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This is a pre-print of the following article *Original Citation:* The Gent model for rubber-like materials: an appraisal for an ingenious and simple idea / Puglisi, Giuseppe; Saccomandi, G.. - In: INTERNATIONAL JOURNAL OF NON-LINEAR MECHANICS. - ISSN 0020-7462. - 68:(2015), pp. 17-27. [10.1016/j.ijnonlinmec.2014.05.007]

Availability: This version is available at http://hdl.handle.net/11589/8076 since: 2022-06-05

Published version DOI:10.1016/j.ijnonlinmec.2014.05.007

Publisher:

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07 May 2024

The Gent model for rubber-like materials: an appraisal for an ingenious and simple idea

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Abstract

We review the main aspects of the celebrated Gent constitutive model for rubberlike materials. Emphasis is placed on the case of damageable materials describing possible damage and deformation localization.

Keywords: Gent model, limiting chain extensibility, damage.

1. Introduction

During 1996 Alan Gent publishes a short note [16] where he proposed a new constitutive equation for the nonlinear elastic behavior of rubberlike materials. Due to its formal simplicity, this model reached a great popularity in various scientific communities interested in large elastic deformations of solids. The aim of this note is to present an appraisal of this simple constitutive model by showing its effectiveness in describing the behavior of traditional and many new elastomeric and biological materials. We remark that the Gent model [16] has been applied successfully in several different fields of material science and in the following we refer only to a small subset of the many possible applications of the simple idea behind the Gent model. For a more detailed survey of the scientific literature related to the Gent model, we refer the reader to the paper by Horgan in this same volume [18].

Rubberlike materials are typically characterized by their ability to undergo very large reversible deformations. As a consequence they are modeled (at least in appropriate ranges of stretches, temperature and time scales) as hyperelastic materials. A general treatment of such an approach was given by

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Rivlin [32] and later by many other authors (see, for example, [25]). This peculiar macroscopic behavior arises from the structure of rubber-like materials at the micro (network) scale and we refer to the classical book by Treloar [34] for an analysis of the amorphous properties of such macromolecular materials at these scales.

To be more explicit, let us consider a deformation $\hat{\boldsymbol{x}}$ of a body Ω , $\Omega \ni \boldsymbol{X} \mapsto \boldsymbol{x} = \hat{\boldsymbol{x}}(\boldsymbol{X})$ and let $\boldsymbol{F} = \operatorname{Grad}(\hat{\boldsymbol{x}})$ be the deformation gradient. Let then $\boldsymbol{B} = \boldsymbol{F}\boldsymbol{F}^T$ be the left Cauchy-Green strain tensor and let

$$I_1 = tr(\boldsymbol{B}), \quad I_2 = rac{I_1^2 - tr(\boldsymbol{B}^2)}{2}, \quad I_3 = \det \boldsymbol{B}$$

be its principal invariants. If a material is hyperelastic and isotropic [25] we may introduce a strain-energy density function $W = W(I_1, I_2, I_3)$. Moreover, because the bulk modulus of rubber is typically significantly higher than the tensile modulus, rubber and rubberlike materials are often modeled as incompressible materials with an energy density depending on only the first two invariants: $W = W(I_1, I_2)$.

As a result, the Cauchy stress tensor T is given by

$$\boldsymbol{T} = -p\boldsymbol{I} + 2\frac{\partial W}{\partial I_1}\boldsymbol{B} - 2\frac{\partial W}{\partial I_2}\boldsymbol{B}^{-1}, \qquad (1.1)$$

where p is the Lagrange multiplier associated with the incompressibility constraint. Moreover, in the absence of body force, the equilibrium equations are

$$\operatorname{div} \boldsymbol{T} = \boldsymbol{0} \tag{1.2}$$

(here div is the usual divergence operator with respect \boldsymbol{x}).

Schematically, we may consider three distinct classes of constitutive approaches proposed in the framework of nonlinear elasticity for rubberlike materials. The first class proposed phenomenological constitutive laws, relating them both to the experimental observations and to the known molecular structure of the material. In this class different simple microstructure based constitutive equations were taken into account to describe the thermomechanical behavior of rubber-like materials. The most *representative* strain energy density function in this class is for sure the basic neo-Hookean model

$$W = \frac{E}{6}(I_1 - 3), \tag{1.3}$$

depending on one single material small strain tensile modulus E that has been related in various ways to the molecular material properties. This macroscopic constitutive law results as a *homogenized* behavior of an isotropic network of ideal Gaussian chains. An introduction to this class of models can be found in the classical work of Treloar [34].

Successively the axiomatic theory of Continuum Mechanics [35] delivered a systematization of the so-called *representation problem* by a systematic use of the methods of Linear Algebra (see for example [32]). Thus, the second class of constitutive models focussed on the *mathematical* determination of specific forms of the general representation formula (1.1). Several new interesting models resulted from the research in this direction among which the most widely adopted is the Mooney-Rivlin model considering an energy function depending linearly also on the second invariant

$$W = C_1(I_1 - 3) + C_2(I_2 - 3).$$
(1.4)

Here C_1 and C_2 are two material moduli. Of course (1.3) is a special case of (1.4).

