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Towards constitutive equation for non-linear mechanics of PDMS-nanosilica

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ABSTRACT: Nanosilica reinforced PDMS is a performing material, but with a complex mechanical response. In our project we aim at modelling its behavior through a multi-scale approach. This paper presents the main advancements in the development of a mechanical constitutive equation from a microscopic physical law. Experimental results prove the modification of the polymer chain dynamics. Mobility reduction is reproduced by gradients in the viscoelastic properties of confined matrix. A wide spectrum of relaxation times allows the representation of a large span of different behaviors by means of one single function.

1 INTRODUCTION

Silica reinforced silicone rubbers are performing materials for many engineering applications. Because of their high chain flexibility and their chemical stability and tailoring, Polydimethylsiloxans (PDMS) are preferred for wide temperature and frequency range specifications. Their mechanical properties are improved by adding nano-silica aggregates, with strong compatibility with the silicone matrix.

At the same time, silica fillers introduce non-linearities and long time evolutions in the PDMS response. Under cyclic solicitation, dependences on the strain amplitude—Payne effect (Clement et al. 2005)—and on the maximum stretch—Mullins effect (Clement 1999)—are observed on filled PDMS, as on other reinforced rubbers [REF]. Stress-strain Lissajous curves show non-linearities resulting from static-strain/precycling-strain couplings (Vincent 2011). Moreover, reinforcement is proven to be temperature dependent and, when mechanically modified, long time recovery is experienced (Vincent 2011). Those strong non-linearities are depending not only on the external solicitation and environmental conditions but also on the morphological structure and filler-matrix interaction (Montes et al. 2010).

To our knowledge, existing mechanical models fail in predicting all these multifaceted behaviours

under multi-axial loadings (Cantournet & Besson 2009, Amin et al. 2006). Macroscopic phenomenological approaches are limited by the amount of parameters which increase with the number of non-linearities. On the other hand, physical interpretations lead to a qualitative description of the overall phenomena, but not a quantitative one (Papon 2012). Thus, they cannot be used for structural prediction.

In our work, we aim at overcoming the limits of the mechanical and of the physical approach by combining them in a multiscale model, linking the microscopic behaviour to the macroscopic one. Firstly, we focus on the experimental characterisation of pure and silica filled PDMS in the linear and non-linear domain. Secondly, a local behaviour based on the modification of the matrix dynamic is set at a microscopic scale. In further developments, the assembly of confined domains to a mesoscopic network is investigated for the homogenisation of the material response.

2 EXPERIMENTAL SECTION

2.1 *Materials*

Pure PDMS and 40phr Silica filled PDMS from Hutchinson are tested on cyclic solicitation. An Anton Paar Physica MCR 501 rheometer with plate-plate configuration is used on cylindrical

specimens (diameter 8mm—thickness 2mm). DSC measurements with a Q800 TA Instrument at 20°C/min increase rate shows a glass transition temperature T_g at -123°C for both materials, while the fusion temperature T_f is -39°C for the pure PDMS and -41°C for the filled PDMS. Stabilised cycles are studied and moduli are computed with first order linear approximation. Temperature sweeps at 1 Hz are performed between -30°C and 130°C , within the linear domain—small strain. Increasing strain amplitude sweeps are performed at temperature 30°C at the same frequency and compared for both materials.

2.2 Results

In the linear domain, filled PDMS exhibit a remarkable enhancement in the storage modulus—more than one order of magnitude—typical of reinforced elastomers.

Figure 1 shows the evolution of the storage modulus with respect to the temperature for filled and unfilled PDMS. A clear difference in the temperature dependence is observed: filled elastomer follows a decreasing trend, while pure silicone rubber shows an increasing storage modulus as predicted by classical entropic elasticity (Treolar 1975).

Fillers modify the viscous response as well. The dissipative factor, in Figure 2, is 3 times larger for filled material. The latter is also more sensible to temperature variation.

In the non-linear domain PDMS-nanosilica composite sample are affected by Payne effect (Fig. 3).

At increasing strain amplitude, filled material shows a drop in storage modulus with respect to the linear behavior observed on unfilled PDMS. This behavior is proven to be temperature dependent. In particular, filled silicone rubber has a large

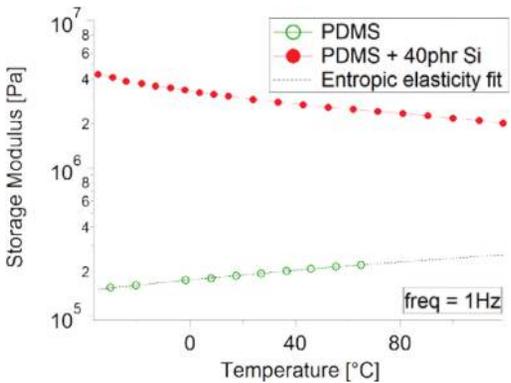


Figure 1. Storage modulus vs. temperature—linear domain: filled PDMS (●); pure PDMS (○); entropic elasticity fit (dashed line).

