# MULTI - SCALE MODELING OF TENSILE RELAXATION BEHAVIOUR OF SEMI-CRYSTALLINE POLYMERS BY DISTRIBUTION OF NONLINEAR RELAXATION APPROACH

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الملخص

يركز هذا البحث على دراسة ومحاكاة السلوك الميكانيكي لبوليمر البولي إيثيلين العالي الكثافة (HDPE) من خلال محورين. الجزء الأول من الدراسة يتضمن دراسة عملية للسلوك اللاخطي واثار الاسترخاء الميكانيكي (Mechanical relaxation) لهذا البوليمر من خلال إجراء مجموعة من اختبارات الشد والضغط الاحادية المحور متضمنة سلسلة من تجارب الاسترخاء (Relaxation tests) عند مستويات انفعال مختلفة، اخذين في الاعتبار ايضا الانفعالات الكبيرة (Large strain). في حين يتضمن الجزء الثاني تطوير نموذج رياضي يهدف لمحاكاة السلوك الميكانيكي للبوليمر تحت ثاتير احهاد الاسترخاء (DNLR) المقارنة بين النتائج النظرية تهدف لدراسة إجراء تعديلات خاصة بنموذج يستخدم علاقات رياضية في الديناميكا الحرارية تهدف لدراسة السلوك اللاخطى لظاهرة الاسترخاء (DNLR)، المقارنة بين النتائج النظرية للنموذج وتلك الموليمر بشكل صحيح.

### ABSTRACT

The aim of the present work is to characterize and model the mechanical behaviour of high density polyethylene (HDPE). Some multiple stress relaxation tests were performed in different sequences of uni-axial tension and compression in large deformation. A non-equilibrium thermodynamic approach, called Distribution of non-linear relaxation (DNLR), is used to model the mechanical behaviour of the polymer in order to predict the experimental results.

The comparisons between the results obtained from the developed model and the experimental data from tensile and relaxation tests demonstrate the ability of this model to correctly describe the nonlinear behaviour of this polymer.

**KEYWORDS**: High Density Polyethylene; Large Strain; Stress Relaxation; Modelling; Thermodynamic Approach

#### **INTRODUCTION**

Of all the semi crystalline polymers, high density polyethylene (HDPE) has received a considerable interest due to the increasing use in various fields of industrial applications, even in the most advanced technology. HDPE pipe has been widely used in potable water, sewer, gas applications for many decades, and its use is steadily increasing. Much research has focused on understanding their nonlinear elastic-viscoplastic behaviour and modelling their mechanical behaviour under different loading conditions [1-4].

Although there are many experimental and mechanical models that have been developed on polymers to characterize the mechanical response at various conditions [1,5-6]. However very limited studies were carried out to investigate the effects of

mechanical relaxation observed during the uniaxial tension and compression in large deformation at different constant strain levels, which can generate very complex memory effects. The modelling of these phenomena would significantly improve the predictive capacities of the constitutive laws.

The aim of the present work is to characterize and model the mechanical behaviour of HDPE. The work consists of two parts: 1) the experimental work which was performed to obtain material data, some relaxation tests were performed in different sequences of uniaxial tension and compression in large deformation; 2) a constitutive model based on the tests data was developed using the thermodynamic approach of nonlinear relaxation phenomena DNLR in order to predict the whole of experimental results.

# **EXPERIMENTAL WORK**

### Material

The material investigated in this study is a high density polyethylene (HDPE), produced by Roechling Company. Its molecular weight distribution is  $M_w = 500 \text{ kg/mol}$ . The glass transition temperature and the melting point are  $-125^{\circ}$ C and  $135^{\circ}$ C respectively. The crystallinity ratio, obtained from differential scanning calorimetry (DSC) and from the x-ray is about 66 %. The density of the material, measured by the hydrostatic weighting is  $\rho=0.964 \text{ g/cm}^3$ .

#### Sample preparation

The tensile specimens were machined from a 30 mm thick wall of HDPE pipe relative to the extrusion direction, following the shape represented in Figure (1). This specific geometry of specimen has been designed, with the median region of cube of 6 mm, in order to control the appearance of necking and to localize the deformation (damage) in the central part where the mechanical variables are determined. The large radius of curvature allows to be freed from the concentrated stresses (free from the stress triaxiality).



Figure 1: General diagram of the Video Traction system, with final geometry of the specimens.

