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Theory and identification of a constitutive model of induced anisotropy by the Mullins effect

G. Machado, G. Chagnon*, D. Favier

UJF-Grenoble1, CNRS, TIMC-IMAG - UMR5525, Grenoble, France.

Abstract

Rubber-like materials present a stress softening phenomenon after a first loading known as the Mullins effect. Some recent experimental data on filled silicone rubber is presented in literature, using uniaxial and biaxial tests to precondition samples thus induce some primary stress softening. A generic modeling based on the polymer network decomposition into an isotropic hyperelastic one, and a stress-softening evolution one, is proposed taking into account the contribution of many spatial directions. A new stress softening criterion tensor is built by means of a tensor that measures the repartition of energy in space. A general form of the stress softening function associated to a spatial direction is written by the way of two variables: one, the maximal eigenvalue of the energy tensor; the other, the energy in the considered direction. Finally, a particular form of constitutive equation is proposed. The model is fitted and compared to experimental data. The capacities of such modeling are finally discussed.

Key words: Mullins effect; stress-softening; strain-induced anisotropy; constitutive equation

1. Introduction

Rubber-like materials present a stress softening after a first loading cycle, known as the Mullins effect (Mullins, 1947). Different definitions have been given to the Mullins effect, in this paper the Mullins effect is considered as the difference between the first and second loadings. Moreover, different studies have highlighted that this phenomenon induces anisotropy, since the stress softening is strongly dependent on the second load direction.

*Corresponding author

Email address: gregory.chagnon@imag.fr (G. Chagnon)

27 In a first approach, many isotropic models were proposed in the literature to describe
28 stress softening. First, physical models taking into account the evolution of the chain net-
29 work were proposed. Govindjee and Simo (1991) proposed a model based on the macro-
30 molecular network evolution by decomposition into a hyperelastic network and an evolving
31 network. Marckmann *et al.* (2002) considered that the macromolecular network can be
32 represented by the eight chains model (Arruda and Boyce, 1993). The model containing
33 chain lengths and chain densities evolving with the maximal principal stretch. In another
34 way, double network theory was developed (Green and Tobolsky, 1946) considering that
35 the rubber-like material can be decomposed into a hard and a soft phase; the hard phase
36 is transformed into soft phase with the stress softening. Different equations were pro-
37 posed (Beatty and Krishnaswamy, 2000; Zuñiga and Beatty, 2002). At the same time, the
38 damage theory was often used to describe the stress softening (Simo, 1987; Miehe, 1995;
39 Chagnon *et al.*, 2004). In another way, Li *et al.* (2008) associated the Mullins effect to the
40 growth of cavities in the material and a compressible model was proposed. In a last point
41 of view, Ogden and Roxburgh (1999) and Dorfmann and Ogden (2003) proposed models
42 based on pseudo-elasticity. All these models fit experimental data more or less accurately
43 in one loading direction, i.e., without changing loading direction between first and second
44 loadings. For a more exhaustive review about these isotropic models, the reader can refer
45 to Diani *et al.* (2009).

46 To improve the modeling and to fit anisotropic stress softening, new approaches were
47 developed taking into account the difference of stress softening in each strain direction.
48 At first, Göktepe and Miehe (2005) generalized the approach proposed by Govindjee and
49 Simo (1991) taking into account a spatial repartition of the chains. In the same way,
50 Diani *et al.* (2006a) proposed a generalization of the Marckmann *et al.* (2002) model by
51 means of chains oriented into 42 or more directions in space. Using a phenomenological
52 damage function, this model can describe different stress softening in different directions,
53 with permanent deformation after unloading. Dargazany and Itskov (2009) proposed a
54 similar approach by taking into account the existence of different chains with different
55 lengths in each direction. They integrate the density of probability in each direction,
56 by taking into account the network evolution at each step. Shariff (2006) proposed an
57 anisotropic damage model that describes transverse anisotropy of Mullins effect, taking
58 into account different damages in the three principal strain directions using a second-order

59 damage tensor. In the same way, Itskov *et al.* (2010) proposed three damage evolution
60 functions for the three principal strain directions. These functions are formulated in terms
61 of material parameters that partly depend on the maximal principal stretch. Recently,
62 Dorfmann and Pancheri (2012) proposed a phenomenological model, based on the theory
63 of pseudo-elasticity, which includes scalar variables in the strain energy function to account
64 for stress softening and changes in material symmetry.

65 Most of the anisotropic models mentioned above are proposed by analyzing successive
66 tensile tests performed along different directions. In spite of that, Machado *et al.* (2012a)
67 has recently performed other original tests based on preconditioning with uniaxial tension
68 and biaxial tension tests. Based on Machado *et al.* (2012a) experimental results using
69 silicone rubber, this paper proposes a new approach for modeling the induced anisotropy
70 by the Mullins effect. In Section 2, the global framework of the Mullins effect modeling
71 is presented. In Section 3, a new approach is proposed to write constitutive equations by
72 introducing a tensor that describes the strain energy repartition in the space directions.
73 The conditions to be verified by the equations are detailed. In Section 4, a first constitutive
74 equation is proposed. It is fitted and compared to experimental data. Finally, Section 5
75 contains some concluding remarks and outlines some future perspectives.

76 **2. Macromolecular approach to model Mullins effect**

77 *2.1. Filled silicone behavior*

78 In the last few years, different tests highlighting the stress softening anisotropy have
79 been presented in the literature for different rubber-like materials, see for example (Mühr
80 *et al.*, 1999; Besdo *et al.*, 2003; Hanson *et al.*, 2005; Diani *et al.*, 2006b; Dorfmann and
81 Pancheri, 2012). In this paper, attention is focused on the largest and most diverse
82 database concerning Mullins effect anisotropy of a rubber-like material to the best of
83 our knowledge. These data concern the results for the RTV3428 filled silicone rubber
84 (Machado *et al.*, 2010, 2012a).

85 First classical experimental tests, i.e., cyclic experiments with an increasing deforma-
86 tion after each cycle, were realized during tensile, pure shear and equibiaxial tensile tests.
87 The data are reported in Machado *et al.* (2010). Second, stress softening anisotropy is
88 presented in Machado *et al.* (2012a) induced by two distinguished preconditioning meth-
89 ods. The first one (noted as TT in the following), consists in a first loading in tension and

90 a second loading also in tension, in four different directions. The second preconditioning
91 method (noted as BT), consists in a first biaxial extension loading with constant principal
92 strain direction. It is followed by a second loading in tension along the two principal strain
93 directions of the first biaxial loading. The originality of these data is that loading states
94 are very different between the first and second loads.

