators having the general form of (15), and satisfying the symmetry condition (16). The determining equations, obtained by inserting (12) and (17) into (16), take the following form

$$\begin{aligned} & -\xi \sum_{j=1}^N \left(\frac{b_j^1 c_j \dot{\varepsilon}}{\tau_j(T)} \right) - \phi_T \sum_{j=1}^N \left(b_j^1 \frac{\partial \tau_j(T)}{\partial T} \frac{z_j - c_j \dot{\varepsilon} t}{\tau_j^2(T)} \right) + \sum_{j=1}^N \left(\frac{\phi_{z_j} b_j^1}{\tau_j(T)} \right) \\ & - E_u (\dot{\phi}_\varepsilon - \dot{\xi}\dot{\varepsilon}) + \dot{\phi}_\sigma - \dot{\xi} \left(E_u \dot{\varepsilon} - \sum_{j=1}^N b_j^1 \frac{z_j - c_j \dot{\varepsilon} t}{\tau_j(T)} \right) = 0 \end{aligned} \quad (18)$$

$$\begin{aligned} & -\xi \sum_{j=1}^N \left(\frac{b_j^2 c_j \dot{\varepsilon}}{\tau_j(T)} \right) - \phi_T \sum_{j=1}^N \left(b_j^2 \frac{\partial \tau_j(T)}{\partial T} \frac{z_j - c_j \dot{\varepsilon} t}{\tau_j^2(T)} \right) + \sum_{j=1}^N \left(\frac{\phi_{z_j} b_j^2}{\tau_j(T)} \right) \\ & + \alpha_u E_u (\dot{\phi}_\varepsilon - \dot{\xi}\dot{\varepsilon}) - \dot{\phi}_s + \dot{\xi} \left(\alpha_u E_u \dot{\varepsilon} + \sum_{j=1}^N b_j^2 \frac{z_j - c_j \dot{\varepsilon} t}{\tau_j(T)} \right) = 0 \end{aligned} \quad (19)$$

$$\begin{aligned}
& -\xi \sum_{j=1}^N \left(\frac{g_{ij} c_j \dot{\varepsilon}}{\tau_j(T)} \right) - \phi_T \sum_{j=1}^N \left(g_{ij} \frac{\partial \tau_j(T)}{\partial T} \frac{z_j - c_j \dot{\varepsilon} t}{\tau_j^2(T)} \right) + \sum_{j=1}^N \left(\frac{g_{ij} \phi_{z_j}}{\tau_j(T)} \right) \\
& - b_i^1 (\dot{\phi}_\varepsilon - \dot{\xi} \dot{\varepsilon}) - \dot{\phi}_{A_i} + \dot{\xi} \left(-b_i^1 \dot{\varepsilon} + \sum_{j=1}^N g_{ij} \frac{z_j - c_j \dot{\varepsilon} t}{\tau_j(T)} \right) = 0 \quad | \quad i = 1..N \quad (20)
\end{aligned}$$

in which we do not insert the expression of the relaxation times (11) for simplicity. The solution of the system of equations (18), (19) and (20) with respect to the unknowns

$$\xi, \phi_\varepsilon, \phi_T, \phi_{z_k}, \phi_\sigma, \phi_s, \phi_{A_k} \quad | \quad k = 1..N \quad (21)$$

is a difficult task in the general case. We focus in the present contribution to a particular set of generators \mathbf{v} , that shall highlight the time temperature equivalence principle.

5 The time-temperature equivalence principle

5.1 Formal approach

Since it is not possible to completely solve the non-linear determining equations (18), (19) and (20), an algorithm to find some particular solution has been implemented. More precisely, a few components of \mathbf{v} are assigned a given value (0, 1, or t for ξ , and 0, 1 or α for ϕ_α , where α is a notation for an element of $\{\varepsilon, T, z_k, \sigma, s, A_k \mid k = 1..N\}$), and one searches the remaining components of \mathbf{v} (see Figure 3 for a schematic representation). For instance, as far as t is concerned, one looks for any generator having the form:

$$\mathbf{v} = \mathbf{v}' \quad \text{or} \quad \mathbf{v} = \frac{\partial}{\partial t} + \mathbf{v}' \quad \text{or} \quad \mathbf{v} = t \frac{\partial}{\partial t} + \mathbf{v}' \quad (22)$$

where \mathbf{v}' has no components in t . This structure of the generator has been used because 0, 1 and α generate three classical Lie groups, see e.g. Olver (1989). Indeed, the first value ($\phi_\alpha = 0$) corresponds to the identity group: $\bar{\alpha} = \alpha$, where $\bar{\alpha}$ is the transformed value of α by the group; the second value ($\phi_\alpha = 1$) corresponds to the group of translation: $\bar{\alpha} = \alpha + \mu$, while $\phi_\alpha = \alpha$ generates the group of dilatation: $\bar{\alpha} = e^\mu \alpha$ (i.e. a translation along the time axis in the $\log E_s$ vs. $\log t$ representation). In practice, a symbolic program (Maple[®]) has been used, and the following particular but interesting solution for the symmetry condition $pr^{(1)} \mathbf{v} \Delta = 0$ has been obtained:

$$\begin{aligned} \xi = t ; \phi_\varepsilon = \varepsilon ; \phi_T = -\frac{RT^2}{RT + \Delta H} \\ \phi_\sigma = \sigma ; \phi_s = s ; \phi_{z_k} = z_k ; \phi_{A_k} = A_k \quad | \quad k = 1..N \end{aligned} \quad (23)$$

