

A NEW FRAME FOR CONSTITUTIVE MODELING OF VISCO ELASTIC POLYMERS; ACCOUNTING THERMAL EFFECTS AND STRAIN INDUCED CRYSTALLIZATION

N. BILLON^{*} AND J. BIKARD[†]

^{*} Center for Materials Forming (CEMEF)
Mines-ParisTech, UMR 7635
BP 207 06904 Sophia Antipolis, France
e-mail: noelle.billon@mines-paristech.fr

[†] Technyl Innovation Center
R&D Solvay Engineering Plastics
Lab. New Tech – CRTL, 85 rue des Frères Perret BP 62 69192 Saint FONS, France
email: Jerome.bikard@eu.rhodia.com

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Abstract. Modelling the mechanical behaviour of polymers is a nontrivial task. Usual macroscopic approaches that decompose global deformation into three elementary components in a “a priori” manner often results in complex and “of limited efficiency” models. This study deals at promoting another concept of visco-hyper-elasticity for polymers close to T_g without arbitrary decomposition into “viscous” and “elastic” stresses or strains. To achieve that point, a hyper elastic model is extended to account for inelastic processes. Those latter are assumed to result in a kinetics of variation of internal variables that have to be accounted for in the energy balance at any time and that induce time effects in the writing. Variables of interest are related to de entanglement and/or strain induced crystallisation through specific kinetics laws. This version uses Edward-Vilgis’ network theory that depends on four physical parameters: the density of fixed network nodes, the density of sliding nodes or entanglements, a parameter ultimately related to chain extensibility and a parameter ultimately representative for level of freedom of entanglements. The stress is written in the framework of Irreversible Processes Thermodynamics (IPT) and in the frame of large strain approximations. Mechanical problem is coupled to thermal problem using Taylor-Quinney coefficient β . Equations are included in a finite difference code (using a θ -method) to calculate temperature and stress through the central section of a sample. Parameters identification is based on the minimisation of a two objectives cost function that accounted for average axial stress in the section and for surface temperature at this section. This latter was written in a mean-square approach. .

1 INTRODUCTION

Constitutive models for polymers have to combine non linear processes that can be elastic or inelastic, highly sensitive to temperature and to strain-rate and that are, sometimes, ruled by discrete relaxations.

Usual macroscopic approaches that arbitrary decompose global deformation into three elementary components (reversible-instantaneous (elastic part), irreversible-not dependent upon strain-rate (plastic part) and irreversible-dependent upon strain-rate (viscous part), respectively) was extensively applied in that field but generally led to models of limited validity.

An exhaustive review would be a tedious task. Let's only say that mathematical writings were built up, either on the basis of 1D-model, further extended to 3D case, or in the continuum thermodynamics frame, in which global behaviour is ruled by energy potentials and dissipation pseudo-potentials. Whatever the route is and despite of some mathematical differences, basic assumptions were equivalent in the most rigorous of those studies. Visco elasticity was considered combining elastic and viscous elementary elements in more or less sophisticated manners. Nonlinearity was addressed at two levels:

- Important strain-hardening in polymers (sometimes related to strain induced crystallization) was often reproduced introducing various hyper-elastic reversible elements.
- Nonlinear viscous effects were introduced through “non Newtonian pseudo plastic, Eyring or Carreau-like elements” or through phenomenological accountings for disentanglement. The dependence upon strain-rate and temperature was “post-introduced” through the dependence of given variables. Those approaches resulted in numerous parameters that are not that easy to identify without specific protocols and without pre-allocating one element or another to one macroscopic phenomenon.

The present study deals at exploring and promoting another concept hoping a reduction in the number of parameters. Starting point was the fact that it is possible to combine the general rubber hyper elastic theory with some evolution of internal variables, potentially induced by microstructure alteration, to model time effects in the constitutive model. This route was already suggested in a totally independent manner in the past. More precisely, our general goal was to model visco-hyper-elasticity and visco-plasticity of polymers above T_g without arbitrary a priori decomposition into “viscous” and “elastic” stresses or strains. Therefore, a hyper elastic model was extended to account for inelastic processes within the frame of continuum thermodynamics. Dissipative processes were assumed to result of a kinetics of variation of internal variables that had to be accounted for in the energy balance at any time and induce time effects in the writing.

Model was validated in its 1-D form using experimental observations on different polymers. However, it was developed in a much more general 3D form, consistent with the large strain mechanical approach and with continuum thermodynamics.

Present paper intends to remind fundamental aspects of this approach and to illustrate its efficiency for various materials (amorphous, semi crystalline or experiencing stain induced crystallization).