95 These new experimental results question the existing anisotropic constitutive equations
96 and the main reasons are detailed here. The first reason is, Diani *et al.* (2006a) and
97 Dargazany and Itskov (2009) models present an important permanent deformation that
98 is related to the stress softening. But here, the material exhibits an important stress
99 softening without permanent deformation. The other reason, for a second tensile loading
100 orthogonal to the first loading, the models of Shariff (2006) and Itskov *et al.* (2010) present
101 a stiffer behavior than the virgin material, which is not the case of the filled silicone
102 rubber. Last, all these models are based on a set of material directions and Mullins effect
103 is controlled in each direction only by the maximum stretch reached during the deformation
104 history along the considered direction. Recently, Merckel *et al.* (2011) analyzed the damage
105 spatial repartition and proposed a softening criterion (Merckel *et al.*, 2012) that is still the
106 maximum stretch in each direction. Therefore, as pointed out in Machado *et al.* (2012a), a
107 maximal deformation criterion that depends only on the considered direction is not enough
108 to describe the stress softening for an arbitrary second load direction. This means that, if
109 the maximal principal direction remains the same during the first and second load cycles,
110 the strain energy can be a measure to quantify the Mullins effect in this direction. In the
111 other directions, a coupling effect exists between different directions and it influences the
112 stress softening. Under these circumstances, a new way to handle Mullins effect should be
113 proposed at the sight of Machado *et al.* (2012a) experimental data.

114 2.2. Two networks theory

115 The results presented using silicone rubber-like materials highlight that unfilled silicone
116 rubbers do not present stress softening (Rey *et al.*, 2013) whereas filled silicone rubbers
117 (Machado *et al.*, 2010) present an important one. For this silicone rubber material, it can
118 be argued that the Mullins effect is principally due to the presence of filler in the material,
119 which is not the case for every rubber-like material. In the light of these findings, a model
120 based on Govindjee and Simo (1991) theory is proposed. The main feature retained from
121 their theory is the additive split of the strain energy into two contributions, motivated

122 by the micromechanical structure represented in the Fig.1. The hypothesis is based on
 123 distinguishing different macromolecular chains in the network, those that are linked to
 124 filler and those that are only linked to other macromolecular chains. It is assumed that
 125 only chains that are linked to fillers are concerned with Mullins effect. In Govindjee and
 126 Simo (1992) authors modified the initial approach into a phenomenological isotropic frame,
 127 introducing a normalized stress function that governs the damage level. Later, Göktepe
 128 and Miehe (2005) conceptually extend the isotropic theory of Govindjee and Simo (1992)
 129 to the anisotropic case where damage history is described by one scalar for each material
 direction.

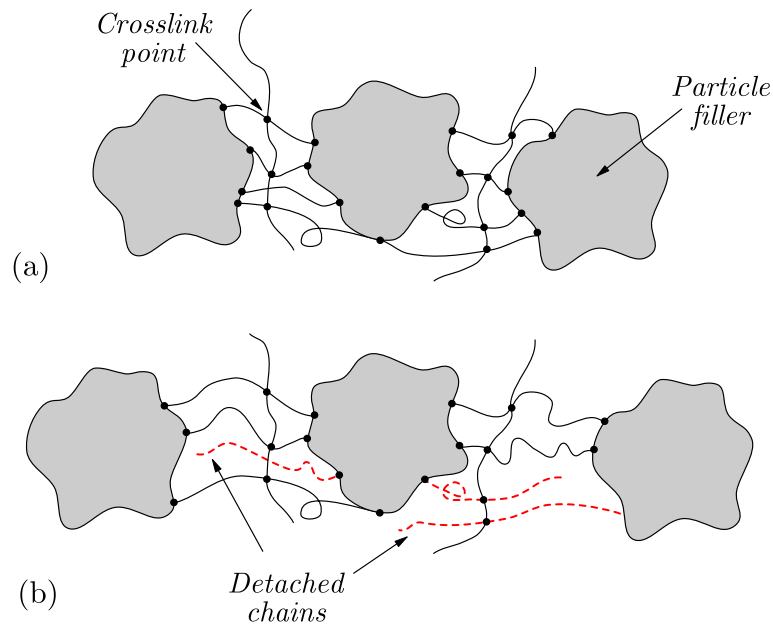


Figure 1: Representation of the silicone organization with macromolecular chains and filler particles

130

131 The same additive split from Govindjee and Simo (1991) is considered here, that means
 132 that the strain energy density (per unit of undeformed volume) over a representative
 133 elementary volume (REV) is decomposed into two parts

$$\mathcal{W} = \mathcal{W}_{cc} + \mathcal{W}_{cf} \quad (1)$$

134 where \mathcal{W}_{cf} and \mathcal{W}_{cc} denote the energy densities of chains linked to filler network and chains
 135 linked to other chains network, respectively. On one hand, as it is considered that chains
 136 linked to other chains do not undergo Mullins effect, \mathcal{W}_{cc} is therefore represented by an
 137 isotropic hyperelastic energy density. On the other hand, \mathcal{W}_{cf} represents the anisotropy of
 138 stress softening induced by Mullins effect contributions in different directions of the REV.

139 **3. Choice of the governing parameters of the Mullins effect**

140 *3.1. Analysis of literature experimental data*

141 The different conclusions identified by Machado *et al.* (2012a) are analyzed and the
142 consequences for the modeling are here in detail. During TT tests (uniaxial tension precon-
143 ditioning followed by second tensile tests) it is shown that whatever is the second loading
144 orientation, the strain-stress curves come back on the first loading curve at the same point
145 corresponding to the maximum tensile stretch encountered during the first tensile loading.
146 Nevertheless the amount of stress softening depends on the angle between the first and
147 second loadings. This means that the return on the tensile virgin curve is controlled by the
148 maximal tensile stretch. However, the amount of stress softening depends on the relative
149 orientation of first and second loadings.