The explicit expression of a one-parameter group G is given by the exponentiation of its infinitesimal generator (Olver (1989)) obtained in the present case by solving the first order differential system resulting from (23)

$$\frac{dt'}{d\mu} = t' ; \frac{d\varepsilon'}{d\mu} = \varepsilon' ; \frac{dT'}{d\mu} = -\frac{RT'^2}{RT' + \Delta H} \quad (24)$$

$$\frac{d\sigma'}{d\mu} = \sigma' ; \frac{ds'}{d\mu} = s' ; \frac{dz'_k}{d\mu} = z'_k ; \frac{dA'_k}{d\mu} = A'_k \quad | \quad k = 1..N$$

where μ is the group parameter, and the superscript “ ’ ” on any variable x means that x' is the transformed of x under the action of the group. The differential system (24) must be completed by the initial conditions

$$t'|_{\mu=0} = t ; \varepsilon'|_{\mu=0} = \varepsilon ; T'|_{\mu=0} = T \quad (25)$$

$$\sigma'|_{\mu=0} = \sigma ; s'|_{\mu=0} = s ; z'_k|_{\mu=0} = z_k ; A'_k|_{\mu=0} = A_k \quad | \quad k = 1..N$$

corresponding to the existence of a neutral element for the group G (Olver (1989)). The solution of the system (24) and (25) corresponds to the one-parameter group of transformations

$$t' = e^\mu t ; \varepsilon' = e^\mu \varepsilon ; z'_k = e^\mu z_k ; \sigma' = e^\mu \sigma ; s' = e^\mu s ; A'_k = e^\mu A_k \quad (26)$$

$$T' = \exp \left(L_W \left(\frac{\Delta H}{R} \exp \left(\frac{\mu T - T \ln(T^*) + \frac{\Delta H}{R}}{T} \right) \right) - \mu + \ln(T^*) - \frac{\Delta H}{RT} \right) \quad (27)$$

where $L_W(x)$ is the Lambert function¹ and T^* is the non-dimensional temperature defined by

$$T^* = \frac{T}{T_0} \quad \text{with} \quad T_0 = 1\text{K} \quad (28)$$

Inverting Equ. (27), it is possible to express the group parameter μ vs T and T' as

$$\mu(T, T') = \frac{\Delta H(T - T')}{RTT'} + \ln \frac{T}{T'} \quad (29)$$

Equations (26) and (27) imply that if the set of functions

$$\varepsilon(t) , T(t) = T , z_k(t) , \sigma(t) , s(t) , A_k(t) \quad | \quad k = 1..N \quad (30)$$

¹ defined as the solution of the equation $L_W(x)e^{L_W(x)} = x$

(the temperature is considered as a constant) satisfies the governing equations (12), then the new set of functions given by

$$\begin{aligned}
\varepsilon'(t') &= e^\mu \varepsilon(t) = e^\mu \varepsilon(e^{-\mu}t') \\
T' &= \exp \left(L_W \left(\frac{\Delta H}{R} \exp \left(\frac{\mu T - T \ln(T^*) + \frac{\Delta H}{R}}{T} \right) \right) - \mu + \ln(T^*) - \frac{\Delta H}{RT} \right) \\
z'_k(t') &= e^\mu z_k(t) = e^\mu z_k(e^{-\mu}t') \quad | \quad k = 1..N \\
\sigma'(t') &= e^\mu \sigma(t) = e^\mu \sigma(e^{-\mu}t') \\
s'(t') &= e^\mu s(t) = e^\mu s(e^{-\mu}t') \\
A'_k(t') &= e^\mu A_k(t) = e^\mu A_k(e^{-\mu}t') \quad | \quad k = 1..N
\end{aligned} \tag{31}$$

also satisfies the constitutive equations (12) for all values of the group parameter μ . It is then possible to highlight an invariance property for the material: noting $\varepsilon_T(t)$ and $\sigma_T(t)$ the strain and the stress values at a given time and temperature, let us define the secant modulus E_s at the time t and for the temperature T by

$$E_s(t, T) = \frac{\sigma_T(t)}{\varepsilon_T(t)} \tag{32}$$

Taking (32) and (31) into account, and considering that the functions $\sigma(t)$ and $\varepsilon(t)$ are associated with T whereas the functions $\sigma'(t')$ and $\varepsilon'(t')$ are associated with T' , one may deduce that

$$E_s(t, T) = \frac{\sigma_T(t)}{\varepsilon_T(t)} = \frac{e^\mu \sigma_T(t)}{e^\mu \varepsilon_T(t)} = \frac{\sigma'_{T'}(t')}{\varepsilon'_{T'}(t')} = E_s(t', T') = E_s(e^\mu t, T') \tag{33}$$

A logarithmic representation of the first relation of (26) leads to

$$\log t' = \log t + \frac{\mu}{\ln 10} \tag{34}$$

Considering (34), Equ. (33) may then be rewritten in the new form

$$E_s(\log t, T) = E_s\left(\log t + \frac{\mu}{\ln 10}, T'\right) \tag{35}$$

This last relationship means that it is possible to deduce the isothermal curve of the modulus $E_s(t, T')$ at T' from the curve of $E_s(t, T)$ at T by a simple translation along the time axis in the log-log representation. The value of the corresponding shift factor $\mu/\ln 10$ is given by Equ. (29). In the next section, these results will be compared to experimental data of a specific polymer.