In compression, to avoid the problem of buckling, an anti-buckling system was used, that allow imposing strain up to 0.5 in traction before returning to compression. After machining, the surfaces and edges are polished with several fine emery papers, before any mechanical tests, samples were submitted to annealing heat treatment for 24 hours at 120°C in a vacuum, then they were cooled slowly to obtain a microstructural state without residual stresses.

#### **EXPERIMENTAL RESULTS**

The stress relaxation behaviour of HDPE was characterized at large deformation under uniaxial tension and compression, followed by several relaxation tests performed at different constant strain levels. The experiments were carried out at controlled temperature of 23°C on a universal hydraulic tensile machine (MTS 810) equipped with a system for measuring the true local strain without any contact with the specimen, called Videotraction extensometer Figure (1). This system gives access to the elastoviscoplastic response of polymer under tensile test. All local measurements of true local strain were performed at the neck. Another important feature of the Videotraction is its ability to keep local strain rate constant [7,8].

This technique based on the measurement of local deformation in representative volume element (RVE), followed up by 7 ink markers printed on the tensile specimen surface in the region where necking develops and which is generally characterized by concentrated of deformation. Five makers were aligned along tensile axis and the two others being aligned with the central dot along the transverse axis. The centre of gravity of these markers were analysed during the test by using CCD camera, and image analysis software computes the strain and tress in real time.

All tests were performed at strain rate of 0.001s<sup>-1</sup> with total time of 20 hr corresponding to stress stabilization. Figure (2) shows the relaxation curves and relaxed stress-strain curves at different strain levels in tension. All curves reveal the existence of fast stress relaxation followed by a very slow rate of relaxation. Comparing the results at different strain levels, it can be seen that the relaxation tests at larger strain levels possess a large decrease in stress, during relaxation, than those at lower strain levels. It can be observed from Figure (2b) that after every relaxation period, the stress did not go back to the value corresponding to the strain without relaxation.



Figure 2: Multiple step stress relaxation tests during uniaxile tension: a) - stress-time curve, b) - stress-strain curve, at strain rate of  $0.001s^{-1}$ .

The equilibrium stats are reached if the duration of relaxation periods is infinitely long. Thus, the stresses measured at the termination point of the relaxation periods are values of relaxed state which is not the true thermodynamic equilibrium state. The relaxed state takes the shape of the tensile response curve. This conforms to the observations reported by [9-11]. The relaxed state and equilibrium state will be further developed in the modelling section. The results of the relaxation tests during uniaxiale compression will be presented with the simulation results.

#### MODELING OF MECHANICAL BEHAVIOUR

The mechanical behaviour of semi crystalline polymers is modelled using a nonequilibrium thermodynamic approach called Distribution of Nonlinear Relaxation, DNLR, [12-14]. It is based on the study of the internal rearrangements such as relaxation processes from a thermodynamic point of view; thermodynamic of irreversible processes. It allows describing, even outside of equilibrium, the evolution of a RVE of materials submitted to the controlled perturbation. Based on the chemical reaction of DE DONDER [15] and the generalization of the fundamental Gibbs equation, one can assume the existence of a thermodynamic potential  $\psi = \psi(\underline{\gamma}, \overline{z})$  which completely describe the state of material. This potential depends on the state variables  $\underline{\gamma}$  (controlled variables necessary to characterize the non dissipation evolution of RVE and on the internal microstructural variables  $\overline{Z}$  (dissipative variables which represent the different internal reorganization) associated to their dual forces  $\underline{\beta}$  and  $\overline{A}$ , respectively.

The global response  $\underline{\beta}$  (observable variables) and the thermodynamic forces  $\overline{A}$  (Affinities of DE DONDER) are defined like the first derivatives of the potential  $\psi = \psi(\gamma, \overline{z})$  which directly leads to the following nonlinear incremental law:

$$\dot{\underline{\beta}} = \underline{\underline{a}}^{u} \cdot \underline{\dot{\gamma}} + \underline{\underline{b}} \cdot \dot{\underline{z}}$$

$$\overline{\dot{A}} = -\underline{\overline{\underline{b}}}^{t} \cdot \underline{\dot{\gamma}} - \overline{\underline{g}} \cdot \overline{\underline{z}}$$

$$(1)$$

Where  $\underline{\underline{a}}^{u} = \partial^{2} \psi_{k}(\underline{\gamma}, \overline{z}) / \partial \underline{\gamma}^{2}$  is Tisza's stability matrix which couples the state variables  $\underline{\gamma}$  and  $\underline{\beta}$  to each others.  $\underline{\overline{b}} = \partial^{2} \psi_{k}(\underline{\gamma}, \overline{z}) / \partial \underline{\gamma} \partial \overline{z}$  and  $\underline{\overline{g}} = \partial^{2} \psi_{k}(\underline{\gamma}, \overline{z}) / \partial \overline{z}^{2}$  are the coupling matrixes. The DNLR approach is characterized by the following two original features:

 The distribution of the dissipative modes including nonlinear effects. The spectrum of relaxation time is statistically obtained by using the Prigogine's equipartition of created entropy theorem [16]. In [12], Cunat showed that, this distribution is characterized by the following equations:

$$P_0^j = B\sqrt{\tau_j^r}$$
 and  $\sum_{j=1}^N P_0^j = 1$ , with  $B = \frac{1}{\sum_{j=1}^N \sqrt{\tau_j^r}}$  (2)

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 $\tau_j^r$  represent the relaxation time of the process j,  $P_0^j$  the relative weight of the process j, N number of dissipative modes, B a normalization constant and the index r means relaxed.

ii) - The modeling of the relaxation time based on activation state theory. This theory rests on the existence of a transient state in a complete thermodynamic non-equilibrium state. The relaxation time of process *j* can then write:

$$\tau_j^r = \frac{h}{k_B T} \exp\left(\frac{\Delta F_j^{+,r}}{RT}\right)$$
(3)

Where,  $\Delta F_j^{+,r}$  represents the activation Helmholtz free energy of the spontaneous fluctuation around the relaxed state for the dissipation mode *j*. *h*, *k*<sub>B</sub> and *R* are constants respectively of Plank, Boltzmann and perfect gases. T represents Kelvin temperature. To take into account the nonlinearity for the situations far from the equilibrium, the relaxation times become dependent on the actual state of the continuous media as:

$$\tau_{j} = \frac{h}{k_{B}T} \exp\left(\frac{\Delta F_{j}^{+,r}}{RT}\right) \exp\left(\frac{\Delta \left(\Delta F_{j}^{+}(t)\right)}{RT}\right)$$
(4)

$$\tau^j = \tau^r_j a_f(t) \tag{5}$$

With 
$$a_f^j(t) = \exp\left(\frac{-V^+(\beta - \beta^r)}{RT}\right)$$
 and  $\tau_j^r = \frac{h}{k_B T} \exp\left(\frac{\Delta F_j^{+,r}}{RT}\right)$ , where  $a_f$  represent the

nonlinearity shift factor, which is the same for all processes  $a_f^j(t) = a_f(t)$ , associated to the activation volume average  $V^+$ . The general constitutive equation of DNLR is given by

$$\underline{\dot{\beta}} = \sum_{j=1}^{N} \underline{\beta}^{j} = \sum_{j=1}^{N} \left( P_{0}^{j} \underline{a}^{u} \cdot \underline{\dot{\gamma}} - \frac{\underline{\beta}^{j} - \underline{\beta}^{j,r}}{a(t)\tau_{j}^{r}} \right)$$
(6)

Where, u and r denote the instantaneous and relaxed values, respectively.

In the field of mechanical engineering, considering the case of tensile test,  $(\underline{\dot{\gamma}} \mapsto \underline{\dot{\epsilon}}, \underline{\dot{\beta}} \mapsto \underline{\dot{\sigma}})$ , at imposed strain  $\dot{\epsilon}$ , the constitutive equation of DNLR approach can be written in the following incremental equation:

$$\dot{\sigma} = \sum_{j=1}^{N} \dot{\sigma}^{j} = \sum_{j=1}^{N} \left( P_0^{j} E^{u} \dot{\varepsilon} - \frac{\sigma^{j} - P_0^{j} \sigma^{j,r}}{a_f(t) \tau_j^r} \right)$$

$$\tag{7}$$

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Where,  $(P_0^j E^u \dot{\varepsilon})$  represents the instantaneous response for a mode j,  $E^u$  is a Young's modulus, and  $(\sigma^j - P_0^j \sigma^{j,r} / a_f(t) \tau_j^r)$  represent the dissipation part of response for a mode j, which is governing the evolution of relaxed state. To complete the modeling, it is necessary to describe the definition and the role of the relaxed state  $\sigma^r$  and the relaxation times  $\tau^j$  (in particular the shift factor  $a_f(t)$ ).