2 THEORETICAL

2.1 Constitutive model [1]

Main hypothesis is that any polymer could be modelled with an equivalent entangled network, at least above or close to Tg. A hyper elastic strain energy density, w , could then be defined that rules the behaviour of the polymer. w -potential depends on temperature, T , and on some variables that reflect the microstructure of the material (m_1, m_2, \dots, m_n) as well as on elastic extension ratios, λ_i^e , or on associated invariants.

During loading, microstructure of the material is altered (disentanglement, crystallisation or crystalline reorganisation), which results in evolution of associated m -variables. This represents a potential change in the energy of the material that has to be compensated for thermodynamics principles to be obeyed. Therefore, some local elastic recovery in the network, $\partial\lambda_i^{re}/\partial t$, have to occur. This is the source of inelastic strain-rate, $\partial\lambda_i^a/\partial t = -\partial\lambda_i^{re}/\partial t$, in the model, i.e. inelastic processes are the fraction of elastic extension that has to be released to compensate change in energy due to microstructural processes. The concept is summarised in Eq. (1):

$$\sum_{j=1}^n \frac{\partial w}{\partial m_j} \frac{\partial m_j}{\partial t} = -\frac{1}{\beta'} \sum_{i=1}^3 \frac{\partial w}{\partial \lambda_i^e} \frac{\partial \lambda_i^{re}}{\partial t} = \frac{1}{\beta'} \sum_{i=1}^3 \frac{\partial w}{\partial \lambda_i^e} \left(\frac{\lambda_i^e}{\lambda_i^a} \frac{\partial \lambda_i^a}{\partial t} \right) \quad \text{with } \beta' \geq 1 \quad (1)$$

where $\partial m_j/\partial t$ is the kinetics of the evolution of m_j -variable. At this point principal elastic extension (e indexes) and principal inelastic extension (a indexes) are assumed to be collinear. β' -parameter, express the fact that part of the released energy could be dissipated into heat (thermo mechanical coupling) or stored via some permanent changes in the microstructure (plastic-like phenomenon).

Edwards-Vilgis' model was chosen as primary network (Eq. (2)) as its efficiency was intensively demonstrated. According to this approach four constitutive parameters are defined. Chains are assumed to have a finite extensibility, which is ultimately controlled by one positive parameter α (0 in the case of a free Gaussian chain). Chains are linked by permanent nodes of density N_c per unit volume and slip links (entanglements) of density N_s per unit volume. Finally, a positive "slipperiness factor", η , is ultimately defined and related to the degree of mobility of slip links. A zero η -value corresponds to permanent nodes. Initial η -value was chosen close to 0.2343 following. So elastic phenomenon are modelled through Eq. (2):

$$w = \frac{N_s^-}{2} \left(\frac{A_{\alpha\eta}}{X_{\alpha\lambda} Y_{\eta\lambda}} Z_{\eta\lambda} + \ln(Y_{\eta\lambda}) + \ln(X_{\alpha\lambda}) \right) + \frac{N_c^-}{2} \left(\frac{(1-\alpha^2)}{X_{\alpha\lambda}} I_1^e + \ln(X_{\alpha\lambda}) \right) \quad (2)$$

$$Y_{\eta\lambda} = 1 + \eta I_1^e + \eta^2 I_2^e + \eta^3; X_{\alpha\lambda} = 1 - \alpha^2 I_1^e; Z_{\eta\lambda} = I_1^e + 2\eta I_2^e + 3\eta^2; A_{\alpha\eta} = (1 + \eta)(1 - \alpha^2)$$

$$I_1^e = \lambda_1^{e2} + \lambda_2^{e2} + \lambda_3^{e2}; I_2^e = \lambda_1^{e2} \lambda_2^{e2} + \lambda_1^{e2} \lambda_3^{e2} + \lambda_2^{e2} \lambda_3^{e2}; I_3^e = \lambda_1^{e2} \lambda_2^{e2} \lambda_3^{e2} = 1$$

where N_s^- and N_c^- are $N_s kT$ and $N_c kT$, respectively, with k the Boltzmann's constant and T , the absolute temperature.

Time dependent effects were introduced in this model through the alteration of parameters, in example an increase in η (disentanglement). Rate of changes were related to the energy that is available in the material in the sense that the more stressed the slip-links the faster the processes (Eq. (3)):

$$\frac{\partial \eta}{\partial t} = \mathfrak{S}(f_s) > 0 \quad (3)$$

$$f_s = \left(\frac{A_{\alpha\eta}}{X_{\alpha\lambda} Y_{\eta\lambda}} Z_{\eta\lambda} + \ln(Y_{\eta\lambda}) + \ln(X_{\alpha\lambda}) \right) - 3 \left[\frac{(1-\alpha^2)}{(1-3\alpha^2)} + \ln(1+\eta) \right] + \ln(1-3\alpha^2)$$

$$\mathfrak{S} = \xi (\exp(f_s - \psi) - 1) \quad \text{if } f_s > \psi, \mathfrak{S} = 0 \quad \text{if } f_s \leq \psi$$