150 The BT tests (biaxial tension followed by second tensile test) use preconditioning cir-
151 cular bulge test. Displacement and strain fields were obtained using three-dimensional
152 image correlation measurements. In the preconditioning step, the circular bulge test spec-
153 imen underwent biaxial loadings with different biaxiality ratios along a meridian. At the
154 top of the bulge specimen, an equibiaxial loading is generated whereas a planar tension
155 state is generated near the grips. Between these two points different biaxial states are
156 generated (Machado *et al.*, 2012b). For different points along the bulge meridian, pairs of
157 specimens were cut along circumferential and meridional directions and they were tested
158 in tension. For each pair, the two different second stress-strain tensile curves, in the same
159 way of TT tests, come back at the same point on the virgin tensile loading curve but
160 with a different amount of stress softening according to the direction (circumferential or
161 meridional). The conclusions are thus the same as TT tests but with a biaxial loading as
162 the preconditioning test.

163 These results encourage to consider that the strain energy in the maximal principal
164 strain direction is the governing parameter for the come-back on the first loading curve
165 whatever is the second loading. Moreover, the stress softening amount in the other di-
166 rections are linked to this parameter but it is attenuated if the direction of the maximal
167 principal strain is not the same between first and second loadings. A measure for these
168 quantities should thus be introduced.

169 3.2. New measure definition to quantify the stress softening

170 The strain energy is often used to describe the Mullins effect (see references in Machado
 171 *et al.* (2010); Diani *et al.* (2009)) but its use is limited to the isotropic approach, since
 172 energy is a scalar global measure of the deformation state. Therefore, to compare the
 173 strain energy in different directions can be the clue. It is thus proposed to introduce a
 174 measure of the strain energy given by the contribution of each material direction.

175 Figure 2 illustrates the kinematics of an infinitesimal cone element extracted from the
 176 initial spherical representative volume element centered in P of radius dR_0 . In the initial
 177 configuration the slant height, surface area and volume are dR_0 , dS_0 and $dV_0 = \frac{1}{3} dR_0 dS_0$
 178 respectively; the unity vector \mathbf{a}_0 defines the material direction in the undeformed REV.
 179 Considering the point Q , lying within an infinitesimal neighborhood of P , defined by the
 180 vector $d\mathbf{x}_0 = dR_0 \mathbf{a}_0$. Under the deformation, this vector is mapped into $d\mathbf{x} = \mathbf{F} d\mathbf{x}_0$,
 181 where \mathbf{F} is the deformation gradient. Thus, one obtains the following relation

$$d\mathbf{x} = \mathbf{F} d\mathbf{x}_0 = dR_0 \mathbf{F} \mathbf{a}_0 \quad (2)$$

182 In the deformed configuration points p and q are referenced by the position vectors \mathbf{x}
 183 and $\mathbf{x} + d\mathbf{x}$ respectively; and the vector normal to the deformed surface dS given by the
 184 Nanson's relation

$$\hat{\mathbf{n}} = \det(\mathbf{F}) \frac{dS_0}{dS} \mathbf{F}^{-T} \mathbf{a}_0. \quad (3)$$

The velocity field within the infinitesimal neighborhood of \mathbf{x} , with respect the reference

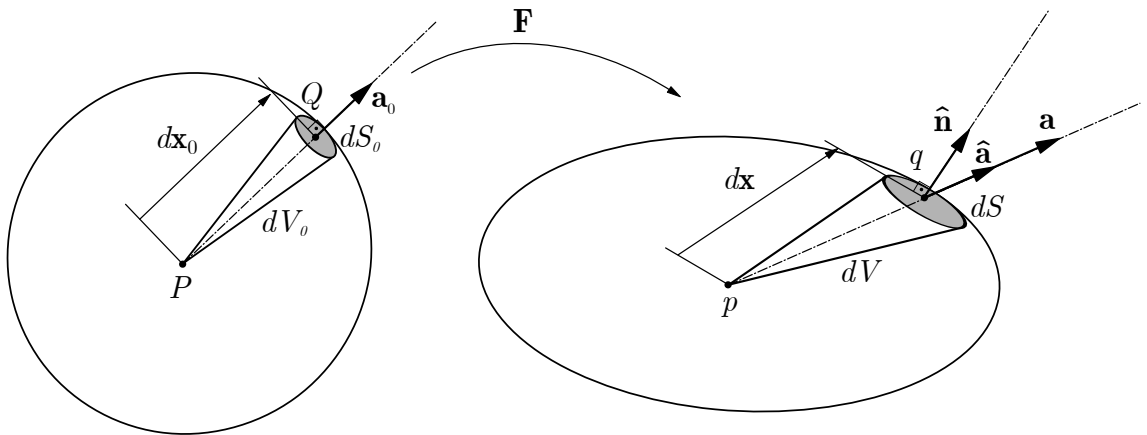


Figure 2: Kinematics of an infinitesimal cone element from the spherical REV.

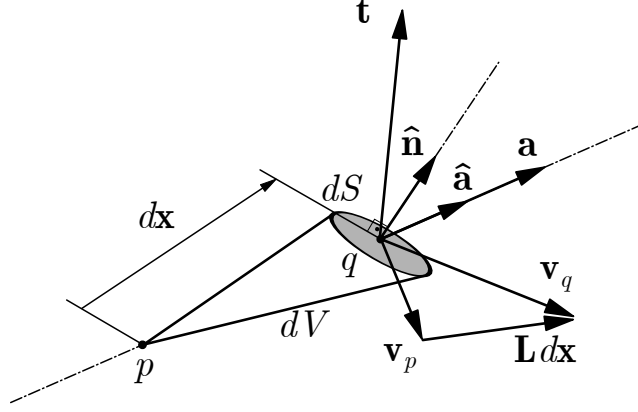


Figure 3: Force and velocity vectors in the deformed REV.