5.2 Validation of the group on the basis of experimental data for dry polyamid 66

In order to model isothermal tensile curves, let us rewrite the first constitutive equation in (6) as

$$\Delta_1 = \dot{\sigma} - E_u \dot{\varepsilon} + \sum_{k=1}^N \frac{\sigma_k - p_k^0 E_r \dot{\varepsilon} t}{\tau_k(T)} = 0 \quad (36)$$

where E_r is the relaxed modulus defined by the equality $p_k^0 E_r = b_k^1 c_k = (k = 1..N)$, see Equ. (6)), in which p_k^0 is the weight of the k^{th} dissipation mode given from the fluctuation theory by (Cunat (2001), Cunat (2000))

$$p_k^0 = \frac{\sqrt{\tau_k(T)}}{\sum_{i=1}^N \sqrt{\tau_i(T)}} \quad | \quad k = 1..N \quad (37)$$

Keeping in mind that the overall stress σ can be written as a sum of N partial stresses σ_j associated with the N dissipative and orthogonal modes

$$\sigma = \sum_{j=1}^N \sigma_j = \sum_{j=1}^N b_j^1 z_j \quad (38)$$

one can compute σ (inserting (38) into (36)). In order to simulate a continuous spectrum by means of a discrete analysis, an arbitrary number N of 20 modes has been considered, with relaxations times equally distributed on a logarithmic scale upon $D = 3$ decades in an interval $[\tau_{min}; \tau_{max}]$ (i.e. $\tau_{max}/\tau_{min} = 10^D$):

$$\log \tau_k = \log \tau_{min} + \frac{(k-1)D}{N-1} = \log \tau_{max} - D + \frac{(k-1)D}{N-1} \quad | \quad k = 1..N \quad (39)$$

The parameters E_u , E_r are adjusted independently on the temperature, whereas the maximum relaxation time τ_{max} is adjusted at each temperature. Four experimental and isothermal tensile curves obtained by Ehrenstein (Ehrenstein and Montagne (1999)) at temperatures between 393K and 454K for dry polyamid 66 (PA66) and the corresponding theoretical modelling (equation (36)) are given in Figure 4. The experimental and theoretical secant moduli $E_s(t)$ versus time at different temperatures T are also represented (see Figure 5). Equation (35) allows to obtain a master curve by translating each curve along the time axes (Figure 6). Using relation (11) (where $\Delta H = \Delta H_j$, $j = 1..N$) and the discrete relaxation times given in (39), one further identifies the value of the free activation enthalpy $\Delta G_j = \Delta H - T\Delta S_j$ for each mode associated with the four temperatures from $T = 393\text{K}$ to 453K , according to the relation

$$\Delta G_j = RT \ln \left(\frac{kT}{h} \tau_j \right) \quad (40)$$

Finally, a linear interpolation of $\Delta G_j = \Delta H - T\Delta S_j$ vs T leads to the value of ΔH . The mean value (that will be discussed in the concluding remarks) obtained from this method is $\Delta H = 13620 \text{ J.mol}^{-1}$, allowing the computation of a theoretical shift factor $\mu/\ln 10$ (Equ. (29)) between two isothermal tensile curves at T and T' . The theoretical shift factors have been compared to the factors measured experimentally at T and T' for the secant modulus (Figure (7)). From Figure 7, one concludes that Equ. (29) may be considered as a good approximation of the experimental homothetic factor.

5.3 Comparison to the Williams-Landel-Ferry empirical law

It is possible to compare the shift factor $\mu/\ln 10$ given by relation (29) to the Williams, Landel and Ferry formulation (see e.g. Ferry (1980)), which empirically states the following equivalence property satisfied by the secant modulus of relaxation

$$E_s(t, T) = E_s(ta_{T' \rightarrow T}, T') \frac{\rho(T)T}{\rho(T')T'} \quad (41)$$

where $\rho(T)$ denotes the mass density at T , and $a_{T' \rightarrow T}$ a shift factor given empirically by the relation

$$\log a_{T' \rightarrow T} = -\frac{C_1(T' - T)}{C_2 + T' - T} \quad (42)$$

The constants C_1 and C_2 are some coefficients depending on the material. In many cases, it is usually assumed that the ratio $\frac{\rho(T)T}{\rho(T')T'}$ is approximatively equal to 1 (e.g. Hotta and Terentjev (2001), Laot (2001)). As a consequence, one can remark that the parameter $\mu(T, T')/\ln 10$ of the group corresponding to Equ. (29) can exactly be identified to the coefficient $a_{T' \rightarrow T}$ given by the WLF empiric relation. Identifying (33) and (41) with $\frac{\rho(T)T}{\rho(T')T'} = 1$, one actually obtains $a_{T' \rightarrow T} \equiv e^{\mu(T, T')}$, which may be rewritten as

$$\frac{\mu(T, T')}{\ln 10} \equiv \log a_{T' \rightarrow T} \Rightarrow \frac{\Delta H(T - T')}{RTT' \ln 10} + \frac{1}{\ln 10} \ln \frac{T}{T'} \equiv -\frac{C_1(T' - T)}{C_2 + T' - T} \quad (43)$$

Consequently, considering the two WLF coefficients C_1 and C_2 (relation (42)) as unknowns, the DLR shift factor given by

$$\frac{\mu(T, T')}{\ln 10} = \frac{\Delta H(T - T')}{RTT' \ln 10} + \frac{1}{\ln 10} \ln \frac{T}{T'} \quad (44)$$

may be fitted to the expression of the WLF shift factor (42) using the least squares method. This leads to the following values of the coefficients

$$C_1 = 3, C_2 = 530\text{K} \quad (45)$$

and the DLR and WLF shift factors compared on Figure 8 are seen to fit well together.