The third, more recent, class of constitutive theories resulted from a critical reassessment of all previous theories searching for a deeper connection between the macroscopic response of rubberlike materials and the behavior at the mesoscopic scale. The aim of these new models was both to cover the gap between the theoretical predictions and the experimental behavior and to generalize the elastic constitutive theories to more general material behaviors (*e.g.* residual strains and Mullin and Payne effects). In this case the main contribution was the introduction of models based on the inverse Langevin function defined as $\mathcal{L}(x) = \operatorname{coth}(x) - 1/x$ [3].

To understand the role of this function, we briefly recall that rubberlike materials are amorphous materials consisting of very long flexible chainlike molecules constituted by a backbone of many non-collinear single valence bonds around which, due to thermal agitation, barrier free rotations are possible. Rubbery materials are composed of a network of thousands of these chains linked through interchain bonds. These topological links deliver the material a *solid behaviour* while allowing the molecules to change their shape easily and continuously at normal temperatures due to their Brownian motion. If a tensile force is applied to the network then the chains assume a somewhat oriented configuration. Several interesting material behaviors descend from this microscale material structure. For example, if the macromolecules in the network are highly regular they are able to finely pack (for stereochemical reasons) so that they easily crystallize due to van der Waals forces. In this case the polymeric material behaves like a crystalline solid exhibiting ductile and plastic behavior. In other cases the monomers may hardly move due to viscous inertial and entanglement effects under thermal agitation and therefore the polymer behaves in a *glassy* way.

The ability of the Gent model to describe important properties of rubberlike materials can be substantially noted by the following observation of the behavior of these materials at the network scale. As described above, rubber materials are constituted by long chains energetically free to switch between a wide variety of conformations through transitions phenomena which are governed mainly by the statistics of random processes. For this reason we say that the elasticity of rubber-like materials is *mainly* entropic in nature, because their elasticity is regulated by the configurational entropy of the chains and not by enthalpic energy contributions. In particular, the statistics that govern the conformation of the macromolecules over short chain lengths is Gaussian, but, when we approach something like one-third of the fully stretched length of the chain (*contour length*), non-Gaussian effects become non-negligible. Macroscopically this is reflected in a large experimental discrepancy of the predictions of a model such as (1.3) based on the Gaussian assumption, or its phenomenological generalization (1.4), with experimental observations.

To overcome this problem, two main methods have been proposed. In one direction more complex phenomenological forms than (1.4) have been proposed. Often the main drawback of these constitutive models is that they contains a large number of empirical parameters that are not always easily determined by fitting procedures with experimental data. The advantage is that they are ready to use in the commercial finite element codes as greatly appreciated by engineers.

The second, successful, direction of research was dedicated to the refinement of the molecular description of the macromolecular network and to the consideration of the non-Gaussian character of the random processes of the chains conformations, taking into account that the probability density function for the end-to-end distance of the chains has compact support, and not infinite tails as in the Gaussian case, since the macromolecules have finite contour lengths. These studies generated several models, among which the most popular is the Arruda-Boyce eight chain model [2] which is indeed based on the inverse Langevin function. The advantage of such models is that they usually contain few constitutive parameters and that such parameters are directly connected to the microscopic properties of the material. On the other hand the main disadvantage is the numerical and analytical complexity of such models and the fact that the stress-strain relationship are usually not expressed in closed explicit form.

The Gent constitutive equation has to be considered in such framework (Paraphrasing Gent himself [16])

a simple, two-constant, constitutive relation, applicable over the

entire range of strains. ...,

Alan Gent, using the typical British understatement, justifies the introduction of his model only on the basis of the simple mathematical feasibility. In reality, it was an ingenious idea that allows, especially because of its mathematical simplicity, exploration of many mechanical issues associated with the elasticity of rubber-like materials. These aspects are reviewed in detail in the paper by Horgan in this issue [18] and we refer to this paper for a more detailed survey of the various results obtained in the literature about the Gent model [18]. The aim of this paper is to show the main features (and limits) of the Gent model by considering the simple deformation classes of simple shear and rectilinear shear. Then we show how the idea of Gent led the derivation of a new generation of models useful also in the description of important biomaterials like spider silk or protein macromolecular biomaterials.

2. The Gent Model

The energy density function proposed by Gent in [16] for incompressible, isotropic, hyperelastic materials is, using his exact formulation,

$$W = -\frac{E}{6}J_m \ln\left[1 - \frac{I_1}{J_m}\right].$$
(2.1)

Here E is the small strain tensile modulus that, for incompressible materials, is related to the infinitesimal shear modulus μ by the relation $\mu = E/3$. Thus, since W depends on the only first invariant of B, the Gent model belongs to the class of the generalized neo-Hookean materials such that $W = W(I_1)$.