186 frame R is given by

$$\mathbf{v}_q(\mathbf{x} + d\mathbf{x})_{/R} = \mathbf{v}_p(\mathbf{x}, t)_{/R} + \mathbf{L}(\mathbf{x}, t)_{/R} d\mathbf{x} \quad (4)$$

187 with $\mathbf{L}(\mathbf{x}, t)_{/R} = \mathbf{W}(\mathbf{x}, t)_{/R} + \mathbf{D}(\mathbf{x}, t)$ where \mathbf{L} , \mathbf{W} and \mathbf{D} are the velocity gradient, spin
 188 and rate of deformation tensors. In any motion, the velocity field is locally decomposed
 189 as a sum of a rigid velocity $\mathbf{v}_p(\mathbf{x}, t)_{/R} + \mathbf{W}(\mathbf{x}, t)_{/R} d\mathbf{x}$ and a straining velocity $\mathbf{D}(\mathbf{x}, t) d\mathbf{x}$.
 190 Considering Figure 3, the power $\mathcal{P}_{/R} = \mathbf{t} \cdot (\mathbf{v}_q)_{/R}$ is expended by a force $\mathbf{t} = \boldsymbol{\sigma} \hat{\mathbf{n}} dS$
 191 acting at point q , where $\boldsymbol{\sigma}$ is the Cauchy stress tensor. The interest is the expended
 192 power associated only with deformations. Then, it is possible to write the strain energy
 193 increment $d\mathcal{M}$ during a time increment dt , excluding rigid velocity, by the scalar product

$$d\mathcal{M} = \boldsymbol{\sigma} \hat{\mathbf{n}} dS \cdot \mathbf{D} d\mathbf{x} dt \quad (5)$$

194 where $\mathbf{D} d\mathbf{x}$ is the straining velocity field associated exclusively to the rate of deformation
 195 tensor \mathbf{D} . Replacing Eq. (3) into Eq. (5), one obtains

$$d\mathcal{M} = 3dV_0 \det(\mathbf{F}) [\mathbf{F}^{-1} \boldsymbol{\sigma} \mathbf{D} \mathbf{F}] : (\mathbf{a}_0 \otimes \mathbf{a}_0) dt \quad (6)$$

Finally, the strain energy contribution in the \mathbf{a}_0 direction is written, per unity of undeformed volume dV_0 , as

$$\mathcal{M}(\mathbf{a}_0) = 3 \left[\int_0^t \det(\mathbf{F}) \mathbf{F}^{-1} \boldsymbol{\sigma} \mathbf{D} \mathbf{F} dt \right] : (\mathbf{a}_0 \otimes \mathbf{a}_0) = 3 \mathbf{M} \mathbf{a}_0 \cdot \mathbf{a}_0 \quad (7)$$

196 This permits to introduce a tensor \mathbf{M} in Eq. (7), defined in the reference configura-

197 tion. It is decomposed into a symmetric \mathbf{M}^{sym} and skew-symmetric \mathbf{M}^{skew} part. Note
 198 that the product of a symmetric tensor and a skew-symmetric tensor has zero trace, i.e.,
 199 $\mathbf{M}^{skew} : (\mathbf{a}_0 \otimes \mathbf{a}_0) = 0$. Thus, in a general formulation, \mathbf{M}^{sym} describes the contribution
 200 of each material direction in the total strain energy. As symmetric tensor \mathbf{M}^{sym} possesses
 201 three real eigenvalues ($M_I > M_{II} > M_{III}$), where the maximal principal value M_I is
 202 connected with an eigenvector determining the direction of maximum strain energy. Dif-
 203 ferent noticeable parameters can be defined. The maximum strain energy for each conical
 204 elementary volume in direction \mathbf{a}_0 along the history is

$$\mathcal{M}_{\max}(\mathbf{a}_0) = \max_{\tau \leq t} \mathcal{M}(\mathbf{a}_0, \tau) \quad (8)$$

205 At the current time t , the maximum instantaneous strain energy in any direction is defined
 206 as

$$\mathcal{I}(t) = M_I(t) \quad (9)$$

207 And last, the maximum strain energy in any direction in the history is defined as

$$\mathcal{G} = \max_{\tau \leq t} M_I(t). \quad (10)$$

208 3.3. Construction of the evolution equation

209 An evolution function \mathcal{F} is introduced along each direction, it describes the evolution
 210 of the network in the considered direction. The global strain energy is then rewritten as

$$\mathcal{W} = \mathcal{W}_{cc} + \int_{V_0^{REV}} \mathcal{F}(\mathbf{a}_0) \mathcal{W}_{cf}(\mathbf{a}_0) dV_0. \quad (11)$$

211 where V_0^{REV} is the undeformed REV volume. At the sight of the silicone filled rubber
 212 experimental data, the function $\mathcal{F}(\mathbf{a}_0)$ can be written as a function of the characteristic
 213 energy measures previously introduced

$$\mathcal{F}(\mathbf{a}_0) = \mathcal{F}(\mathcal{M}(\mathbf{a}_0), \mathcal{M}_{\max}(\mathbf{a}_0), \mathcal{I}, \mathcal{G}) \quad (12)$$

214 The main difference with the models from the literature is that the function \mathcal{F} does not
 215 only depend on what happens in the considered direction \mathbf{a}_0 but also on the global strain
 216 energy in the material, i.e., \mathcal{I} and \mathcal{G} . Then, different forms can be proposed.

217 In this paper, the concept for evolution function (Beatty and Krishnaswamy, 2000;
 218 Zuñiga, 2005; Zuñiga and Rodríguez, 2010) is used. This concept describes the Mullins
 219 effect by comparing the current deformation state and the maximum one, that means
 220 that the evolution function depends on the difference between the maximum and current
 221 deformation state. Thus, the value of introduced function remains one during the first
 222 load and it decreases when the current state differs from the maximum state. Thus, during
 223 a first loading $\mathcal{I} = \mathcal{G}$ the function $\mathcal{F}(\mathbf{a}_0)$ should not evolve if the material is stretched in
 224 a given direction for the first time, then

$$\mathcal{F}(\mathcal{M}(\mathbf{a}_0), \mathcal{M}_{\max}(\mathbf{a}_0), \mathcal{I} = \mathcal{G}, \mathcal{G}) = 1 \quad (13)$$

225 During a second loading curve the function evolves, as the difference between the current
 226 and the maximum strain increases, in the interval given by

$$\mathcal{F}(\mathcal{M}(\mathbf{a}_0), \mathcal{M}_{\max}(\mathbf{a}_0), \mathcal{I}, \mathcal{G}) \in [0, 1] \quad (14)$$

227 This approach leads to a dependence in $(\mathcal{G} - \mathcal{I})$ and $(\mathcal{M}_{\max}(\mathbf{a}_0) - \mathcal{M}(\mathbf{a}_0))$ of the constitutive
 228 equation. Moreover, the amount of stress softening is directly linked to the orientation
 229 of the loading, the ratio of what happens in each direction compared to the maximum
 230 deformation should be taken into account. In this way, a general form is proposed as
 231 follows

$$\mathcal{F} = 1 - \mathcal{F}_1(\mathcal{G} - \mathcal{I}) \mathcal{F}_2(\mathcal{M}_{\max}(\mathbf{a}_0) - \mathcal{M}(\mathbf{a}_0)) \mathcal{F}_3\left(\frac{\mathcal{M}_{\max}(\mathbf{a}_0)}{\mathcal{G}}\right) \quad (15)$$