5.4 Discussion

If the activation enthalpy ΔH is not the same for all the modes, then the particular group given by Equ. (23) does not represent a symmetry for the constitutive equations. A physical interpretation of this breaking of symmetry may be due to the temperature which only affects the kinetics of the reactions described by the internal variables \mathbf{z} . Furthermore, the linear interpolation $\Delta G_j = \Delta H - T\Delta S_j$ is possible if ΔH and ΔS_j are temperature independent. In our opinion, this assumption is acceptable for most of time-dependent materials, especially in the case of monotonic and uniaxial loading conditions. For cyclic loading paths, Mrabet et al. (2005) showed that the consideration of a non-linear dependence of the time spectrum $\{\tau_k, k = 1..N\}$ with the loading conditions is unavoidable to capture well the mechanical behaviour of the tested polymer. The values of $C_1 = 3$ and $C_2 = 530\text{K}$ previously identified are quite different from the universal values $C_1 = 17.4$ and $C_2 = 51.6\text{K}$ proposed by Ferry (Ferry (1980)) and suitable for several polymers when the chosen reference temperature is the glass transition temperature. However, the author also showed that a better adjustment can be obtained when these coefficients are specially chosen for each polymer. From Ferry (Ferry (1980)) and e.g. Hotta (Hotta and Terentjev (2001)) *et al* or Laot (Laot (2001)), the “typical” values of the WLF coefficients are in the following ranges

$$2 \lesssim C_1 \lesssim 30 \quad (46)$$

$$35\text{K} \lesssim C_2 \lesssim 220\text{K}$$

We surmise that the difference between (46) and the present values $C_1 = 3$ and $C_2 = 530\text{K}$ is due to the independence of E_u and E_r with respect to the temperature. This assumption can be considered as true only in a small range of temperature above the glass transition (Ehrenstein and Montagne (1999)). It can be shown that a better fit of experimental data with Equ. (36) can be obtained, considering a small decrease of E_u and E_r with the temperature. The value of ΔH may also be compared with the value calculated using WLF model, for which the apparent activation energy E_a is defined as (e.g. Laot (2001))

$$\frac{E_a}{R} = \frac{d(\ln a_{T' \rightarrow T})}{d\left(\frac{1}{T'}\right)} = \frac{T'^2 C_1 C_2 \ln 10}{(C_2 + T' - T_g)^2} \quad (47)$$

where $T_g = 363\text{K}$ is the glass transition temperature of the considered polymer. From the correspondence between DLR and WLF models written as

$\ln a_{T' \rightarrow T} \equiv \mu(T, T')$, one obtains by a derivation of (29) with respect to $1/T'$

$$\frac{d\mu(T, T')}{d\left(\frac{1}{T'}\right)} \equiv \frac{d(\ln a_{T' \rightarrow T})}{d\left(\frac{1}{T'}\right)} \Rightarrow \Delta H \equiv \frac{RT'^2 C_1 C_2 \ln 10}{(C_2 + T' - T_g)^2} - RT'^* \quad (48)$$

where T'^* is the non dimensional value of T' , coming from the derivation of the logarithmic term of (29). One can notice that this WLF equivalent value of ΔH increases with the temperature T' , from a value of 12038 J.mol⁻¹ for $T' = 413\text{K}$ to a value of 12522 J.mol⁻¹ for $T' = 453\text{K}$. These values are close to the estimated value $\Delta H = 13620$ J.mol⁻¹ obtained for the DLR approach.

A discussion about the determination of the theoretical shift factor μ is also in order: it results from the exponentiation of a particular generator the components of which satisfy the determining system. In the present range of mechanical loading, the particular solution obtained with the group of dilatation for t (that is, with $\xi = t$) is found to be unique for the considered constitutive equations. However, for other testing conditions (e.g. different loading paths: relaxation, creep, etc...), the constitutive equations may not be adequate to reproduce experimental data and we cannot stipulate *a priori* that the solution (23) will still be valid. More generally, for a given set of constitutive equations, one could identify several symmetry groups each having a generator of the form $t \frac{\partial}{\partial t} + \mathbf{v}'$. In this case, the problem of discriminating one or another solution is not trivial and still open.

From a broader point of view, the powerfullness of the present methodology based on symmetry groups is to provide a mathematical frame to establish and predict master curves, as done in this work for the time-temperature superposition principle. Indeed, finding the Lie symmetries of a given set of constitutive equations allows the writing of mapping rules that leave its solution invariant. More precisely, the fundamental ideas of the present contribution may be summarized in the following steps:

- find a suitable set of constitutive equations that fit the experimental data obtained at given levels of some parameters (e.g. temperature, strain rate...),
- for these equations, write and solve the corresponding determining system to obtain the Lie symmetries,
- extrapolate or interpolate experimental data for other values of the loading parameters.

One should keep in mind that the extrapolation could be debatable if different internal processes are involved in the considered range of the controlled variables.