### Application of DNLR to the mechanical behaviour of HDPE

The mechanical behaviour of semi crystalline polymers as characterized by elasto-viscoplastic deformation is intimately related to their two phase microstructures, constituted by amorphous and crystalline phases. The elasto-viscoplastic behaviour strongly depends on the degree of cristalinety, the initial crystallographic texture and molecular orientation, as well as the evolution of this microstructure during the deformation [1,17-19]. Thus, in our case of HDPE, one must take into account the existence of two phases which is the key in determining the overall macroscopic mechanical behaviour of HDPE.

Based on the deformation mechanisms of HDPE [1,18,20-22], the constitutive model can be obtained after considering three distinct internal reorganization families. The first family is denoted  $\bar{z}$  and it is related to the relaxation mechanisms that depend on the imposed strain rate (viscous process), mainly due to the amorphous phase. The other one is denoted ( $\bar{\rho}$ ) for the mechanisms, non viscous, that are independent of this strain rate due to the fragmentation of the crystallites (plastic process). A third family ( $\bar{e}$ ) is corresponding to the phenomena of damage by cavitation.

In the present work, the case of unidirectional mechanical tests was considered. One can chose, thus, a new thermodynamic potential as  $\phi = \phi(\varepsilon, T; \overline{z}; \overline{\rho}; \overline{e})$ . The system of constitutive equations that take into account these three types of internal reorganizations can be written in the DNLR form as:

$$\begin{pmatrix} \dot{\sigma} \\ -\bar{A}_{z} \\ -\bar{A}_{\rho} \\ -\bar{A}_{e} \end{pmatrix} = \begin{pmatrix} E^{u} & b_{\varepsilon z} & 0 & b_{\varepsilon e} \\ b_{\varepsilon e} & g_{z z} & g_{z \rho} & 0 \\ 0 & g_{\rho z} & g_{\rho \rho} & 0 \\ b_{e\varepsilon} & 0 & 0 & g_{ee} \end{pmatrix} \begin{pmatrix} \dot{\varepsilon} \\ \bar{z} \\ \bar{\rho} \\ \bar{e} \end{pmatrix}$$
(8)

The experimental observations of ROGUET et al [11] and MRABET et al [9] show that, for semi crystalline polymer, the relaxed state differs from the true thermodynamic equilibrium state. The relaxation state, which is accessible via relaxation test, tends to the true equilibrium state after a very long relaxation time. Note that, the shapes of relaxed stress – strain curve and the tensile response curves are similar, with the fact that the relaxed stress is independent of the applied strain rate.

Thus to complete the modeling, one admit that the spectrum of the relaxation time associated to the dissipation of viscoplastic modes exhibits the same spectrum of damage modes, and the fragmentation of crystallites which occurs much later on the time scale depending on another spectrum. These observations and hypotheses, with the analysis steps of DNLR approach (presented in details in [14,23], lead to the following differential equation:

$$\dot{\sigma} = \sum_{j=1}^{N} \dot{\sigma}^{j} = E^{u} \dot{\varepsilon} - \sum_{j=1}^{N} \frac{(\sigma_{1}^{j} - P_{j}^{0} \sigma^{j,r})}{\tau_{j}^{r}}$$
(9)

The relaxed stress evolution is governed by the following relation in DNLR form as:

$$\dot{\sigma}^{r} = \sum_{j=1}^{N} \dot{\sigma}^{j,r} = E^{r,eff} \dot{\varepsilon} - \sum_{j=1}^{N} \frac{(\sigma^{j,r} - P_{j}^{r} \sigma^{j,eq})}{\tau_{j}^{eq}}$$
(10)

Where  $E^u$  is the instantaneous modulus of elasticity,  $E^{r,eff}$  the damaged modulus of elasticity at relaxed state.  $\sigma^r$  and  $\sigma^{eq}$  are respectively the relaxed and equilibrium stress, corresponding to their relaxation time  $\tau_j^r$  and  $\tau_j^{eq}$  of the j<sup>th</sup> mode. The global response of the material is the sum of each modal stress represented by  $\sigma^j$ . The weight of each mode is obtained by  $p_j^r = p_j^0 + (p_j^u - p_j^0)/2$ , with  $p_j^u = 1/N$  [9].