232 where \mathcal{F}_1 , \mathcal{F}_2 and \mathcal{F}_3 are functions to be determined. This multiplicative decomposition,
 233 also used in Rebouah *et al.* (2013), is principally phenomenological, since stress softening
 234 is treated as a multiplicative function of the strain energy, see Eq.11. The conditions
 235 evoked in Eq. (13) lead to

$$\mathcal{F}_1(\mathcal{G} - \mathcal{I}) = 0 \quad \text{if} \quad \mathcal{G} = \mathcal{I} \quad (16)$$

$$\mathcal{F}_2(\mathcal{M}_{\max}(\mathbf{a}_0) - \mathcal{M}(\mathbf{a}_0)) = 0 \quad \text{if} \quad \mathcal{M}_{\max}(\mathbf{a}_0) = \mathcal{M}(\mathbf{a}_0). \quad (17)$$

236 Now, different constitutive equation forms can be proposed for each function \mathcal{F}_1 , \mathcal{F}_2 and
 237 \mathcal{F}_3 in Eq. (15).

238 **4. The anisotropic constitutive equation**

239 *4.1. Hyperelastic constitutive equation*

240 The advantage of such formulation is that the first loading curve is independent of the
 241 evolution function on the contrary of damage mechanics (Lemaitre and Chaboche, 1990).
 242 Thus, the choice of the hyperelastic energy only depends on the first loading curves. In a
 243 first approach, it is proposed to use the classical Mooney (1940) constitutive equation to
 244 represent the isotropic energy density, then

$$\mathcal{W}_{cc} = C_1(I_1 - 3) + C_2(I_2 - 3) \quad (18)$$

245 For the anisotropic part of the constitutive equation the material could be represented
 246 by an infinite number of directions, introducing a probability density. But in this study, it
 247 is preferred to use a distribution of n -direction $\mathbf{a}_0^{(i)}$ oriented in any direction throughout
 248 the three-dimensional space instead of an integral formulation (Eq. 11). Bazant and Oh
 249 (1986) proposed different orientation schemes, that define the set of vectors $\mathbf{a}_0^{(i)}$ with
 250 different weight $\omega^{(i)}$ for each direction to obtain a material as close as possible to an
 251 isotropic material when all the chains have the same mechanical behavior. \mathcal{W}_{cf} is then
 252 written as

$$\mathcal{W}_{cf} = \sum_{i=1}^n \omega^{(i)} \mathcal{F}^{(i)} \mathcal{W}_{cf}^{(i)}(\mathbf{a}_0^{(i)}) \quad (19)$$

253 where n is the number of considered directions and $\mathcal{W}_{cf}^{(i)}(\mathbf{a}_0^{(i)})$ is the hyperelastic strain
 254 energy of the chain in the initial direction $\mathbf{a}_0^{(i)}$. The classical centrally symmetric $n = 2 \times 21$
 255 scheme was chosen to represent the material directions. The vector and weight of each
 256 direction can be found in Bazant and Oh (1986). All the other direction distribution
 257 schemes could also be used. A comparative study of recently proposed integration schemes
 258 in application to a full network model of rubber can be found in Ehret *et al.* (2010).

259 The non-Gaussian theory is classically used to capture the anisotropy. Diani *et al.*
 260 (2006a) and Dargazany and Itskov (2009) use the Langevin chain representation for $\mathcal{W}_{cf}^{(i)}$
 261 energy. The great advantage of this choice is that it brings physical understanding to the
 262 modeling and it presents two main consequences. The first is that the zero-stress state is
 263 only ensured by the compensation of all the directions contribution as $\partial \mathcal{W}(\lambda^{(i)}) / \partial \lambda^{(i)} \neq 0$
 264 if $\lambda^{(i)} = 1$. Hence, this formulation could hardly be used for an initially non-isotropic

265 material. The second one is that it allows to capture an important permanent deforma-
 266 tion of the material after a loading cycle. However, in filled silicone experiments, it was
 267 shown that the permanent deformation is quite negligible. To this purpose, the classi-
 268 cal hyperelastic anisotropic approach using the strain invariant $I_4^{(i)} = \mathbf{a}_0^{(i)T} \mathbf{C} \mathbf{a}_0^{(i)}$ is used,
 269 where $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ is the right Cauchy-Green strain tensor. The function should verify the
 270 following conditions

$$\mathcal{W}_{cf}^{(i)}(I_4^{(i)}) = 0 \quad \text{if} \quad I_4^{(i)} = 1 \quad (20)$$

$$\frac{\partial \mathcal{W}_{cf}^{(i)}(I_4^{(i)})}{\partial I_4^{(i)}} = 0 \quad \text{if} \quad I_4^{(i)} = 1. \quad (21)$$

271 In a first approach, an ordinary constitutive equation is used, considering that the chains
 272 are only stretched by tensile stresses. Otherwise, it is considered that compressive stretches
 273 lead to buckling. Thus, one may write

$$\mathcal{W}_{cf}^{(i)} = \frac{K^{(i)}}{2} \left(I_4^{(i)} - 1 \right)^2 \quad \text{if} \quad I_4^{(i)} \geq 1 \quad \text{else} \quad 0. \quad (22)$$

274 This formulation can be adapted to non-initially isotropic materials by choosing different
 275 functions for $\mathcal{W}_{cf}^{(i)}$. As the filled silicone rubber is initially isotropic, every $\mathcal{W}_{cf}^{(i)}$ is initially
 276 the same in all directions, i.e., $\forall i, j \quad K^{(i)} = K^{(j)}$.

277 4.2. stress softening constitutive equation

278 In part 3.3, a multiplicative decomposition was postulated in Eq. (15). The use of
 279 simple power functions, for \mathcal{F}_1 , \mathcal{F}_2 and \mathcal{F}_3 , is proposed to represent the stress softening,
 280 given by

$$\mathcal{F}^{(i)} = 1 - \eta \sqrt{\frac{\mathcal{G} - \mathcal{I}}{\mathcal{G}}} \sqrt{\frac{\mathcal{M}_{\max}^{(i)} - \mathcal{M}^{(i)}}{\mathcal{G}}} \left(\frac{\mathcal{M}_{\max}^{(i)}}{\mathcal{G}} \right)^2 \quad (23)$$

281 where η is a material parameter. The functions \mathcal{F}_1 and \mathcal{F}_2 are normalized according to
 282 the maximum strain energy \mathcal{G} to ensure a normalized evolution function for each second
 283 loading curve. It is important to note that, even if the objective is to describe Mullins effect
 284 anisotropy, the constitutive equation for stress softening only depends on one parameter η .
 285 All the other parameters describe the hyperelastic first loading. The evolution functions
 286 have the same form in all directions, but this approach could be extended to non-isotropic
 287 stress softening function by defining different values for the parameter η in the different

288 directions.