6 Conclusion

The general programme of exploiting the postulated Lie group structure of the constitutive response of dissipative materials to predict the material's response when some control parameters vary (strain rate, temperature) has been followed in the present contribution. A set of isothermal viscoelastic-like equations has been identified and validated from experimental data on the dry polyamid (PA66), involving a temperature-dependent spectrum of relaxation times and assuming constant apparent activation enthalpy and entropy. It has been shown that the symmetry analysis of the constitutive equations written within a thermodynamical framework of relaxation leads to a time-temperature equivalence principle. Thereby, the characteristic system allowing the determination of the corresponding Lie symmetries has been formulated and a particular solution has been highlighted, based on a specific algorithm focusing on three classical groups (identity, translation, dilatation). The exponentiation of the group generator leads to the formulation of a theoretical shift factor that reveals the existence of a master curve, encapsulating the material's response for the considered range of temperatures. This master curve can be obtained by translating curves of the material response in terms of the secant modulus $E_s(t, T)$ at different temperatures along the time axis in a logarithmic representation. It has been shown that the theoretical expression of the predicted shift factors and the Williams-Landel-Ferry empirical relation exhibit similar evolutions in the considered range of temperatures. Works to extend the approach to cyclic loadings paths and to validate it on experimental tests are in progress.

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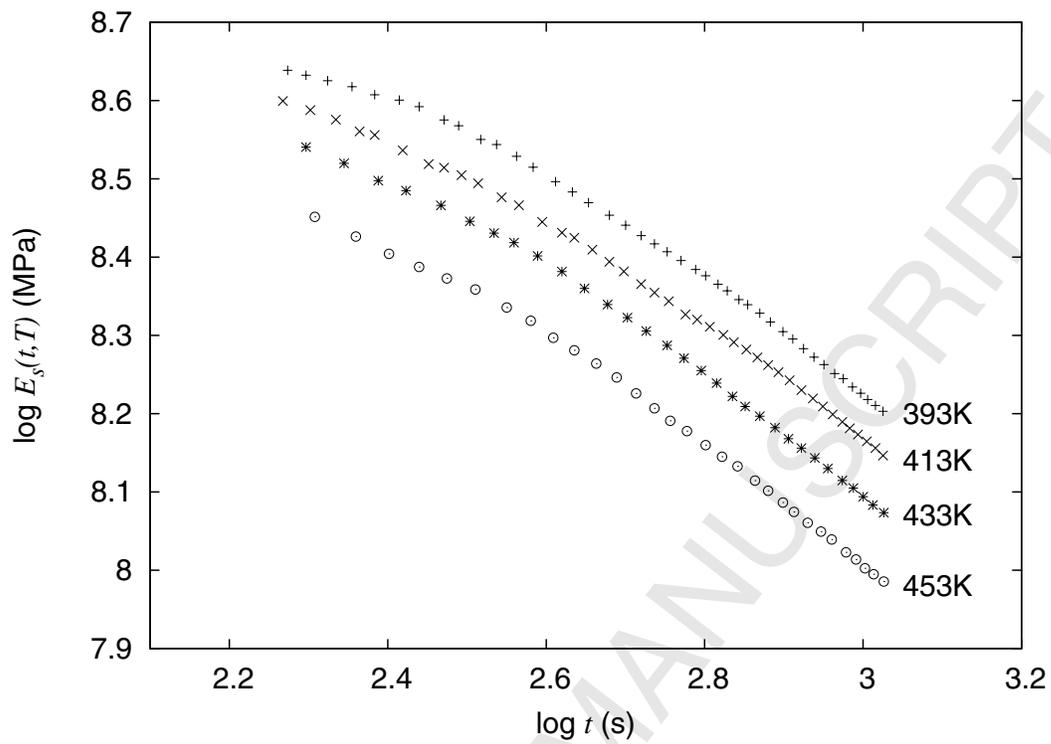


Figure 1. Experimental secant modulus $E_s(t, T)$ vs time t (log-log representation) for PA66 at different temperatures.

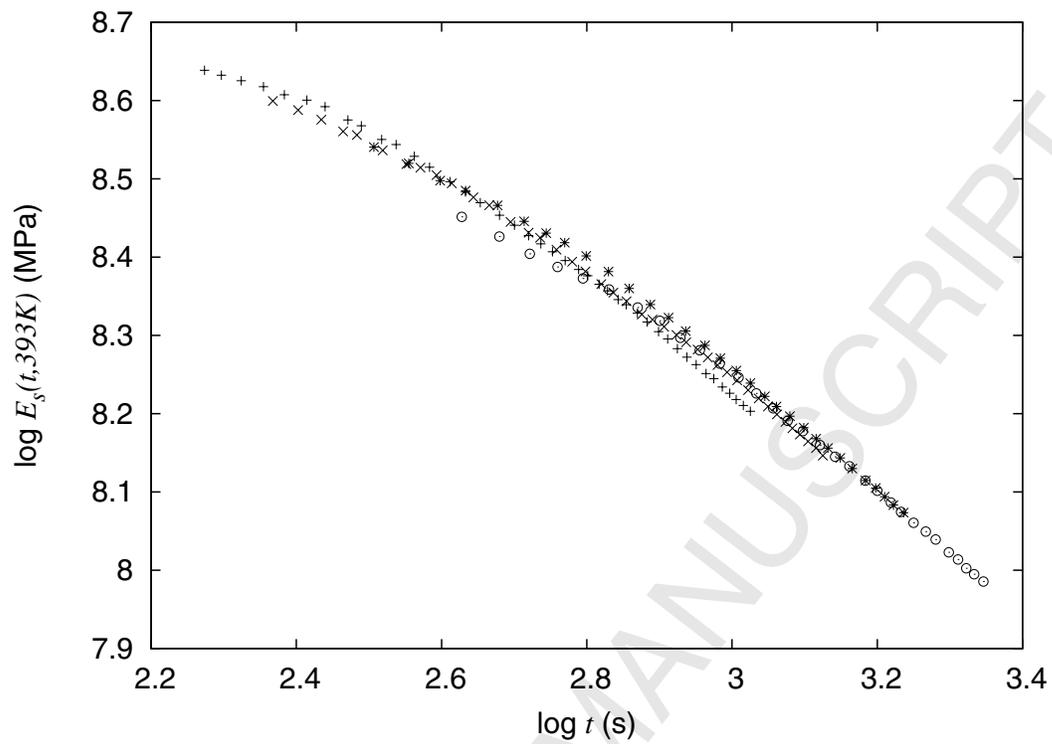


Figure 2. Master curve obtained at 393K by translation of curves of Figure 1 along the time axis.

