Supplementary Material

Viscoelastic / hardening parallel model

1. *Introduction*

The model used to fit the large strain extension is based on a combination of a classical model in rheology of non-newtonian polymeric fluids and a model used for crosslinked rubbers. It is clear that there is a certain degree of arbitrariness in that choice and we do not claim that these are the best models available to capture fully the behaviour of these complex deformable materials. Rather they are the simplest combination of models able to capture the physics in a quantitative way (for a given strain rate) and provide physically meaningful parameters to compare materials with a good sensitivity.

The model basically consists of a parallel association of a Maxwell branch with a spring in series with a dashpot for the softening description and a nonlinear spring with a finite extensibility to capture the necessary strain hardening at large strains (Figure A-1). In this study, we have targeted heterogeneous latex based soft adhesives but the methodology used can be generalized to all viscoelastic crosslinked materials.

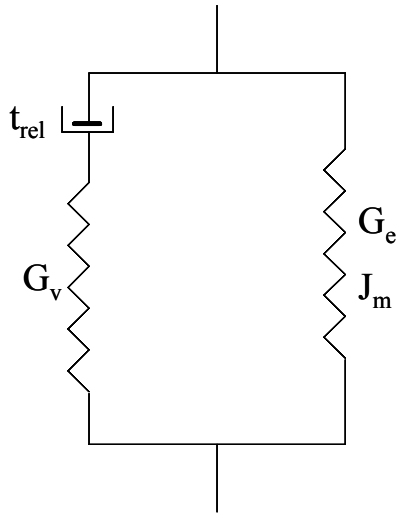

Figure A-1. Schematic of the model used for the mechanical properties of viscoelastic and slightly crosslinked materials.

2. Modeling of the viscoelastic part

The viscoelastic part of the model is an Upper-Convected Maxwell (UCM) model which is a generalization of the Maxwell model for the case of large deformations of polymers. The related constitutive equation can be written as:

$$t_{rel}\frac{\delta \underline{\tau}}{\delta t}+\underline{\tau}=2G_v t_{rel}\underline{D} \qquad \text{Eq. A-1}$$

where $\underline{\tau}$ is the stress tensor, t_{rel} the relaxation time, $\frac{\delta \underline{\tau}}{\delta t}$ the upper convected time derivative of $\underline{\tau}$, G_v the shear modulus of the viscoelastic part and $\underline{D}$ the strain rate tensor:

$\underline{D}=\frac{1}{2}\left(\underline{L}+\underline{L}^T\right)$ where $\underline{L}=\frac{\delta v_j}{\delta x_i}$ is the tensor of velocity derivatives for the fluid.

The upper convected time derivative, also called Oldroyd derivative, is the rate of change of some tensor property of a small element of material written in the Eulerian coordinate system rotating and stretching within the sample. The operator is specified by the following formula:

$$\frac{\delta \underline{A}}{\delta t} = \dot{\underline{A}} - \underline{L}A - A\underline{L}^{T} \qquad \text{Eq. A-2}$$

where $\underline{A}$ is a tensor field, $\dot{\underline{A}}$ the substantive derivative of $\underline{A}$. This upper convected derivative is widely use in polymer rheology for the description of the behaviour of a viscoelastic fluid under large deformations.

In the case of a uniaxial elongation and using the coordinate system shown on Figure , the UCM can be written as the following equation system:

$$\begin{cases} t_{rel}\dot{\tau}_{zz} + (1 - 2t_{rel}\dot{\varepsilon})\tau_{zz} = 2t_{rel}G_v\dot{\varepsilon} \\ t_{rel}\dot{\tau}_{xx} + (1 + t_{rel}\dot{\varepsilon})\tau_{xx} = -t_{rel}G_v\dot{\varepsilon} \\ t_{rel}\dot{\tau}_{yy} + (1 + t_{rel}\dot{\varepsilon})\tau_{yy} = -t_{rel}G_v\dot{\varepsilon} \end{cases} \qquad \text{Eq. A-3}$$

with $\dot{\varepsilon}$ the Hencky's strain rate.

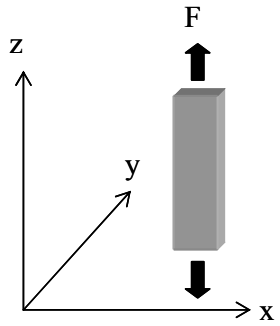

Figure A-2. Definition of coordinate system used in the case of a uniaxial elongational stretching.