289 There remains to verify that the presented model is in agreement with the requirements
 290 of thermodynamics (see e.g. Coleman and Gurtin, 1967). If only isothermal processes is
 291 considered, the Clausius-Duhem inequality must be satisfied by the conditions

$$-\frac{\partial \mathcal{W}}{\partial \mathcal{M}_{\max}^{(i)}} \dot{\mathcal{M}}_{\max}^{(i)} \geq 0 \quad (24)$$

$$-\frac{\partial \mathcal{W}}{\partial \mathcal{G}} \dot{\mathcal{G}} \geq 0 \quad (25)$$

292 where $\dot{\mathcal{M}}_{\max}^{(i)} \geq 0$ and $\dot{\mathcal{G}} \geq 0$. By means of straightforward manipulations of Eqs. (11), (24)
 293 and (25) one can easily establish the above relations in terms of the evolution function
 294 $\mathcal{F}^{(i)}$. It is also important to show that

$$\frac{\partial \mathcal{F}^{(i)}}{\partial \mathcal{M}_{\max}^{(i)}} \leq 0, \quad \forall i \quad (26)$$

$$\frac{\partial \mathcal{F}^{(i)}}{\partial \mathcal{G}} \leq 0, \quad \forall i. \quad (27)$$

295 Considering the form of Eq. (23), the explicit form for Eq. (26) is given by

$$-\eta \sqrt{\frac{\mathcal{G} - \mathcal{I}}{\mathcal{G}}} \frac{1}{\mathcal{G}} \left[\frac{1}{2} \left(\frac{\mathcal{M}_{\max}^{(i)} - \mathcal{M}}{\mathcal{G}} \right)^{-\frac{1}{2}} \left(\frac{\mathcal{M}_{\max}^{(i)}}{\mathcal{G}} \right)^2 + 2 \left(\frac{\mathcal{M}_{\max}^{(i)}}{\mathcal{G}} \right) \sqrt{\frac{\mathcal{M}_{\max}^{(i)} - \mathcal{M}}{\mathcal{G}}} \right] \leq 0, \quad \forall i. \quad (28)$$

296 First, an elementary study of the Eq.(28) shows that all fractions terms are positive.
 297 Second, when the stress softening evolves, i.e., \mathcal{G} increasing, the maximum instantaneous
 298 strain energy \mathcal{I} is equal to the maximum \mathcal{G} . Thus, the function remains equal zero and
 299 the condition of Eq. (26) is automatically satisfied. In this way, the choice of \mathcal{F} respects
 300 the conditions of Eqs.(26) and (27) and consequently the Clausius-Duhem inequality is
 301 satisfied.

302 4.3. Comparison of the modeling with experimental data

303 The model is fitted on all the experimental data presented in Machado *et al.* (2010,
 304 2012a), i.e., tests where the principal stretch directions remain unchanged during first
 305 and second load or tests where the principal stretch directions are not necessarily the
 306 same during first and second loads. First, the parameters of the hyperelastic constitutive
 307 equations are fitted on the different first loading curves. Different parameters can be
 308 chosen according to the repartition of the strain energy between \mathcal{W}_{cc} and \mathcal{W}_{cf} .

309 Considering a second tensile loading immediately before the sample rupture, the most
 310 stress softening level is obtained and this state corresponds to the strain energy of chains
 311 that were not affected by the Mullins effect. Thus, to ensure a good balance between \mathcal{W}_{cc}
 312 and \mathcal{W}_{cf} the portion \mathcal{W}_{cc} , i.e., the Mooney model, is fitted on the beginning of the second
 313 tensile loading curve at the higher deformation achieved before rupture.

314 Next, the part of \mathcal{W}_{cf} is fitted to complete the stress amount of the first loading curves.
 315 The fitted parameters are presented in Table 1.

Table 1: Values of the constitutive equation parameters

Parameter	Value
C_1	0.05 MPa
C_2	0.03 MPa
$\forall i \ K^{(i)}$	0.20 MPa
η	1.0

316 The last parameter that describes the stress softening is fitted on the second loading
 317 curves for all the tests, the value $\eta = 1.0$ is obtained. The condition in Eq. (14) must be
 318 satisfied, and as explained the function $\mathcal{F}^{(i)}$ cannot be negative. If its softening is too
 319 large, i.e., $\mathcal{F}^{(i)} < 0$, the value $\mathcal{F}^{(i)} = 0$ is imposed. That means that in the considered
 320 direction a great number of chain–filler links were broken. In the second load, for the
 321 same direction, the suspended chains are no longer acting enough to impose a force on
 322 the macromolecular network, i.e., they do not contribute to the network entropic energy
 323 any more and their energy is thus lost (Dargazany and Itskov, 2009). This assumption
 324 is consistent with the two networks theory and justified for relative short chains. Note
 325 that for longer molecular chains bonded at different places to fillers this assumption can
 326 be relaxed, for example, to take into account permanent set.

327 The simulations of the cyclic uniaxial tensile, pure shear and equibiaxial tensile tests
 328 are presented in Fig. 4. Concerning the first load, it appears that the model describes
 329 adequately uniaxial and pure shear tests whereas equibiaxial tests are underestimated.
 330 This phenomenon is due to the hyperelastic equation and not to stress softening equation.
 331 As pointed out by Marckmann and Verron (2006) and Boyce and Arruda (2000), there
 332 are very few hyperelastic constitutive models able to simultaneously simulate the both
 333 multi-dimensional data with a unique set of material parameters. Concerning the cyclic
 334 behavior, the form of the stress softening for all tests is quite well described. For uniaxial

335 tensile and pure shear curves, the model has a slight tendency to underestimate stress
 336 softening and it is even more pronounced for equibiaxial tensile test.