One of the objectives in this modeling is to take into account the effect of strain rate, with respect the independency of the relaxed state of the strain rate which agrees with the experimental results. We propose to introduce this effect in the nonlinearity shift factor,  $a_v(\dot{\varepsilon})$  which will take place in both  $\tau_j^r$  and  $\tau_j^{eq}$ . The relaxation spectrums which control the phenomenon of relaxation from the instantaneous state to the relaxation state and from the relaxation state to the equilibrium state are:

$$\tau_{j}^{r} = \frac{h}{k_{B}T} \exp\left(\frac{\Delta F^{+}}{RT}\right) \exp\left(\frac{-V\left|\sigma - \sigma^{r}\right|}{RT}\right) \left(\frac{\dot{\varepsilon}_{0}}{\left|\dot{\varepsilon}\right|}\right)^{1/m}$$
(11)

$$\tau_{j}^{eq} = \frac{h}{k_{B}T} \exp\left(\frac{\Delta F^{+,eq}}{RT}\right) \exp\left(\frac{-V^{eq} \left|\sigma^{r} - \sigma^{eq}\right|}{RT}\right) \left(\frac{\dot{\varepsilon}_{0}}{\left|\dot{\varepsilon}\right|}\right)$$
(12)

With

$$\tau_{\max}^{r} = \frac{h}{k_{B}T} \exp\left(\frac{\Delta F^{+}}{RT}\right) \text{ and } \tau_{\max}^{eq} = \frac{h}{k_{B}T} \exp\left(\frac{\Delta F^{+,eq}}{RT}\right)$$
(13)

Where  $\exp\left(-V\left|\sigma - \sigma^{r}\right|/RT\right)$  and  $\exp\left(-V^{eq}\left|\sigma^{r} - \sigma^{eq}\right|/RT\right)$ , the nonlinearity shift factor  $a_{f}(t)$ .

The term  $(\dot{\varepsilon}_0/|\dot{\varepsilon}|)^{l/m}$  represents the effect of strain rate,  $a_v(\dot{\varepsilon})$ , m is the strain rate sensitivity factor. Indeed m=1 when the material behaviour is independent of strain rate as in the relaxed state.  $\dot{\varepsilon}_0$  is the critical strain rate below which the tensile behaviour is no more dependent on the strain rate [11].  $V = V_0 \exp(k_1 \varepsilon^{k_2})$ , where  $V_0$  is the activation volume which increasees with deformation (damage effect),  $k_1$  and  $k_2$  are the

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parameters.  $V^{eq}$ , the activation volume which is related to the fragmentation /orientation mechanisms of crystallites lamellae.

The modeling of equilibrium stress,  $\sigma^{eq}$ , is based on a statistical model with eightchain as proposed by Arruda and Boyce [24], which is related to hyperelastic hardening at large strain of rubber and other polymers, and due to changes in molecular chains configuration.

$$\sigma_{i}^{eq} - \sigma_{j}^{eq} = \frac{Nk_{B}T}{3\lambda_{c}} n^{0.5} \left(\lambda_{i}^{2} - \lambda_{j}^{2}\right) \ell^{-1} \left(\frac{\lambda_{c}}{n^{0.5}}\right), \quad i, \ j = 1, 2, 3$$
(14)

With  $\lambda_1 = \exp(\varepsilon)$ ,  $\lambda_2 = \exp(-\varepsilon/2) = 1/\sqrt{\lambda_1}$ ,  $\lambda_c = \sqrt{\lambda_1^2 + 2\lambda_1^2/3}$ , and  $\ell^{-1}(\lambda_c/n^{0.5})$  is the inverse of the Langevin function. The term  $Nk_BT$  represents the initial shear modulus, and n the number of rigid segments per macromolecular chain [9].

The damage may be represented by an elastic modulus change. In empirical way, the evolution of  $E^{r,eff}$  can be modelled by considering two physical phenomena, the first contribution (microcavities) leading to fall of the elastic modulus and the second representing their increase (reorientation of chains) [5].

$$E^{r,eff} = E^r \left[ 1 - \left[ \alpha_1 \left( 1 - \exp(-\beta_1 \varepsilon_1) \right) - X \ \ell^{-1} \left( \frac{\lambda_c}{n^{0.5}} \right) \right] \right]$$
(15)

The above equation can be written in the following form:

$$E^{r,eff} = E^r \left[ 1 - D \right] \tag{16}$$

Where *D* is the damage variable resulting from the two contributions  $D = D_{cavitation} + D_{orientation}$ , with  $X = \sqrt{\frac{1}{n^{0.5}} \frac{3n - 1}{n - 1}}$ ,  $\alpha_1$  represents the level of maximum damage,  $\beta_1$  is a parameter to be adjusted.