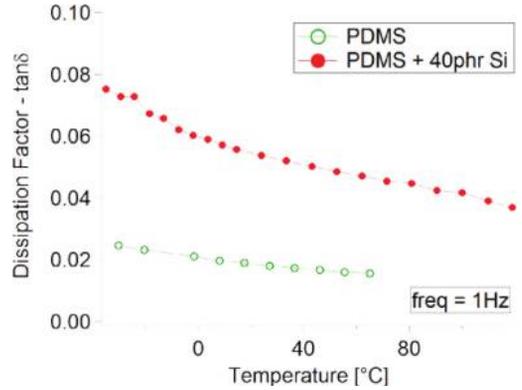


Figure 2. Dissipation factor vs. temperature—linear domain: filled PDMS (●) and pure PDMS (○).

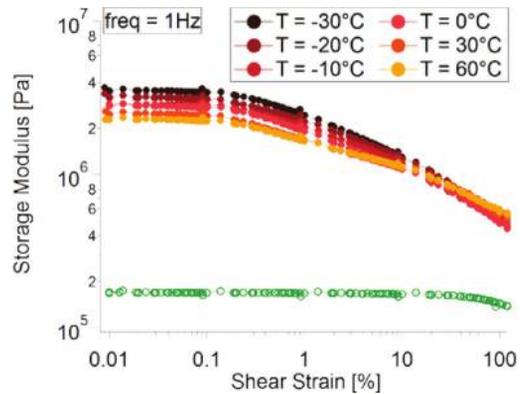


Figure 3. Storage modulus vs. strain amplitude: pure PDMS (○); filled PDMS (●) at different temperatures.

strain trend which is the opposite of small strain one—linear domain. It is rather similar to the one observed on the unfilled matrix.

2.3 Discussion of the experimental results

The empirical analysis put into evidence the temperature dependence of the reinforcement phenomenon. Filler addition has an influence other than the simple hydrodynamic effect (Guth 1945), since it affects the dynamical response of the matrix. At a microscopic level, physico-chemical interactions induce a reduction of polymer chain mobility, thus, leading to an increase of the elastic and viscous responses. Confined zones have reasons to be regions where the presence of silica has a stronger effect.

The mobility reduction is proven to depend on many factors. Figure 4 sums up the outlines of the



Figure 4. Fillers modify matrix dynamical response: chain mobility reduction: sum up scheme of the chain mobility reduction observations.

experienced dependences. In the following section, we aim at building a microscopic scale model that takes the observed behaviors as key element of the mechanical description. At the current state, a quantitative comparison is not developed yet, though the main principles may be applied to other filled systems, other than silicone rubber based ones.

3 MICROSCOPIC MODEL

3.1 Local viscoelastic behavior

In the previous section, silica filler is proven to modify the dynamical response of the matrix. Filler-matrix interactions cause a reduction in chain mobility of the matrix surrounding the aggregate (Berriot et al. 2002, Papon et al. 2011). This modification is modeled by means of a glass transition temperature gradient of few nanometers wide, represented by the formula:

$$T_g(z) = T_g^\infty \left[1 + \left(\frac{\delta}{z} \right)^{\frac{1}{\nu}} \right] \quad (1)$$

where T_g^∞ = glass transition temperature at the bulk (without solicitation); δ = filler-matrix interaction coefficient [in nm]; ν = gradient exponent; and z_i = distance from the particle surface within the glassy bridge.

Wherever aggregates are sufficiently close, a confinement condition is attained, with thermodynamic properties different from the bulk polymer, typically an enhanced glass transition temperature. These regions are modeled as overlaps of multiple

glass transition gradients: a rigid connection, called glassy bridge, establishes a preferential path for force transmission between aggregates. The set of glassy bridges forms a temperature depending percolation network, responsible of the reinforcement effect at the macroscopic scale (Montes et al. 2003).