The important parameter J_m represents the maximum value of I_1 with the energy that grows to infinity as $I_1 \rightarrow J_m$. To better understand its mechanical meaning we may recall a simple result by Kearsley [22] that states that I_1 "is equal to three times the square of the stretch ratio of an infinitesimal line element averaged over all possible orientations". As a consequence J_m can be seen as a fair (and natural) measure of the average contour length of the chains composing the polymeric network.

Observe also that, in analogy with the entropic models for molecular chains, showing that the non-Gaussian models converge to a Gaussian one when the contour length grows to infinity, we observe that when $J_m \to \infty$ (2.1) reduces to (1.3) corresponding to the averaged behavior of an isotropic network of Gaussian chains. We may then see the Gent model as a simple and direct generalization of the neo-Hookean strain energy density that takes into account the non-Gaussian character of the macromolecular chains with finite contour length. The stress-strain relation for (2.1) is easily obtained as

$$\boldsymbol{T} = -p\boldsymbol{I} + \frac{E/3}{1 - I_1/J_m}\boldsymbol{B},$$
(2.2)

and the generalized shear modulus function $\hat{\mu}$ is given by

$$\hat{\mu} = \frac{E/3}{1 - I_1/J_m} \tag{2.3}$$

and is a function of the only first invariant.

2.1. Simple shear

To describe the behavior of the Gent model we begin by fixing the ideas on the simple, analytically clear case of simple shear deformations

$$x = X + \kappa Y, \quad y = Y, \quad z = Z. \tag{2.4}$$

Here κ is the shear deformation parameter. This deformation is probably the simplest example of finite deformation although it is a deformation which is difficult to produce experimentally due to the required boundary conditions such as surface tractions.

In this case, given the energy $W = W(I_1, I_2)$ the components of the Cauchy stress are given by

$$T_{11} = -p + 2(1 + \kappa^2)W_1 - 2W_2, \quad T_{12} = 2\kappa(W_1 + W_2),$$

$$T_{13} = T_{23} = 0,$$

$$T_{22} = -p + 2W_1 - 2(1 + \kappa^2)W_2, \quad T_{33} = -p + 2W_1 - 2W_2,$$

(2.5)

where $W_i = \frac{\partial W(I_1, I_2)}{\partial I_i}$, i = 1, 2. In the case of Gent material (2.2) the shear stress is given by

$$T_{12} = \mu \frac{\kappa}{1 - (\kappa^2 + 3)/J_m}.$$
(2.6)

To point out the effect of the parameter J_m we observe that

 $T_{12} \to \infty$, when $\kappa \to \sqrt{J_m - 3}$

and

$$T_{12} \to \mu \kappa$$
, when $J_m \to \infty$

The behavior is reproduced in Fig.1 where we show a comparison also with the 8-chain Arruda-Boyce model [3] for which after easy calculations one gets

$$T_{12}^{8c} = \frac{\mathcal{L}^{-1}\left(\sqrt{\frac{3+k^2}{3n}}\right)}{2\sqrt{\frac{3+k^2}{3n}}}\,\mu\,k,$$

where n is the number of links in the chain.



Figure 1: Comparison of the shear stress/strain curves for the Gent model, the neo-Hookean model and the 8-chain model. Here the values $J_m = 21$ and n = 7 have been chosen to let the Gent and 8-chain model attain the same limiting extensibility.

We observe that the Gent model behaves as the neo-Hookean model at low strain. Moreover the model, while keeping its fundamental analytical simplicity, approximates very well the macroscopic 8-chain model. This last model is deduced from a molecular chain model of the inverse Langevin type as attained under a freely jointed chain behavior hypothesis [3].

It is important to observe that the generalized shear modulus for the Gent material is a rational function. In this respect we observe that in typical phenomenological models polynomial (Taylor series) approximations are considered for the constitutive laws. As a result, these models lose the possibility of describing well the asymptotic behavior assigned by the contour length threshold. On the other hand, it is possible to introduce better approximations using rational functions of given orders such as the *Padé approximants* [4] that are usually more accurate than Taylor expansions and are able to take into account the presence of singularities (such as the limiting value of the admissible amount of shear in (2.6)). The first to use a rational approximation for the inverse Langevin function was, to the authors knowledge, Treloar [34]. Moreover, a Padé approximation was first introduced by Cohen in 1991 [5] and required the introduction of sixth-order terms. Interestingly, later Horgan and Saccomandi in [20] realized that by fixing J_m (the maximum average contour length) the Padé approximant of the the eight-chain model proposed by Arruda and Boyce [2] delivers exactly the Gent model. This result gives a natural *molecular* interpretation of the Gent model.