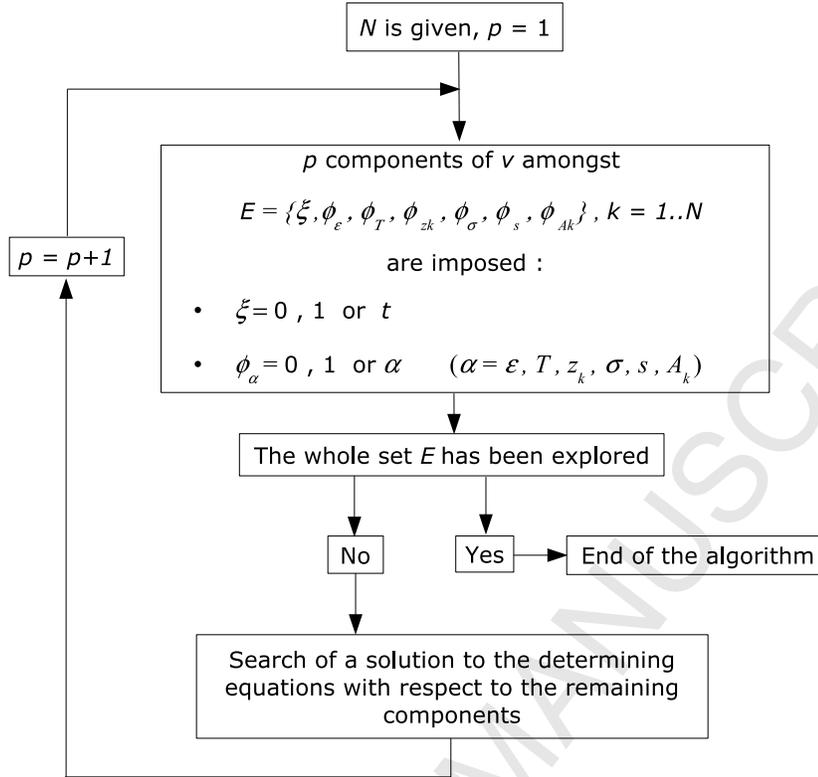


Figure 3. Algorithm to partially solve the determining equations.

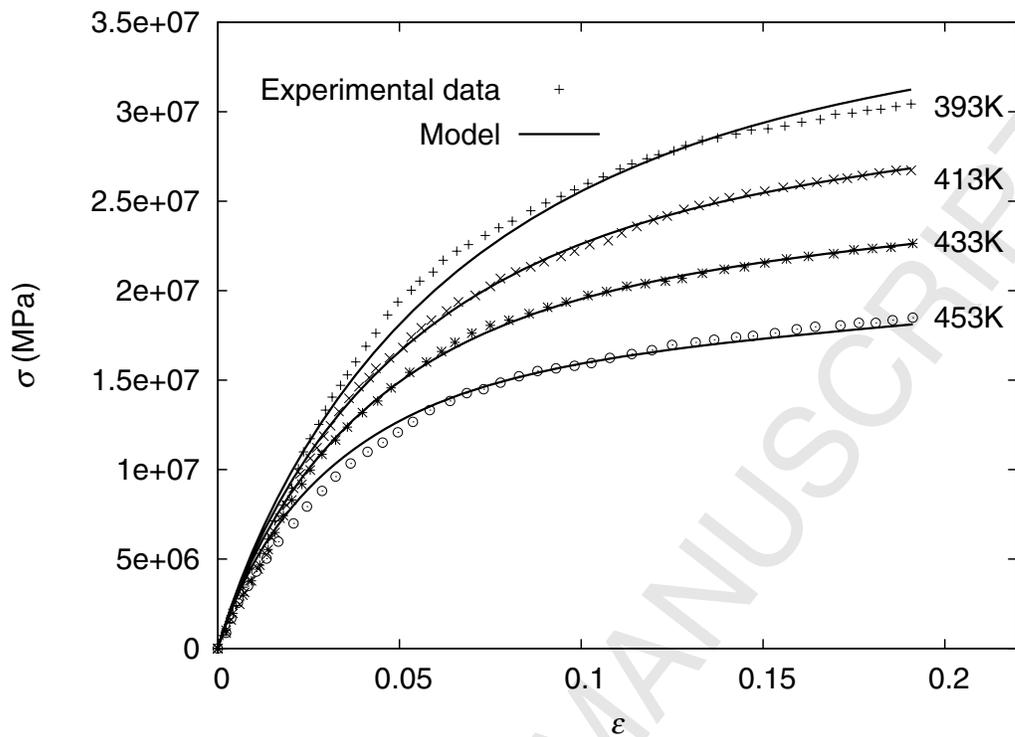


Figure 4. Experimental and DNLr simplified version (called DLR) stresses (see Equ. 36) vs strain curves for PA66 at different temperatures, $\dot{\epsilon} = 0.00018 \text{ s}^{-1}$.