#### **Model Validation**

To demonstrate the ability of the model to predict the elasto-viscoplastic behaviour of HDPE, an explicit integration schema in Matlab was used to numerically integrate our model of nonlinear differential equation. Fourteen parameters must be identified to run the model, the values of the required material parameters for HDPE were obtained using the SiDolo software.  $E^u = 1150$  MPa,  $V_0 = -1254 cm^3/Mol at$ ,  $k_1 = 0.65$ ,  $k_2 = 1.99$ ,  $\tau_{max}^r = 20100$  sec,  $E^{r,eff} = 300$  MPa,  $\alpha_1 = 0.899$ ,  $\beta_1 = 18$ ,  $\tau_{max}^{eq} = 15 \times 10^7$  sec,  $V^{eq} = -520 cm^3/Mol at$ ,  $\dot{\varepsilon}_0 = 10e^{-7}$  sec, m= 0.18,  $Nk_BT = 0.53$  MPa, n= 90. Note that, all simulations were obtained by using the same set of parameters.

Figures (3 & 4) present the simulated stress response of simple relaxation experiments in uniaxial tension and compression at different strain levels. Most features of stress – strain behavior during the tests, initial stiffness, nonlinear response during loading and unloading and hardening zone were well predicted over the complete range of the test program. Figures (3a & 4a) show the model prediction for multi constant strain levels of stress relaxation were in an excellent agreement with experimental observations even through compression tests.



Figure 3: Numerical simulations of multiple step stress relaxation test during uniaxile tension at different strain levels and strain rate of  $0.001s^{-1}$ . a) – stress relaxation -time curve, b) – stress-strain curve.



Figure 4: Numerical simulations of multiple step stress relaxation test during uniaxile compression at different strain levels and strain rate of  $0.001s^{-1}$ . a) – stress relaxation -time curve, b) – stress-strain curve.

### CONCLUSIONS

The relaxation behaviour of high density polyethylene cut out from a thick – walled pipe has been investigated over a range of different strain levels, by using a series of relaxation tests under uniaxial and compression.

In order to describe the nonlinear behaviour of this polymer, an elasto-viscoplastic model for the constitutive behavior of semi-crystalline polymers has been developed. The DNLR approach was used and modiefied. Such model is physically based on a thermodynamic formalism of irreversible process. To take into account both the morphology (amorphous and crystalline phases) and deformation mechanism, a new thermodynamic potential was coupled with DNLR approach. The introduction of two spectrum of relaxation time, allowed to describe the relaxation and equilibrium states. The theoretical simulations have shown the ability of the modified model to correctly describe the experimental observation in large strain, even during the complex loading path.

### Nomenclature

- $\overline{Z}$  Internal (Dissipative) variables
- $\overline{A}$  Affinities (J m<sup>-3</sup>)
- a<sup>u</sup> Tisza's stability matrix
- $\overline{\underline{b}}, \overline{\underline{g}}$  Coupling matrixes
- $P^{j}$  Relative weight of the process j
- $\Delta F^+$  Activation Helmholtz free energy (J/mol at)
- *h* Plank's Constant (J  $s^{-1}$ )
- $k_B$  Boltzmann's Constant (J K<sup>-1</sup>)
- *R* Constants of perfect gases (J mol<sup>-1</sup>  $K^{-1}$ )
- *T* Kelvin temperature (K)
- $a_f$  Nonlinearity shift factor
- $V^+$  Activation volume average (cm<sup>3</sup>/Mol at)
- $E^{u}$  Instantaneous modulus of elasticity (MPa)
- $E^{r,eff}$  Damaged modulus of elasticity at relaxed state (MPa)
- $V_0$  Initial activation volume (cm<sup>3</sup>/Mol at)
- $k_1$ ,  $k_2$  Material's parameters
- $Nk_BT$  Initial shear modulus (MPa)
- n Number of rigid segments per macromolecular chain
- *D* Damage variable

#### Greek symbols

- $\psi$  Thermodynamic potential
- $\dot{\varepsilon}$  Imposed strain rate (s<sup>-1</sup>)
- $\dot{\varepsilon}_0$  Critical strain rate (s<sup>-1</sup>)
- $\sigma$  True stress (MPa)
- $\sigma^r$  Relaxed stress (MPa)

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- $\sigma^{eq}$  Equilibrium stress (MPa)
- $\underline{\gamma}$  Control variables
- $\beta$  Observable variables
- $\tau$  Relaxation time (s)
- $\alpha_1, \beta_1$  Material's parameters

### **Superscripts**

- J associated to mode j
- U referred to instantaneous state
- r referred to relaxed state
- *eq* referred to equilibrium state
- m Strain rate sensitivity factor
- N Number of dissipative modes

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