2.2. Limits of the Gent model

As typical of very simple models, the constitutive assumption (2.1) was an ingenious intuition, but because it uses only two constitutive parameters to describe many properties of a huge class of complex statistical models, it has some important limits. In this section we briefly analyze some of them. We remark, anyway, that the limits we describe in the following are indeed shared with all members of the class of generalized neo-Hookean models, *i.e.* materials with an energy density depending on the only first invariant: W = $W(I_1)$. Therefore, the resulting unpleasant features that will be discussed in the following are shared also with models of the Arruda-Boyce type [2, 3].

To be specific, consider again the simple shear deformation and the associated universal relations [33] that are assigned by the two trivial conditions $T_{13} = T_{23} = 0$ plus the celebrated Rivlin universal relation

$$T_{11} - T_{22} = \kappa T_{12}. \tag{2.7}$$

As a result, if experimentally (2.7) is not satisfied then one may conclude that the material under investigation is not an isotropic Cauchy elastic material.

Consider now a rectangular elastic body, under the shear deformation (2.4) and suppose that the two faces perpendicular to the Z direction respect the boundary conditions $T_{33} = 0$. Using (2.5) we obtain

$$p = 2(W_1 - W_2).$$

As a result we have

$$T_{11} = 2\kappa^2 W_1, \quad T_{12} = 2\kappa (W_1 + W_2),$$

 $T_{22} = -2\kappa^2 W_2, \quad T_{13} = T_{23} = T_{33} = 0.$

Now we have three trivial universal relations $T_{13} = T_{23} = T_{33} = 0$ plus (2.7). If then we suppose that $W = W(I_1)$ (generalized neo-Hookean material), we

obtain

$$T_{11} = 2\kappa^2 W_1, \quad T_{12} = 2\kappa W_1$$

 $T_{22} = T_{12} = T_{22} = T_{22} = 0$

This means that the new trivial universal relation $T_{22} = 0$ arises from the peculiar case of generalized neo-Hookean materials.

By comparing these theoretical results with experimental data the authors in Pucci and Saccomandi [28] and in McKenna et al. [17], could conclude that

it is shown that at moderate ratios, the eight-chain model does not provide even qualitative agreement with the experimental stressstrain data for both the dry and swollen states.

Similar comments can be extended also to the Gent model.

Despite these limitations, the role played in the development of the theory of rubber-like elasticity by the Gent model has been fundamental due to its simplicity and its relation with the inverse Langevin function models. As a result the Gent model has been, in the last decade, a true motor towards interesting models able to connect the macroscopic scale behavior to the mesoscopic structure of polymeric networks. Horgan and Saccomandi (see [18]) and other co-workers have shown that using the model (2.1) it is possible to solve analytically a huge class of boundary value problems. Moreover, the simple structure of the Gent model may be generalized to obtain interesting three-dimensional continuum versions of various molecular models such as the widely adopted worm-like chain model for biological materials [26].

2.3. Rectilinear Shear

The main effect of the parameter J_m on the solution of a boundary value problem is here exemplified by considering the simple case of rectilinear shear deformations

$$x = X + f(Y), \quad y = Y, \quad z = Z,$$

where f(Y) is a function that must be determined from the balance equations.

To be specific, consider the rectangular body schematized in Fig.2_a under a constant load q with fixed boundaries at the edges Y = 0, 1. The averaged total potential energy of the system is $(\bar{G} = \frac{G}{\mu} = \frac{3G}{E})$

$$\bar{G} = \int_0^1 \left(-\frac{1}{2} J_m \ln\left(1 - \frac{\kappa^2 + 3}{J_m}\right) - \bar{q}f \right) dY, \qquad (2.8)$$

where $\bar{q} = \frac{q}{\mu} = \frac{3q}{e}$ and the shear κ is now defined as $\kappa = \frac{df}{dY}$. If we consider the Dirichlet boundary conditions

$$f(0) = 0, \quad f(1) = 0,$$
 (2.9)

by integrating the Euler-Lagrange equilibrium equations we obtain the balance equation

$$\frac{\kappa}{1 - (\kappa^2 + 3)/J_m} + \bar{q}Y = c_1 \tag{2.10}$$

where c_1 is an integration constant.

Observe that, since for $J_m > 3$ the energy density (2.1) is a strictly convex function of κ and the coercivity condition $W \geq J_m \ln\left(\frac{J_m}{J_m-2}\right) + \frac{J_m}{J_m-2}\kappa^2$ is satisfied, the solution to the BVP we are considering exists and it is unique in a suitable deformation space [1]

To search for the explicit solution, we first observe that since the problem is symmetric around Y = 1/2 the considered BVP can be recast as the standard IVP

$$\frac{\kappa}{1 - (\kappa^2 + 3)/J_m} = \bar{q}\left(\frac{1}{2} - Y\right), \quad \hat{f}(0) = 0.$$

Thus, by using simple algebraic methods, we may obtain by quadrature the exact solution in terms of the function

$$\Phi(Y) = \frac{J \log\left(\left|Y - \frac{1}{2}\right|\right) - J \operatorname{arcsinh}\left(\frac{J}{\sqrt{J - 3\bar{q}}|2Y - 1|}\right)}{2\bar{q}} - \frac{\sqrt{J^2 + 4(J - 3)\bar{q}^2(Y - 1)Y + (J - 3)\bar{q}^2}}{2\bar{q}}$$

as

$$f(Y; J_m; \bar{q}) = \Phi(Y, J_m, \bar{q}) - \Phi(0, J_m, \bar{q}).$$
(2.11)

This solution is represented in Fig.2.