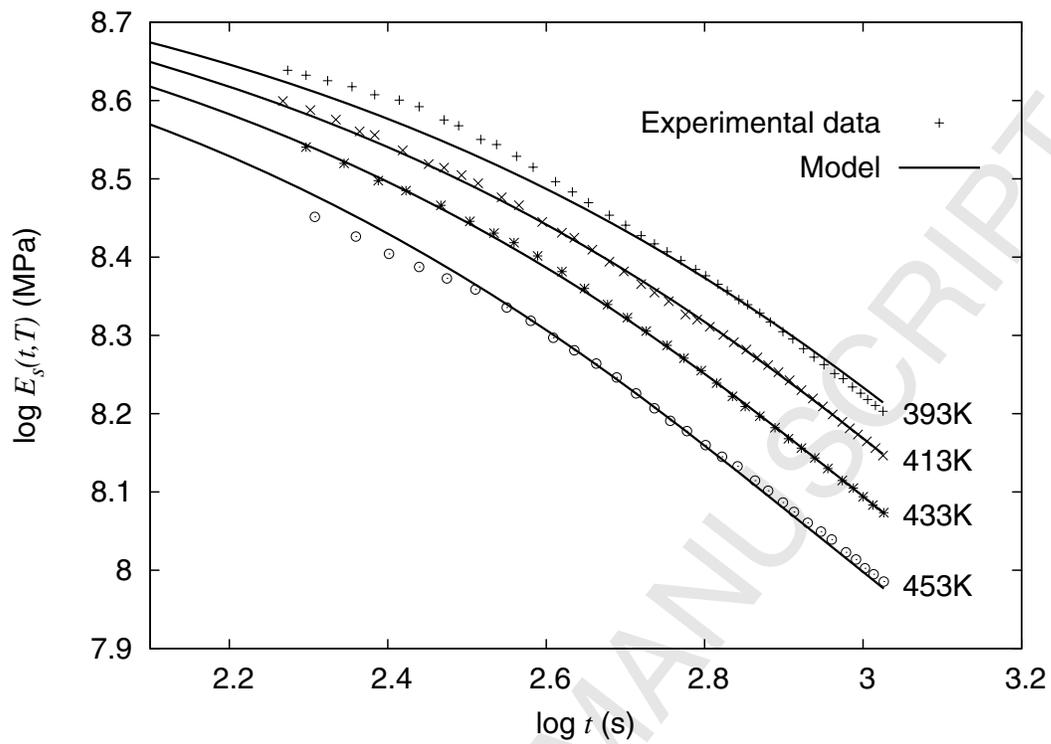


Figure 5. Experimental and modelling secant modulus $E_s(t, T)$ (see Equ. 32) vs time for different temperatures.

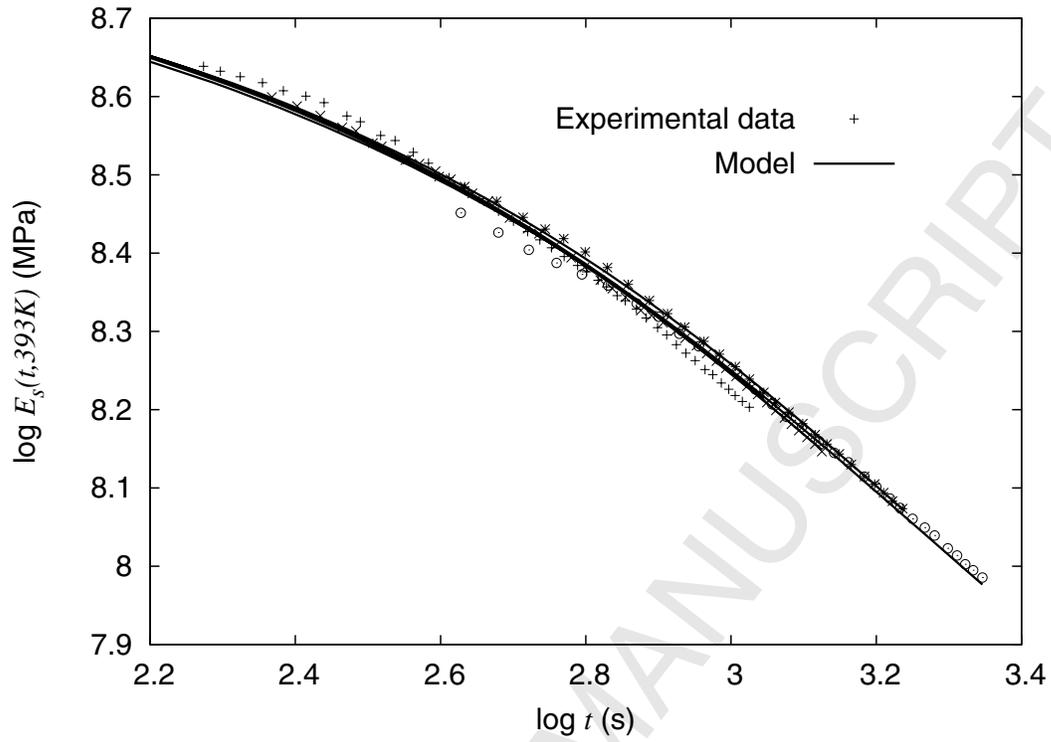


Figure 6. Experimental and modelling master curves for the secant modulus obtained from a time shift (see Equ. (35)).