According to the framework of Irreversible Processes Thermodynamics (IPT) and in the frame of large strain approximations the stress is given in Eq.(4) /

$$\sigma = 2F_e \left(\frac{\partial w}{\partial I_1^e} \frac{\partial I_1^e}{\partial C_e} + \frac{\partial w}{\partial I_2^e} \frac{\partial I_2^e}{\partial C_e} + \frac{\partial w}{\partial I_3^e} \frac{\partial I_3^e}{\partial C_e} \right) F_e^T - p'I \quad (5)$$

where p' is an arbitrary pressure due to incompressibility (compressible model will be further presented), F_e is the elastic extension tensor and C_e is the Cauchy-Green stress tensor;

Parameters can depend on temperature and strain-rate but it was possible to combine those two dependences in a unique dependence upon equivalent strain-rate at reference temperature, T_{ref} , as classically defined in the usual WLF's approach [1]. To summarise parameters depends on the fictitious strain-rate:

$$\dot{\tilde{\epsilon}} = a_{T/T_{ref}} \dot{\epsilon}_{eq} = a_{T/T_{ref}} \sqrt{\frac{2}{3} D : D} \quad (6)$$

where D is the total strain-rate tensor. $a_{T/T_{ref}}$ is the so-called shift factor:

$$\log a_{T/T_{ref}} = -\frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (7)$$

C_1 and C_2 are material characteristics that depends on T_{ref} an arbitrary reference temperature.

2.2 Thermomechanical coupling

Thermomechanical coupling was introduced in energy equation (Eq. (8)) in a classical manner accounting for dissipation potential, ϕ_{int} , related to inelastic strain:

$$\rho C_p \dot{T} = \lambda \Delta T + T \frac{\partial \sigma}{\partial T} : D_e + \phi_{int} \quad (8)$$

where D_e is the elastic strain-rate tensor, λ is the heat conductivity, C_p is the heat capacity and ρ the specific mass of the polymer.

Dissipation potential was related to disentanglement (Eq. (3)) and is rewritten as:

$$\phi_{int} = A^{D_v} : D_v + A^\eta \dot{\eta} \geq 0 \quad (9)$$

$$A^{D_v} = 2C_e \frac{\partial w}{\partial C_e} : D_v$$

$$A^\eta = -\frac{\partial w}{\partial \eta} \dot{\eta}$$

where D_v is the inelastic strain-rate tensor. A^{D_v} and A^η are the thermodynamics forces associated to the inelastic deformation process, respectively.

This approach is consistent with Clausius-Duheim inequality and is compatible with the Generalized Standard Materials (GSM) approach. Novelty relies on the fact that the inelasticity results from the consumption of some elastic energy to promote changes in the internal variables.

Eq. (9) depicted the case of an athermal process where there is no heat dissipation. A Taylor-Quinney coefficient β was introduced in the intrinsic dissipation in a general manner making not any assumption concerning its value (Eq. (10)):

$$\phi_{int} = A^{D_v} : D_v + A^\eta \dot{\eta} = \beta (D_e, a_T \dot{\epsilon}_{eq}) A^{D_v} : D_v \geq 0 \quad (10)$$

where $\beta(A^{D_v} : D_v)$ is the energy transformed into heat. Two extreme values for β exist:

- β close to 1 (but not 1): inelasticity is mainly converted into heat;
- $\beta=0$ there is no heat dissipation, inelastic energy is stored in changes in microstructure only.

In consequence, the energy equation can be rewritten as Eq. (11):

$$\rho C_p \dot{T} = \lambda \Delta T + T \frac{\partial \sigma}{\partial T} : D_e + \beta A^{D_v} : D_v \quad (11)$$

2.3 Coupling with strain induced crystallization

Ability of some initially amorphous polymers (such as PET, PLA) to develop semi-crystalline microstructure under mechanical loading above glass transition has been intensively studied. Parallel to crystallisation a spectacular strain-hardening is observed, which an important phenomenon to reproduce in constitutive models is. This latter point was addressed through the models presented here.

A precise experimental protocol, involving exact thermo-mechanical descriptions of the deformation as well as coolings as rapid and as controlled as possible [2], allowed us to conclude that this crystallization does not obey the classical schematic of simple two steps process: nucleation and growth of the spherulites. According to these measurements crystallisation is a more progressive phenomenon with intermediate stages: orientation, lateral packing of the molecules and lamellae formation. Mechanical strain hardening is not due to the appearance of well defined crystals and crystallinity ratio as measured after cooling is not a relevant descriptor for the entities responsible for strain hardening. As a matter of fact, the increase in stress occurs during the very first stage of the crystallisation when only some traces of micelle-like entities can be detected.