The peculiarity of this solution, first proposed in [27], is obtained in the limit $\bar{q} \to \infty$ (see Fig.2). Indeed, while for the neo-Hookean material the solution blows up as $\bar{q} \to \infty$, the asymptotic solution for (2.11) is given by

$$f(Y; J_m; \bar{q} \to \infty) = \frac{\sqrt{J_m - 3}}{2} (1 - |2Y - 1|),$$

$$k(Y; J_m; \bar{q} \to \infty) = \sqrt{J_m - 3},$$

$$\bar{G}(Y; J_m; \bar{q} \to \infty) \to \infty.$$
(2.12)



Figure 2: Rectilinear shear for a rectangular body of a Gent material (here we assumed $J_m = 21$). a) scheme of the deformation class and assigned load q. b) displacement, c) shear strain, and d) energy density fields at different values of the load \bar{q} .

Observe that in the limit of growing load the system tends to a solution that is uniform everywhere up to a point where the amount of shear has a jump. A clear phenomena of *localization* of the strain, but what is more important is that everything happens with finite values of strain and stress with possible important applications in fracture mechanics: a first attempt in this direction has been provided in [19] and with more details and interesting insights in [23]. The results contained in such papers confirm that the use of the idea of limiting chain extensibility may be a possible solution for some of the paradoxes of classical fracture mechanics.

3. Beyond elasticity

As remarked above the constitutive parameter J_m is connected to a mesoscopic characteristic of the polymeric material (contour length). As a consequence it is natural to extend the Gent model (2.1) to capture stress-softening and healing effects related to the variations of this mesoscale parameter. Specifically, we point out that *damage* in polymeric and many biological materials represents a macroscopic homogenized effects of complex phenomena of breaking [10] and re-crosslinking [6] at the network scales related to the evolution during the history of deformation of the average length of the macromolecular chains. The analysis of such behavior at network scales suggested the introduction of microstructure inspired approaches such as the ones proposed in [29] and [10]. These models have been shown to be effective in describing the complex history dependent dissipative behavior of rubberlike materials also in non-trivial inhomogeneous deformation histories [9], showing the ability of describing experimentally verified damage localization effects [11, 7] or instabilities observed in rubberlike balloons [8].

In this perspective and in relation to the Gent model, we remark that recent advances in experimental techniques, that allow the analysis of the behavior of single macromolecule thermomechanical behavior [30, 31], showed the fundamental role in the macroscopic dissipation of the continuous variations of the chain contour length. These variations are accompanied by entropy variations revealed at the micro scale by a sequence of stress drops in the chains. Based on these observations an energetic microstructure inspired approach [12] or statistical mechanics multiscale approaches [13, 14] have recently been proposed to describe the dissipative behavior of macromolecular materials undergoing unfolding phenomena. Despite the ability of these models to deliver a direct connection between the microstructure properties and the macroscopic behavior of these materials, fundamental in particular in the field of the design of new bio-inspired materials, the possibility of models as simple as the Gent model, with a clear connection with the microstructure properties of the material, appears appealing both for numerical computations and for the clearness of the resulting analytical interpretations. This suggests extending the Gent model to non-elastic behavior of biological and rubberlike materials [21].

The aim of this section is to show how it is possible to modify the constitutive equation (2.1) to take into account damage. In the framework of the internal variable Thermodynamics, under the hypothesis of isotropic damage, we may simply introduce an internal damage variable α with a new history dependent energy density function $W = W(\mathbf{F}, \alpha)$. In this approach the main problem is the deduction of the dependence of the energy density on the internal variable itself and of its evolution equation. In [7, 14] the authors showed the possibility of deducing such informations by considering multiscale approaches.

Another, more phenomenological approach is to consider evolution equations reflecting the macroscopic hysteretic and damage behavior of the system [15] or to deduce, knowning the energy density function, the evolution equation of the damage variable based on a hypothesis of maximization of the dissipation rate (see [29]). To be more explicit, consider the usual definition of the dissipation rate

$$\xi = \mathbf{T} \cdot \mathbf{D} - \dot{W} = \left(\mathbf{T} - \frac{\partial W}{\partial \mathbf{F}} \mathbf{F}^{T}\right) \cdot \mathbf{L} + g\dot{\alpha}, \qquad (3.1)$$

where $\mathbf{L} = \dot{\mathbf{F}} \mathbf{F}^{-1}$, the stretching tensor is defined as $\mathbf{D} = (\mathbf{L} + \mathbf{L}^T)/2$ and $g := -\frac{\partial W}{\partial \alpha}$ is the generalized force working for the damage increment [36]. To maximize the dissipation rate subjected to the isochoricity condition

$$\boldsymbol{L}\cdot\boldsymbol{I}=0$$

and to the requirement

$$\xi \ge 0, \tag{3.2}$$

representing the Clausius-Duhem dissipation inequality [36], we introduce the Lagrangean function

$$\mathcal{L} = \xi + \eta_1 \left\{ \left(\mathbf{T} - \frac{\partial W}{\partial \mathbf{F}} \mathbf{T}^T \right) \cdot \mathbf{L} + g\dot{\alpha} - \xi \right\} + \eta_2 \mathbf{L} \cdot \mathbf{I}.$$