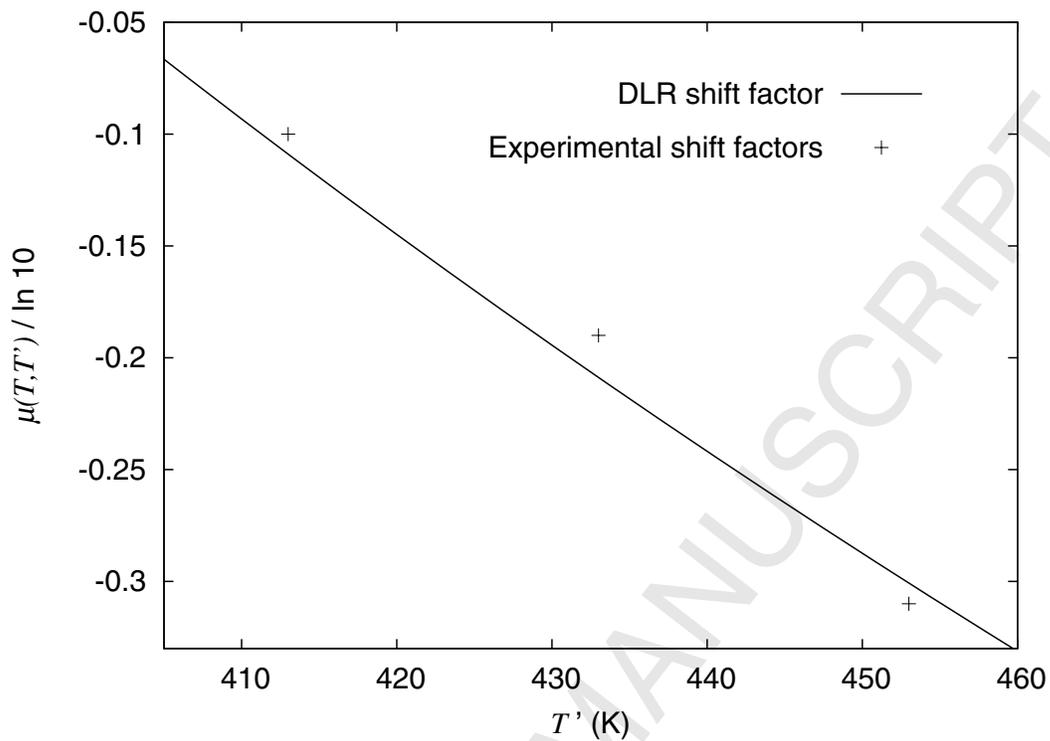


Figure 7. Comparison between the DLR shift factor $\mu(T, T')/\ln 10$ (Equ. (44)) and the experimental shift factors measured for the three values $T' = 413\text{K}$, $T' = 433\text{K}$, $T' = 453\text{K}$, assuming $T = 393\text{K}$.

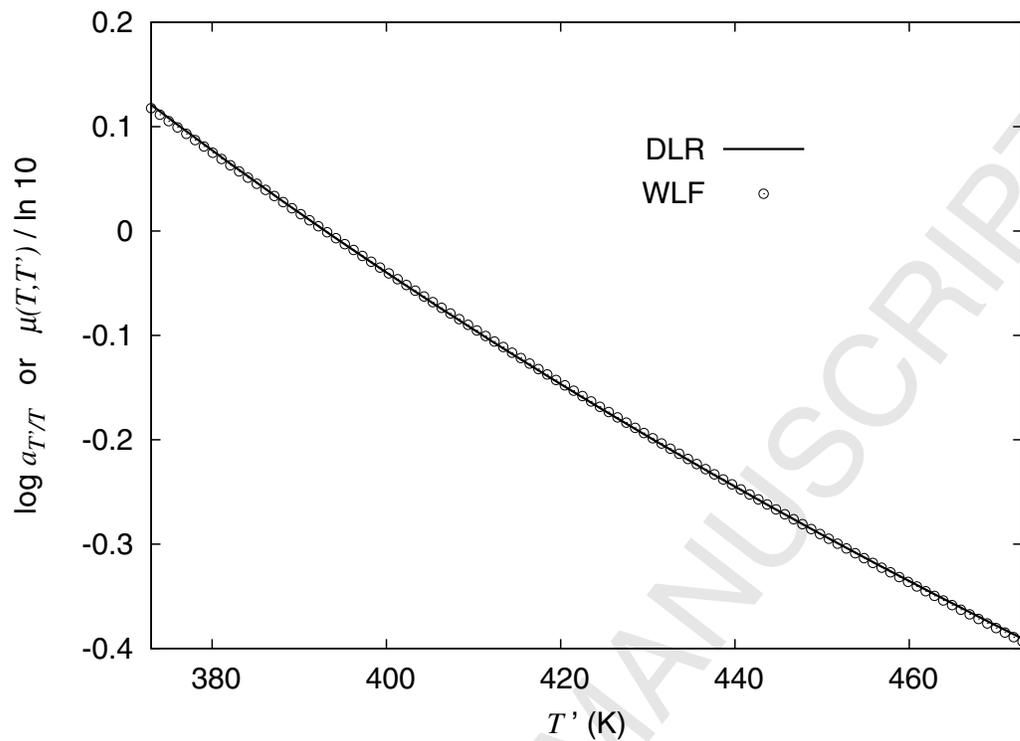


Figure 8. Comparison between the DLR shift factor $\mu(T, T')/\ln 10$ (Equ. (44)) and the WLF shift factor $\log a_{T' \rightarrow T}$ (Equ. (42)) vs T' for $T = 393\text{K}$.