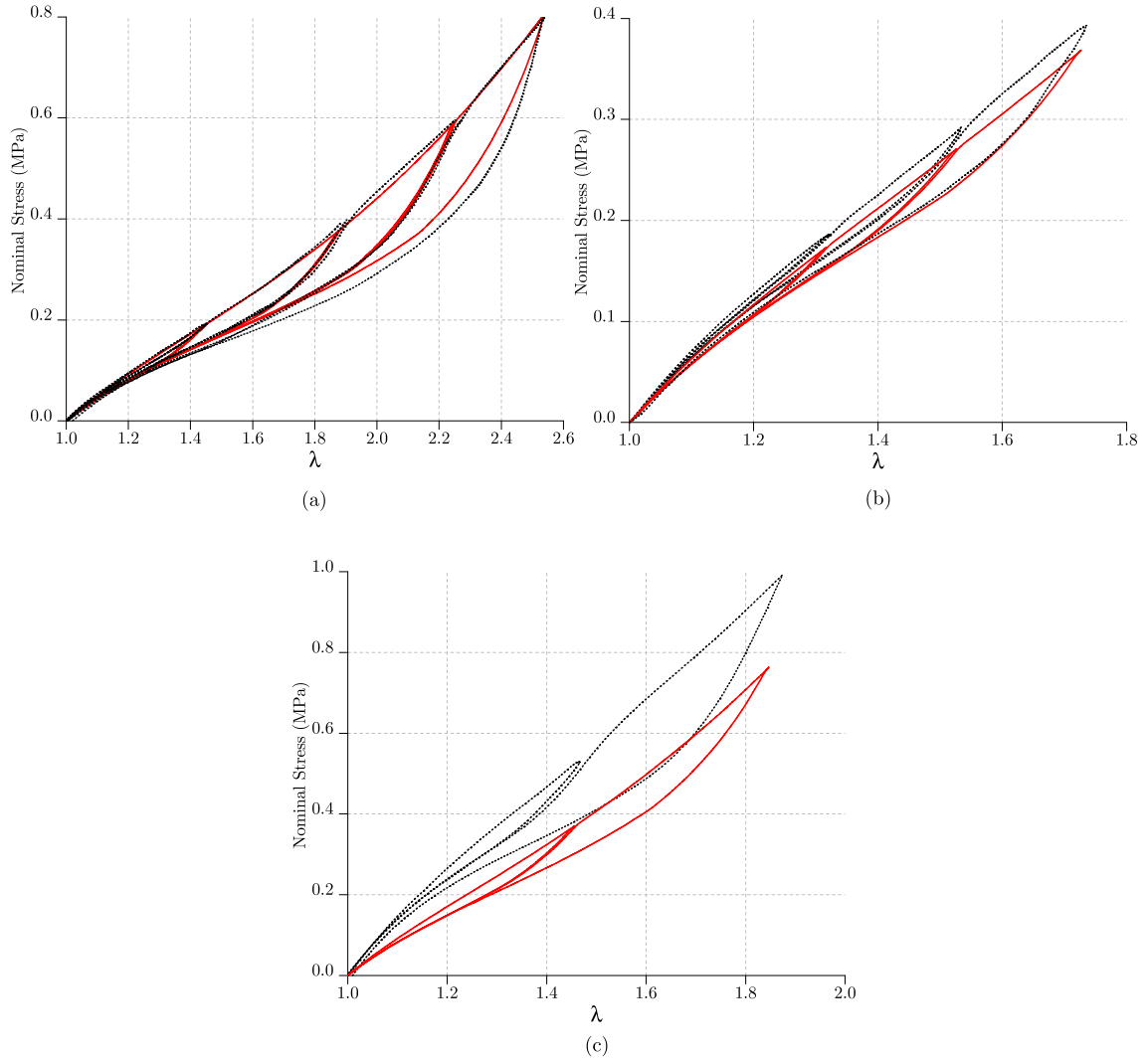


Figure 4: Comparison of the model (solid lines) with experimental data from Machado *et al.* (2010) (dotted lines) for: (a) cyclic uniaxial tensile test, (b) cyclic pure shear test and (c) cyclic equibiaxial test.

337 Next, tensile tests with a change of loading direction between the first and second
 338 loads are confronted. A simulation of the modeling is presented in Fig. 5(a). It appears
 339 that the trend of simulations are exactly what experimentally happens. All the second
 340 loading curves come back on the same point of the first loading curve and the amount of
 341 stress softening is directly linked to the angle between the principal stretch directions of
 342 the first and second loads. A detailed comparison with experimental data is presented in
 343 Fig. 5(b-f). The model does not superpose perfectly all experimental data, but all trends
 344 are quite well described.