The Euler-Lagrange necessary condition (modulo a relabeling of the Lagrange multipliers η_1, η_2) delivers the usual formula for the Cauchy stress tensor of incompressible materials

$$\boldsymbol{T} = -p\boldsymbol{I} + \frac{\partial W}{\partial \boldsymbol{F}} \boldsymbol{F}^{T}, \qquad (3.3)$$

where $p = -\frac{\eta_2}{\eta_1}$ and the relationship

$$\eta \frac{\partial \xi}{\partial \dot{\alpha}} = g$$

where $\eta = \frac{1+\eta_1}{\eta_1}$. As a result we have

$$\xi = g\dot{\alpha} = \eta \frac{\partial\xi}{\partial\dot{\alpha}}\dot{\alpha}.$$
(3.4)

This equation defines the rate of damage depending on the rate of dissipation of the material.

Since here we are interested in the description of materials showing a rate-independent behavior we assume that the driving force $g = g(\alpha)$ is independent of $\dot{\alpha}$. Moreover, since with the progression of the damage the average contour length of the macromolecular network increases we assume that

$$J_m(\alpha) = J_m^0 + \alpha J_m^1, \qquad \alpha \in (0, 1)$$
(3.5)

so that in this context the damage of the material coincides with a variation of the parameter J_m . Here $J_m = J_m^0$ represents the value of J_m for the undamaged material, whereas $J_m = J_m^0 + J_m^1$ is the value of J_m at damage saturation. As a result we have

$$g = g(I_1, \alpha) = \frac{I_1 + (J_m - I_1)\log(1 - I_1/J_m)}{6(J_m - I_1)} EJ_m^1 > 0, \qquad (3.6)$$

so that, using (3.1), (3.2), and (3.3), we obtain the reduced dissipation inequality

$$\xi = g\dot{\alpha} \ge 0,\tag{3.7}$$

showing that in this simple setting the Clausius-Duhem inequality for this simple model is respected iff damage grows:

 $\dot{\alpha} \geq 0$

or, using (3.5), equivalently

 $\dot{J}_m \ge 0.$

Regarding the choice of the *evolution* law, it must be fixed through a phenomenological approach or deduced by an analysis of the behavior at the network scale [14]. Here we are interested in describing deterioration effects in materials such as rubber showing a Mullins type damage effect [24] whose memory is restricted to the only maximum values of the attained stretches. Then, based on the Gent idea, on the microstructure considerations reported above and on the results in [13] and [14], we assume that the damage variable α depends only on the maximum attained value of the first invariant, I_1^{max} . In particular we may simply choose a growing function of I_1^{max} (see again [14] for a microstructure justification of this choice or [21] for the application of this simple idea to describe the Mullins effect). As a result the system undergoes damage only when $I_1 = I_1^{max}$, with a dissipation potential

$$D = g(\alpha, I_1^{max})\dot{\alpha}.$$

The maximization of the entropy production associated with this type of potential delivers the conditions (3.3), (3.4) and the consistency condition

$$(g(\alpha, I_1^{max}) - g(\alpha, I_1))\dot{\alpha} = 0$$

that, due to the fact that g grows with I_1 , ensures that damage is attained only when $I_1 = I_1^{max}$. As a result we obtain the history dependent elastic domain $I \in (3, I_1^{max})$.

Now, if we fix again our attention on the simple shear deformation class, we may for the sake of algebraic simplicity assume the following monotonic damage law, depending only on the maximum previously attained value of the shear strain k_{max} :

$$\alpha = 1 - \exp\left\{-\beta \left(\sqrt{\kappa_{max}^2 - \kappa_0^2}\right)^{\gamma}\right\},\tag{3.8}$$

where β and γ are positive material parameters, and $\kappa_0 < \sqrt{J_m^0 - 3}$ is the activation shear threshold. As a result we deduce the shear stress-shear strain relation

$$T_{12} = \begin{cases} \frac{\kappa \mu}{1 - \frac{\kappa^2 + 3}{J_m^0}} & \text{if } k_{max} < k_0 \\ \frac{\kappa \mu}{1 - \frac{\kappa^2 + 3}{J_m^0 + \alpha J_m^1}} & \text{if } k_{max} \ge k_0. \end{cases}$$
(3.9)

The corresponding stress-strain curves are represented in Fig. 3 for the two different damage functions represented in Fig. $3_{a,c}$. Interestingly, according to the choice of this function, two different scenarios of damage evolution can be obtained. If the contour length grows slowly as I_1^{max} grows, the system shows a continuous damage evolution up to damage saturation as shown in Fig. 3_c . If instead the contour length grows fast the corresponding softening can prevail with a non monotone stress-strain diagram. This possibility was evidenced in the microstructure inspired damage model proposed in [11] where the authors showed the resulting possibility of damage and deformation localization. The analytical variational approach in this case (non-convex energy densities) can be found in [7] where damage localization for antiplane shear deformations was described.