It could then be concluded that the occurrence of strain hardening can be due to the extension of chains and the increase in the interaction between molecules. So a concept of locking up of an amorphous network was chosen as a relevant concept for mechanical modelling.

Therefore, within the frame of Edwards & Vilgis' potential, it was assumed that the density of permanent node increased as a function of elastic energy in the material. Parallel to that extensibility of chains increased as a consequence of a lost of conformational freedom. Obviously, disentanglement still exists in not crystalline zones through an increase of η . Eq. (1) could then be rewritten as:

$$\frac{\partial w}{\partial \eta} \frac{\partial \eta}{\partial t} + \frac{\partial w}{\partial N_c} \frac{\partial N_c}{\partial t} + \frac{\partial w}{\partial \alpha^2} \frac{\partial \alpha^2}{\partial t} = \frac{1}{\beta'} \sum_{i=1}^3 \frac{\partial w}{\partial \lambda_i^e} \left(\frac{\lambda_i^e}{\lambda_i^a} \frac{\partial \lambda_i^a}{\partial t} \right) \quad \text{with } \beta' \geq 1 \quad (12)$$

Model can then be tracked as previously and allowed combining inelastic processes due to amorphous phase as well as that induced by the texturation.

3 IDENTIFICATION OF PARAMETERS

Experimental data consisted in tensile and shearing tests where local strain field and surface temperature field were measured. DIC on random painted patterns were used for the former an IR camera allowed the latter. From those measurements local strain and temperature were deduced in the necking zone allowing the extraction of true stress vs. true

strain and surface temperature vs. true strain curves that was used to identify parameters of the model.

To achieve that point the above equations were included in a finite difference code (using a θ -method) to calculate temperature and stress through central section of the sample [3]. Concerning temperature a through the thickness 1D-modelling was used to model the experiments with a convection with surrounding air boundary condition.

In addition, this numerical model was associated to an inverse analysis, based on the simplex algorithm available in MATLAB® software. The identification was based on the minimisation of a two objectives cost function that accounted for average axial stress in the section and for surface temperature at this section. This latter was written in a mean-square approach.

In consequence, parameters to be identified were: mechanical parameters (N_c , N_s , α , η) and parameters controlling evolution of η , N_c and α^2 , parameter β and their dependence upon $\tilde{\epsilon}$ and, finally, h , the convection coefficient. The thermal conductivity, the heat capacity and the density of the material were issued from the literature and were assumed to be constant.

4 CONCLUSION

Using such approach, it is possible to reproduce both the mechanical and thermal properties of the polymer over the wide range of experimental sets using only 12 parameters.

The use of equivalent strain-rate at a reference temperature made it possible to model the behavior of various

It was also possible to reproduce the drastic strain hardening of PET under tensile test performed above T_g (Figure 1) and the change in the inelasticity regime when “crystallization” occurs.

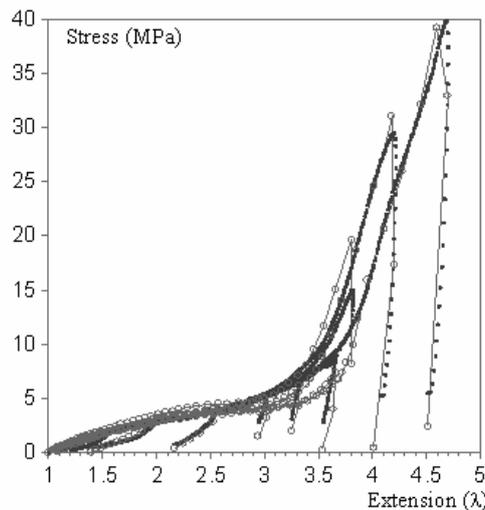


Figure 1 Typical uploading unloading true stress vs. true strain (Henky's strain) at 86 °C and 0.01 s⁻¹. Dots represents experimental data, lines correspond to calculation with the model.

REFERENCES

- [1] Billon, N. New constitutive Modelling for tiem-dependant mechanical behaviour of polymers close to glass transition: Fundamentals and experimental validation. *J. Appl. Polym. Sci.* (2012) **125**:4390-4401.
- [2] Gorlier, E., Haudin, J-M. and Billon, N. Strain-induced crystallisation in bulk amorphous PET under uni-axial laoding. *Polymer* (2001) **42**: 9541-9549.
- [3] Maurel-Pantel, A., Baquet, E., Bikard, J. and Billon, N. Coupled thermomechanical characterisation of polymers based on inverse nalysis and IR measurements. *Applied Mechanics and Materials* (2011) **70**: 393-398.