Our tensile experiments are performed at constant crosshead velocity implying a constant nominal strain rate but decreasing Hencky's strain rate. However, to provide a simple analytical solution and to avoid the numerical solving of the differential equations, we assumed a constant Hencky's strain rate. This simplification is justified by the fact that the viscoelastic contribution is most important at low strains where the constant Hencky's strain rate approximation should not be bad (an estimate of errors as a consequence of this approximation is discussed later). Analytical solutions for the stress can thus be written as:

$$\begin{cases} \tau_{zz}(t) = \dfrac{2t_{rel}G_v\dot{\varepsilon}}{1-2t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\left(1-2t_{rel}\dot{\varepsilon}\right)\dfrac{t}{t_{rel}}\right)\right) \\ \tau_{xx}(t) = \tau_{yy}(t) = -\dfrac{t_{rel}G_v\dot{\varepsilon}}{1+t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\left(1+t_{rel}\dot{\varepsilon}\right)\dfrac{t}{t_{rel}}\right)\right) \end{cases} \quad \text{Eq. A-4}$$

For $\dot{\varepsilon}$ to be constant, the deformation λ is defined as:

$$\lambda(t) = exp(\dot{\varepsilon}t) \text{thus, } t = \frac{ln\,\lambda}{\dot{\varepsilon}} \quad \text{Eq. A-5}$$

The true stress contribution of the viscoelastic part is:

$$\sigma_{T,v} = \tau_{zz} - \tau_{xx} \quad \text{Eq. A-6}$$

Therefore, the nominal stress evolution as a function of λ can finally be written as:

$$\sigma_{N,v}(\lambda)=\left(\frac{2G_v t_{rel}\dot{\varepsilon}}{1-2t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\frac{1-2t_{rel}\dot{\varepsilon}}{\dot{\varepsilon}t_{rel}}ln\,\lambda\right)\right)+\frac{G_v t_{rel}\dot{\varepsilon}}{1+t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\frac{1+t_{rel}\dot{\varepsilon}}{\dot{\varepsilon}t_{rel}}ln\,\lambda\right)\right)\right).\lambda^{-1} \quad \text{Eq. A-7}$$

$$\sigma_{N,v}(\lambda)=\left(\frac{2G_v t_{rel}\dot{\varepsilon}}{1-2t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\frac{1-2t_{rel}\dot{\varepsilon}}{\dot{\varepsilon}t_{rel}}ln\,\lambda\right)\right)+\frac{G_v t_{rel}\dot{\varepsilon}}{1+t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\frac{1+t_{rel}\dot{\varepsilon}}{\dot{\varepsilon}t_{rel}}ln\,\lambda\right)\right)\right).\lambda^{-1}$$ Eq.

points out the important role played by the $t_{rel}\dot{\varepsilon}$ product. This quantity represents the product of the strain rate and the relevant relaxation time for flow of the polymer and can be viewed as en effective Deborah number called D_e. Hence we can rewrite equation A-7 as:

$$\sigma_{N,v}(\lambda)=\left(\frac{2G_v D_e}{1-2D_e}\left(1-exp\left(-\frac{1-2D_e}{D_e}ln\,\lambda\right)\right)+\frac{G_v D_e}{1+D_e}\left(1-exp\left(-\frac{1+D_e}{D_e}ln\,\lambda\right)\right)\right).\lambda^{-1} \quad \text{Eq. A-8}$$

3. Modeling of the strain hardening part

The strain hardening is captured by a nonlinear spring with a finite extensibility added in parallel to the viscoelastic Maxwell model (Figure). Several limiting chain extensibility constitutive models have been developed on using phenomenological continuum mechanics approaches. One such model, the Gent model for incompressible hyperelastic materials, is particularly simple and has been chosen within the present work. In this model, the strain energy density depends only on the first strain invariant I_1 of the Cauchy-Green strain tensor, is a simple logarithmic function of I_1 and involves just two material parameters, the shear

modulus G_e and a parameter J_m which measures a limiting value for I_1-3 = J_1 reflecting limiting chain extensibility[38].

The strain energy density has been proposed to be as:

$$W = -\frac{G_e}{2} J_m \, ln\left(1 - \frac{J_1}{J_m}\right) \qquad \text{Eq. A-9}$$

In the case of a uniaxial elongation, $J_1 = \lambda^2 + 2/\lambda - 3$. Thus the nominal stress contribution from the elastic part can be written as:

$$\sigma_{N,e}(\lambda) = \left(\frac{G_e}{1 - \frac{\lambda^2 + 2/\lambda - 3}{J_m}} \left(\lambda^2 - 1/\lambda\right) \right) \lambda^{-1} \qquad \text{Eq. A-10}$$

Finally, the overall nominal stress of the system can be written as:

$$\sigma_N(\lambda) = \sigma_{N,v}(\lambda) + \sigma_{N.e}(\lambda) \qquad \text{Eq. A-11}$$

which is used in the fits shown in **Fig. 6** of the main paper.