4. Concluding Remarks

In the theory of polymer mechanics many constitutive forms of the strainenergy density have been proposed, but only few of these constitutive equation delivered true breakthroughs. An example is the Mooney-Rivlin strain



Figure 3: Shear stress - shear strain diagrams for a damageable Gent material under simple shear. Here we assumed $\mu = 1$, $J_m^0 = 3.5$, $J_m^1 = 1.0$. In b) we show the behavior for a material with a damage function represented in a) assigned by $\delta = 1$ and n = 2. In d) we show the non monotone shear stress-strain corresponding to the damage function in c) corresponding to $\delta = 4$ and n = 6.

energy density function at the basis of the Rivlin research on finite elasticity. Another example is the Ogden strain energy density function, the first functional form that allowed to fit in a careful way the experimental data for a variety of deformations and a significant range of strains. Such constitutive equations were at the base of clear advancements in rubber constitutive modeling in various directions. On the same pathway the Gent model, because of its mathematical feasibility, was at the base of a new impetus of research analyzing the multi-scale behavior rubber-like materials.

The use of models based on the inverse Langevin function is clearly re-

stricted by the fact that even for very simple deformation fields it is not possible to obtain results in closed form. On the other hand, the Gent model which has the same accuracy in fitting experimental data as the Arruda-Boyce model based on the inverse Langevin function, allows closed form solutions for a huge class of deformations with a much clearer mechanical interpretation.

Moreover, the simple and clear mathematical structure of the Gent model allows us to understand how it is possible to generalize constitutive theories beyond classical Taylor expansions. Interestingly the damage extension of the Gent model here proposed, considering a history dependent parameter J_m , let us describe complex phenomena such as the transition from homogeneous to localized damage configurations, relating them to microstructure properties such as the rate of contour length variations of the chains. The clear interpretation of the material moduli involved in the Gent model is the key ingredients for such an intuitive way of extending this model.

We are sure that the Gent model will continue to stimulate in the next decades many interesting researches in the field of macromolecular materials and, as we have tried to show in this paper, not only in the framework of nonlinear elasticity, but also in its extension to dissipative behaviors.

All people engaged in the mechanics of elastomeric materials have to be grateful to the simple idea of Alan Gent a true gentleman who has always communicated his findings professionally, with enthusiasm, humility and an open mind.

Acknowledgements This paper is dedicated to the memory of Alan Gent. G.P and G.S. have been partially supported by GNFM of Istituto Nazionale di Alta Matematica. G.S. is grateful to C. O. Horgan and E. Pucci for sharing many good ideas about the Gent model during the last fifteen years. We thanks Ray Ogden for helpful criticisms.

References

- ANTMAN S.S. (1995) Nonlinear Problems of Elasticity, Springer-Verlag, New York.
- [2] ARRUDA E.M., BOYCE M.C. (1993) A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials, J. Mech. Phys. Solids 41, 389–412.
- [3] ARRUDA E.M., BOYCE M.C. (2000) Constitutive models of rubber elasticity: a review, *Rubber Chem. Techn.* **73**, 504–523.