Moreover, external solicitation modifies matrix properties within the confined region. Glass transition temperature is proven to depend on the stress field (O’Connell & McKenna 1997). For a glassy bridge scale under applied strain, viscous flow phenomena take place, leading to energy dissipation and Payne effect at macroscopic scale (Montes et al. 2003). Local glass transition temperature is, thus, expressed within a glassy bridge by:

$$T_g(z_i, \tilde{\sigma}) = T_g^\infty \left[1 + \left(\frac{\delta}{z_i} \right)^{\frac{1}{\nu}} \right] - f(\sigma_{eq}) \quad (2)$$

where z_i = distance from the surface of the i th particle of the glassy bridge; and $f(\sigma_{eq})$ is a scalar function of an equivalent local stress.

In the glass transition gradient approximation, the mechanical behavior of the polymer surrounding the particle gives responses spanning from the pure rubber up to the glassy state. The local viscoelasticity is reproduced by means of a Zener model (Fig. 5): on one side a hyperelastic function describes the purely rubbery behavior—with modulus of the order of few MPa—; on the other side a glassy elastic term—modulus of few GPa—is coupled with a locally variable relaxation time τ , whose expression is directly deduced from

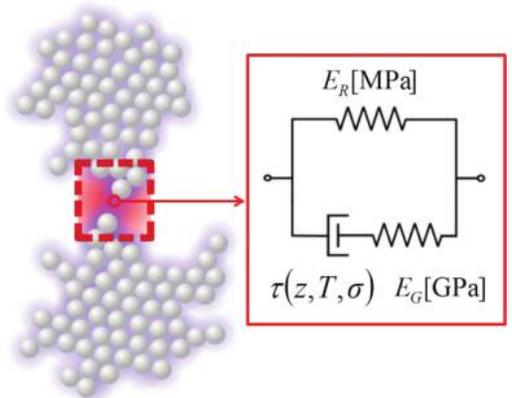


Figure 5. Chain mobility reduction is modeled by a local Zener large strain viscoelasticity: a relaxation time function depending on filler-matrix interaction, stress tensor and temperature is applied.

the William-Landell-Ferry law and the glass transition temperature gradient:

$$\text{Log} \left[\frac{\tau(T, z_i, \tilde{\sigma})}{\tau_g} \right] = - \frac{C_1 [T - T_g(z_i, \tilde{\sigma})]}{C_2 + [T - T_g(z_i, \tilde{\sigma})]} \quad (3)$$

where the local shift factor $a_T^{T_g}$ is expressed as the ratio between the local relaxation time and the relaxation time at the glass transition temperature; C_1 and $C_2 =$ WLF material parameters; and $T =$ temperature.

The present assumption allows the description with a unique and simple model of all the behaviors between two antithetical trends. Moreover, it includes a wide relaxation spectrum of relaxation time which may be able to reproduce long time recovery phenomena.

Previous equations have been implemented in the Finite Element code Z-set (<http://www.zset-software.com>) in large strain formulation. The axis of the glassy bridge between two silica particles has been reproduced by a stick of concatenated cubic c3d20 elements, where the glassy bridge height—minimum particle to particle distance—is denoted h_0 (Fig. 6).

3.2 Preliminary results

In the first instance, cyclic stretching simulations are performed from an unsolicited configuration with a glass transition temperature gradient law, with no stress dependence (Equation 1), at temperature $T_g + 20$ K. Figure 7 shows the profile of the relaxation times along the axis, for a 2 nm glassy bridge. Filler-matrix interaction parameters are chosen $\delta = 0.1$ nm and $\nu = 0.88$. Similar behaviors

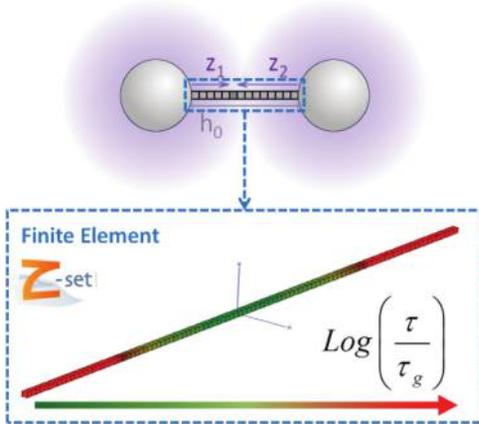


Figure 6. The axis of a glassy bridge confined between two particles is represented by a stretched stick of cubic elements and tested by Finite Element Method.