4. *Constant Hencky strain rate vs. constant nominal strain rate solutions*

It is important to compare numerical modeling and analytical solutions obtained considering a constant Hencky strain rate and a constant nominal strain rate respectively. The same values of G_v and t_{rel} have been used in a numerical simulation program and in the preceding analytical equation

$$\sigma_{N,v}(\lambda)=\left(\frac{2G_v t_{rel}\dot{\varepsilon}}{1-2t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\frac{1-2t_{rel}\dot{\varepsilon}}{\dot{\varepsilon}t_{rel}}ln\,\lambda\right)\right)+\frac{G_v t_{rel}\dot{\varepsilon}}{1+t_{rel}\dot{\varepsilon}}\left(1-exp\left(-\frac{1+t_{rel}\dot{\varepsilon}}{\dot{\varepsilon}t_{rel}}ln\,\lambda\right)\right)\right).\lambda^{-1}$$ (Eq.). Some results obtained are shown on Figure . One can note that the analytical solution tends to predict that the maximum is reached a bit later and at a lower level of stress. This means that the analytical solution underestimates t_{rel} and overestimates G_v. The discrepancy between both solutions seems to be linear with G_v and t_{rel}. To get an idea of the numerical value of t_{rel}, analytical fitting result should be multiplied by 1.9 while for G_v it should be divided by 1.7.

Those differences are however shadowed at large strains when the hardening contribution is added for the calculation of global nominal stress.

Since the main objective was here to compare materials and not to get exact molecular parameters, it makes sense to keep raw values of t_{rel} and G_v obtained from the simple analytical equation as tools for comparisons.

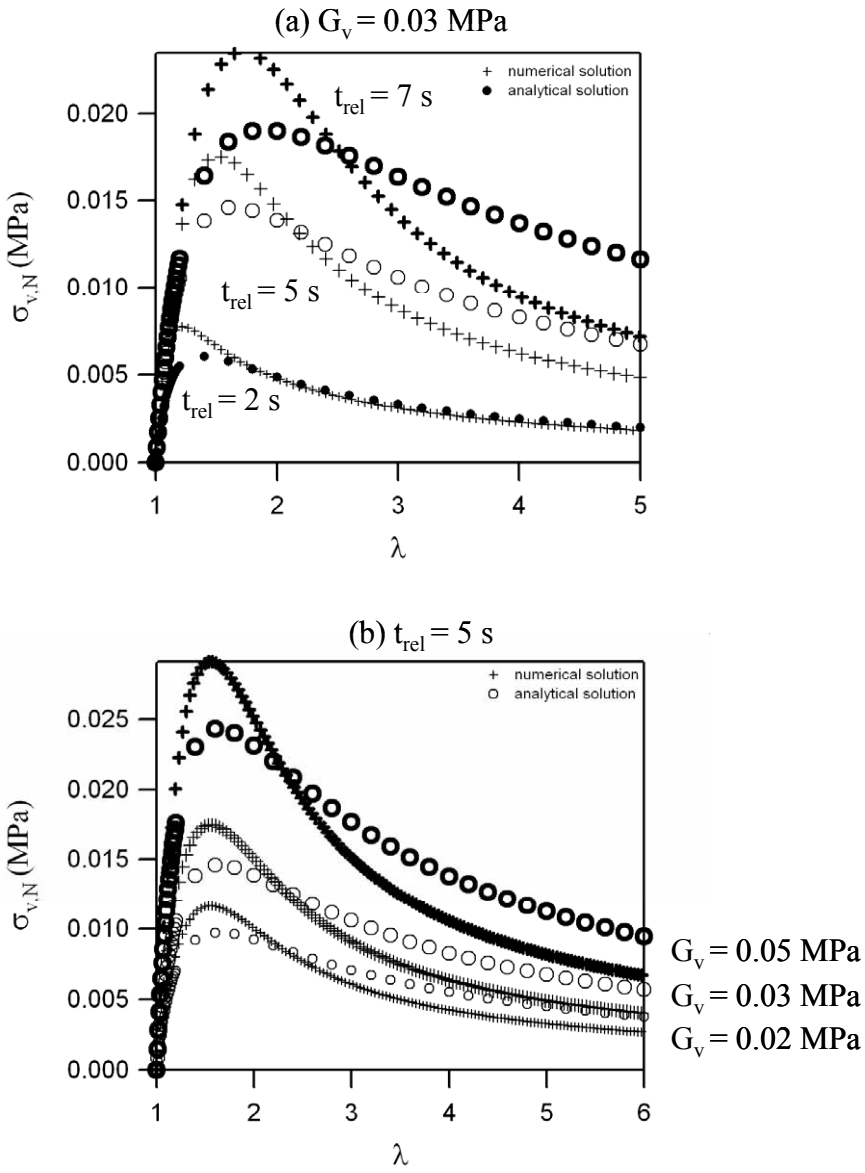

Figure A-3. Comparison between analytical solution considering a constant nominal strain rate (crosses) and numerical solution obtained considering a constant Hencky's strain rate (circles). (a) Results obtained with three different relaxation times and a fixed value of G_v = 0.03 MPa (t_{rel} = 2 s, 5 s and 7 s). (b) Results shown are obtained with three different shear moduli G_v = 0.02 MPa, 0.03 MPa and 0.05 MPa (t_{rel} = 5 s).