- [4] BAKER, G. A. JR. ,GRAVES-MORRIS P. (1996) Padé Approximants. Cambridge U.P., Cambridge
- [5] COHEN A. (1991) A Padé approximant to the inverse Langevin function, *Rheologica Acta* 30, 270–273.
- [6] D'AMBROSIO P., DE TOMMASI, D., FERRI D., PUGLISI, G. (2007) A phenomenological model for healing and hysteresis in rubber-like materials, *Int. J. Eng. Science* 46, 293–30.
- [7] DE TOMMASI D., MARZANO. S., PUGLISI G., SACCOMANDI G. (2010) Localization and stability in damageable amorphous solids, *Cont. Mech. Therm.* 22, 47–52
- [8] DE TOMMASI D., MARZANO. S., PUGLISI G., ZURLO G. (2009) Damage and healing effects in rubber-like balloons, Int. J. Sol. Struct. 46, 223-23
- [9] DE TOMMASI, D., PUGLISI, G. (2007) Mullins effect for a cylinder subjected to combined extension and torsion, J. Elasticity 86, 85–99.
- [10] DE TOMMASI, D., PUGLISI, G., SACCOMANDI G. (2006) A micromechanics-based model for the Mullins effect, J. Rheology 50, 495– 512.
- [11] DE TOMMASI, D., PUGLISI, G., SACCOMANDI G. (2008) Localized versus diffuse damage in amorphous materials, *Phys. Rev. Lett.* 100, 085502.
- [12] DE TOMMASI, D., PUGLISI, G., SACCOMANDI G. (2010) Damage, self-healing, and hysteresis in spider silks, *Biophysical J.* 98, 1941–1948.
- [13] DE TOMMASI D., MILLARDI N., PUGLISI, G., SACCOMANDI G. (2013) An energetic model for macromolecules unfolding in stretching experiments, J. Roy. Soc. Int. 10, 20130651.
- [14] DE TOMMASI D., PUGLISI, G., SACCOMANDI G. (2014) A multiscale model for macromolecular materials with unfolding domains. Preprint.
- [15] DORFMANN A., OGDEN R.W. (2004) A constitutive model for the Mullins effect with permanent set in particle-reinforced rubber, Int. J. Sol. Struct. 41 1855–1878.
- [16] GENT A. (1996) A new constitutive relation for rubber. Rubber Chem. Techn. 69 59–61.

- [17] HAN, W.H., HORKAY, F., MCKENNA, G.B. (1999) Mechanical and swelling behaviors of rubber: a comparison of some molecular models with experiment. *Math. & Mech. Solids*, 4, 139–167.
- [18] HORGAN C.O. (2014) The remarkable Gent constitutive model for hyperelastic materials, Int. J. Nonlin. Mech., this issue.
- [19] HORGAN C.O., SACCOMANDI G.(2001) Anti-plane shear deformations for non-Gaussian isotropic, incompressible hyperelastic materials, Proceedings of the Royal Society A-457, 1999–2017.
- [20] HORGAN C.O., SACCOMANDI G. (2002) A molecular-statistical basis for the Gent model of rubber elasticity, J. Elasticity, 68, 167–176.
- [21] HORGAN C.O., OGDEN R.W., SACCOMANDI G. (2004) A theory of stress softening of elastomers based on finite chain extensibility, *Proc. Roy. Soc. Lond. A*, 460, 1737–1754.
- [22] KEARSLEY E.A. (1989) Strain invariants expressed as average sStretches, J. Rheol. 33 757–760;
- [23] LONG, R., HUI C. Y. (2011) Effects of finite chain extensibility on the stress fields near the tip of a mode III crack *Proc. R. Soc.*, A 467, 3170-3187
- [24] MULLINS L., TOBIN N. (1953) Theoretical model for the elastic behavior of filler-reinforced vulcanized rubber, *Rubber Chem. Technol.* 30 551571
- [25] OGDEN R.W. (1984) Nonlinear elastic deformations, Ellis Horwood, Chichester.
- [26] OGDEN R.W., SACCOMANDI G., SGURA I. (2006) On worm-like chain models within the three-dimensional continuum mechanics framework, *Proc. R. Soc.*, A 462, 749–768.
- [27] PUCCI E., SACCOMANDI G. (1999) Some remarks on the Gent model of rubber elasticity, Proceedings 1st Canadian Conference on Nonlinear Solid Mechanics, June 16-20, 1999, University of Victoria Press, 163– 172.
- [28] PUCCI E., SACCOMANDI, G. (2002) A note on the Gent Model for rubber-like materials, *Rubber Chemistry and Technology*, **75**, 839–851.

- [29] RAJAGOPAL K.R., SRINIVASA A.R., WINEMAN A.S. (2007) On the shear and bending of a degrading polymer beam, *International Journal* of Plasticity, 23, 1618–1636.
- [30] RIEF M., OESTERHELT F., HEYMANN B., GAUB H.E. (1997) Single molecule force spectroscopy on polysaccharides by atomic force microscopy, *Science*, **275**, 1295–97.
- [31] RIEF M., GAUTEL M., OESTERHELT F., FERNANDEZ J.M., GAUB H.E. (1997) Reversible Unfolding of Individual Titin Immunoglobulin Domains by AFM, *Science*, **276**, 1109-1112.
- [32] RIVLIN R. S. (1948) Large elastic deformations of isotropic materials IV. Further developments of the general theory, *Phil. Trans. Roy. Soc.* A241, 379–397.
- [33] SACCOMANDI G. (2001) Universal results in finite elasticity, in Nonlinear Elasticity: Theory and Applications Eds. Y. B. Fu & R. W. Ogden. Cambridge: Cambridge University Press Lecture Notes in Mathematics 283.
- [34] TRELOAR L. R. G. (1975) The physics of rubber elasticity Oxford University Press, Oxford and New York.
- [35] TRUESDELL C., NOLL W. (1965) The non-linear field theories of mechanics. Handbuch der Physik, Bd. III/3, Springer Berlin
- [36] ZIEGLER, H. (1983). An introduction to Thermomechanics. North-Holland.