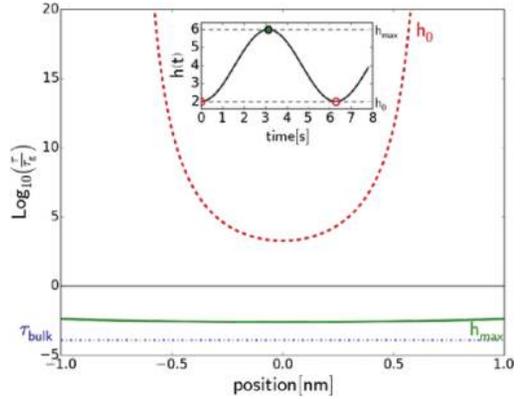


Figure 7. Relaxation time vs. position on the axis for a 2 nm glassy bridge—mobility reduction induced from glass transition gradient overlap $T_g(z_i)$: unstretched configuration (dashed line); stretched configuration (full line); bulk behavior (point line).

are observed at different glassy bridge height h_0 , for different temperature.

At the unsolicited state, relaxation time profile is much higher than the relaxation time of the bulk matrix. As a consequence, the glassy bridge behaves as a rigid element.

Under stretching, relaxation time undergoes a smooth reduction till the point of viscoelastic transition between the glassy and rubbery behavior. The bridge behavior is soft at maximum stretch.

Finally, if no stress dependence in present the initial relaxation time profile and stiffness is established.

In the case of a stress dependent glass transition temperature (Equation 2), the stiffness reduction is anticipated by a viscous flow phenomenon. Figure 8 shows the traction force under uniaxial stretch at a constant strain rate of 10^{-4} s^{-1} and at temperature $T_g + 7$ K.

The behavior in absence of mobility reduction corresponds to the one at high temperature: the mechanical response is the one of a pure rubber matrix. The addition of a mobility reduction by mean of a glass transition temperature gradient (Equation 1) increase of 3 orders of magnitude the mechanical response and introduce a dissipative term within the system. The stress dependence glass transition temperature (Equation 2) leads to a yielding-like phenomenon, with a viscous flow behavior induced by the implicit interdependence of stress and relaxation time.

3.3 Discussion of the numerical results

The strong non-linearities are induced by both confinement and stress dependence $f(\sigma_{eq})$. The reduction of chain dynamics observed by the

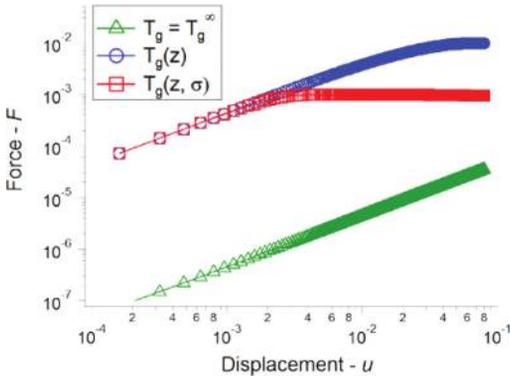


Figure 8. Force vs. displacement—mechanical response for a 2 nm glassy bridge under constant rate stretch (10^{-4} s^{-1}) and $T = T_g + 7\text{K}$: no mobility reduction (Δ); mobility reduction and dissipation (\circ); stress induced loss in the mobility reduction (\square).

experiments is reproduced by taking into consideration the filler-matrix interaction. Rigid-like behavior is simulated at temperature higher than the glass transition temperature. Hence, the local stiffness is temperature dependent.

The application of an external solicitation modifies the relaxation times profiles on two aspects. On one side it changes the glassy layer overlap, affecting the scope of the filler-matrix interaction. On the other side it forces a viscous behavior, leading to a softening of the glassy bridge and strong dissipation within the material.

In conclusion, the dynamical dependencies experimentally observed are here reproduced with one single physical law at the microscopic level.

4 CONCLUSION

In the present paper we discuss the actual advancement in the definition of a mixed physical-mechanics approach, which aims at describing the complex macroscopic behaviour of reinforced elastomers. The experimental characterisation brings us to the conclusion that the reinforcement observed for silica filled PDMS is driven by the modification of the dynamical response of the matrix. Environmental parameters, external solicitation and morphological organisation are main factors on the composite response.

Chain mobility reduction is reproduced by means of a function of glass transition temperature within confined regions, called glassy bridges. From a glass transition temperature gradient approximation, we develop a local mechanical model. One single law is used to represent the set of dependencies observed at the empirical level.

From this microscopic physical law we aim at building a multi-scale homogenisation approach. In future perspective the computed law will be applied on a Representative Elementary Volume of the filler-elastomer morphology (Jean et al. 2010, 2011). The network of glassy bridges is used to obtain a macroscopic response.

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