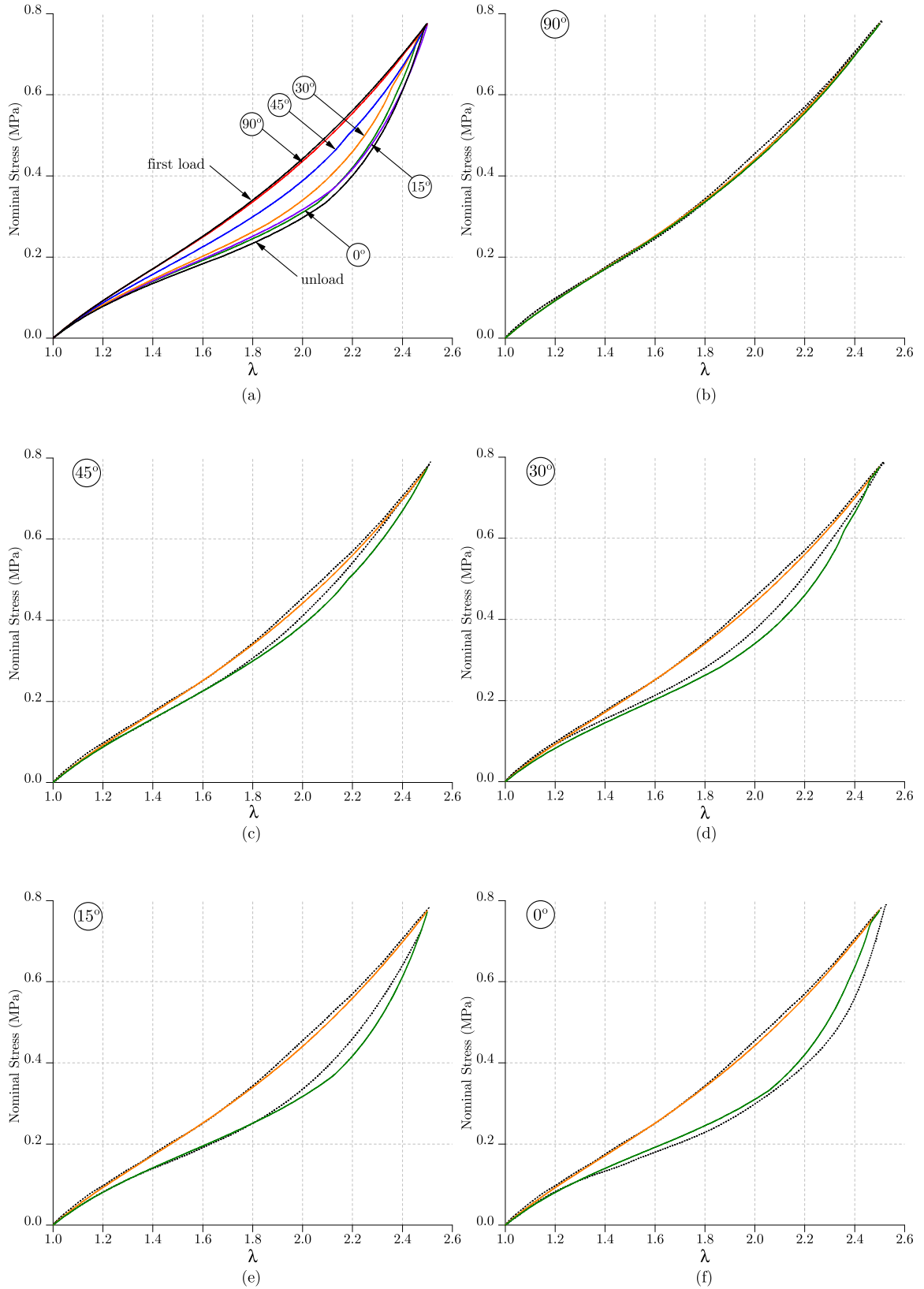


Figure 5: Comparison of the model (solid lines) with TT uniaxial prestretching experimental data (dotted lines). (a) simulation of the model for different orientations of the second load. Details of the experimental (dotted lines) and modeled (solid lines) first and second load curves with an angle between stretch direction of: (b) 90°, (c) 45°, (d) 30°, (e) 15° and (f) 0°.

345 To finish, the model is used to simulate BT tests, the first load being a biaxial test
 346 and the second load being a tensile test. The comparison of the second loading curves is
 347 presented in Fig. 6. It appears that stress softening is moderately overestimated by the
 348 model, however the come-back on the first loading curve is perfectly described.

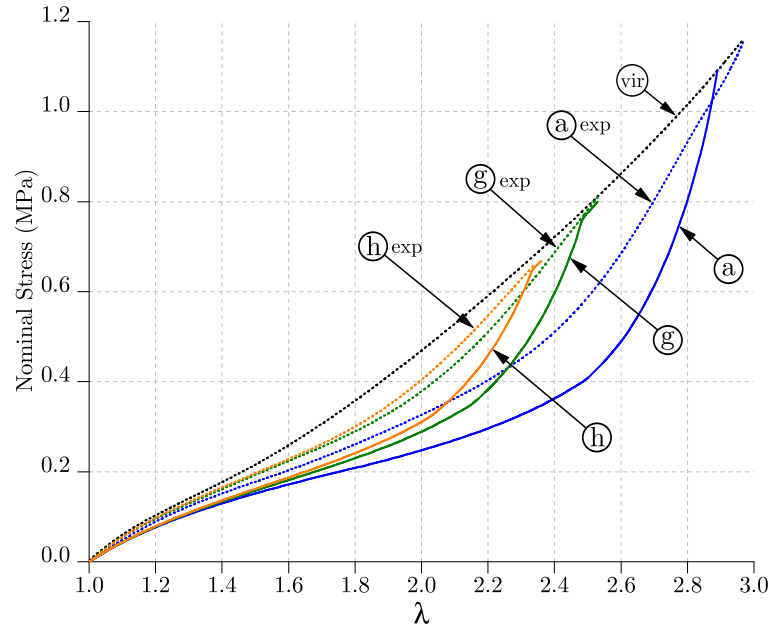


Figure 6: Comparison of the model (solid lines) with BT biaxial prestretching experimental data (dotted lines). Curve *a*: simulation of the model for the second tensile load after an equibiaxial test; curve *g*: simulation of the model for the second load after a biaxial test of biaxiality ratio $\mu = 0.7$; curve *h*: simulation of the model for the second load after a biaxial test of biaxiality ratio $\mu = 0.5$

349 All these simulations emphasize that the use of this new elongation energy measure is
 350 a good point to describe the come back of the second loading curves on the virgin one.
 351 The amount of stress softening is well described for cyclic loading experiments and for
 352 TT tests, where the principal stretch directions were not the same during first and second
 353 loads. Nevertheless, the stress softening during BT test is overestimated. As observed
 354 in Fig. 4(c), stress was underestimated for the equibiaxial state, but this is due to the
 355 underestimation of hyperelastic strain energy obtained at the first load.

356 It can be noticed that the model describes correctly all the experimental tests with a
 357 simple constitutive equation that only depends on one parameter. Evidently, the results
 358 can be improved by proposing more complex constitutive equations, that consequently
 359 would lead to a significant increase in the number of parameters. Nevertheless, the pre-
 360 sented results allowed to demonstrate the efficiency of this new approach.

361 **5. Conclusion**

362 This paper presents an original approach to model the stress induced anisotropy by the
363 Mullins effect, by the definition of a tensor to measure the repartition of the strain energy
364 in space. The comparison of the strain energy in different directions with the maximal
365 principal strain energy permits to create a new formulation for stress softening modeling.
366 In this approach, the constitutive equation is written in function of the variation of strain
367 energy in each direction and the variation of strain energy in the maximal principal strain
368 direction. This new approach captures the principal characteristics of the Mullins effect
369 underlined in literature. This new way of describing Mullins effect anisotropy can be a
370 good starting point to elaborate new constitutive equations.

371 In this paper, a simple constitutive equation to describe the stress softening evolution
372 was proposed. It clearly appears that the results are quite encouraging for a model that
373 can describe many different types experimental tests, with very different strain histories,
374 and the models presents only one material parameter. Of course, the agreement with
375 the experimental data can be improved by using more sophisticated constitutive equation
376 forms.

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