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A NEW MODELLING OF THE MULLINS EFFECT AND THE VISCOELASTICITY OF ELASTOMERS BASED ON A PHYSICAL APPROACH

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The mechanical behaviour of elastomers is known to be highly non-linear, time-dependent and to exhibit hysteresis and stress-softening known as the Mullins effect (Mullins, 1948) upon cyclic loading. These phenomena are classically studied and modelled independently. Some studies are based on physical approaches (Arruda and Boyce, 1993; Bergström and Boyce, 1998; Marckmann *et al*., 2002) in which macroscopic constitutive equations are build in regards with the physics of polymeric chains. In this context of physical considerations, the aim of the present paper is to study independently each phenomenon involved in rubber-like materials and to assemble them in a global constitutive equation.

First, the hyperelastic behaviour of elastomers is modelled by the physical approach of Arruda and Boyce (1993), widely known as the eight-chains model. This model accurately reproduces the large strains elastic behaviour of elastomers under different types of deformation. Second, the hysteretic time dependent behaviour is approached by the model developed by Bergström and Boyce (1998) that considers the separation of the network in two phases: an elastic equilibrium network and a viscoelastic network that captures the non-linear rate-dependent deviation from equilibrium. This model is quite simple and successfully reproduces the rate-dependent hysteretic properties of elastomers. Last, as shown in the bibliography, the Mullins stress-softening effect can be considered as a damage phenomenon which only depends on the maximum stretch attained during the deformation history (Govindgee and Simo, 1992). In the present approach, the physical theory of Marckmann *et al*. (2002) based on an alteration of the polymeric network is adopted. This theory was introduced in the eight-chains hyperelastic model and successfully simulates the decrease of the material stiffness between the first and the second loading curves under cyclic loading. As these three models are based on the physics of the polymeric network, they are gathered in a new efficient constitutive equation. This model is able to reproduce simultaneously the Mullins effect and the time-dependent hysteretic behaviour of elastomers. Finally, the constitutive parameters of this new model are identified by fitting experimental data.

Key Words: Natural Rubber, hyperelastic, Mullins effect, hysteresis, physical approach.

1. INTRODUCTION

The fatigue of elastomers has become a key point in automotive industry. Indeed, the prediction of the fatigue behaviour of automotive parts, such as engine mounts or bump stoppers, is a necessary prerequisite to the development of new products. In this context, the numerical modelling, for example the finite element method, takes an important role and the development of efficient constitutive equations for elastomers is of prime necessity.

Elastomers are known to exhibit a highly non linear elastic behaviour under static load; a rate dependent or viscoelastic behaviour including hysteresis under cyclic loading; and a so-called Mullins effect which can be described as a stress-softening phenomenon observed during the first cycles under fatigue loading conditions. Another phenomenon, the Payne effect, involves the thixotropic behaviour under dynamic loading (Lion, 1998). Our study is devoted to the modelling of the behaviour of a carbon black filled natural rubber. It is well known that the addition of filler particles leads to an increase of the material stiffness and to an improvement of the ultimate properties of the material (ultimate stress and maximum extensibility). Moreover, it has to be noted that the Mullins effect and the hysteretic nature of the rubber is amplified by the presence of fillers. Considering cyclic experiments, the Mullins effect is measured through the area between the first and the second loading curves and the hysteretic behaviour is characterised by the area between loading and unloading curves.

The aim of the present paper is the development of a rubber-like constitutive equation that is able to simulate both these two phenomena. A physical approach has been adopted for the development of the model. In section 2, classical hyperelastic constitutive equations are first recalled. Then, the models adopted for the Mullins effect and the hysteresis are independently presented. Finally, a combination of these two sub-models is developed. Section 3 presents the identification of the previous model. The comparison between experimental data and theoretical results is performed for both uniaxial tensile and pure shear tests. Section 4 is devoted to concluding remarks.

2. CONSTITUTIVE EQUATION

2.1. HYPERELASTIC MODEL

Rubber like materials are classically considered isotropic, incompressible and hyperelastic. They are characterised by a strain energy function *W*. Thus, the definition of a hyperelastic model consists in defining the form to *W*. Two different points of view can be adopted to define *W*: phenomenological or physical. In the former case, many authors proposed models based on strain invariants. Mooney (1940) developed a linear model of the strain invariants which was generalised by Rivlin and Saunders (1951). Others forms of *W* were considered by Gent and Thomas (1958) and Hart-Smith (1966). Principal stretches based model were proposed by Valanis and Landel (1967) and Ogden (1972). All these constitutive equations are based on both experimental data and mathematical developments. In the later case, the definition of *W* is based on the physics of the polymeric chains network. Treloar (1943) used Gaussian statistics applied to the network in order to describe the macroscopic behaviour of rubber-like materials. These physical considerations lead to the neo-Hookean constitutive equation. This model is not dedicated to large deformations. In order to overcome the limitations of the neo-Hookean approach, authors used non-Gaussian statistics to describe molecular chains deformations. Kuhn and Grün (1942) described the stretching limit of the chains. Their developments are the basis of the chains models like the full network model of Wu and van der Giessen (1992), the three chains model of James and Guth (1943), the four chains model of Flory (1944) and the eight chains model of Arruda and Boyce (1993). The network configuration corresponding with the eight-chains model is presented in Figure 1.

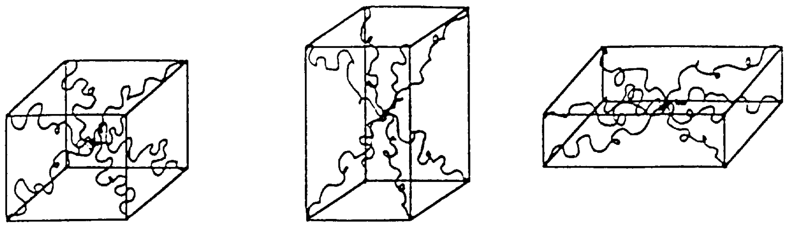

Figure 1. Spatial representation of the eight chains model.

In our study, we consider the eight chains model because of its simplicity and its good capability of describing the strain-hardening of the material. The corresponding expression of *W* is given:

$$W = C_r.N\left[\frac{r_{chain}}{Nl}\beta + \ln\frac{\beta}{\sinh\beta}\right] \tag{1}$$

Where

$$\begin{cases} C_r = nk\theta \\ r_{chain} = \dfrac{1}{\sqrt{3}}\sqrt{N}l(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{1/2} \\ \beta = \boldsymbol{L}^{-1}\left[r_{chain}/Nl\right] \end{cases} \tag{2}$$

In which $\boldsymbol{L}$ is the Langevin function defined by $\boldsymbol{L}(\beta) = \coth(\beta) - 1/\beta$.

2.2. MULLINS EFFECT

It is well known that elastomers exhibit a reduction of stiffness after the first loading cycle of a fatigue experiment. This phenomenon was observed, first, by Bouasse ad Carrière (1903), studied in details by Mullins (1969) and is widely known as the Mullins effect. Under quasi-static condition, the viscoelastic behaviour of elastomers does not influence the material response and the behaviour can be considered as purely elastic and submitted to the Mullins effect. The corresponding stress-strain curves are presented in Figure 2. The undamaged (or virgin) material is first stretched to the extension ratio λ_I and the stress follows the path I in Figure 2(b). Then the unloading from λ_I to 0 follows the path I'. The second loading from 0 to $\lambda_{II} > \lambda_I$ first follows the path I' until $\lambda = \lambda_I$ then it follows the path II. The second unloading from stretch ratio λ_{II} to 0 follows the path II' which is different than path I'. At a given stretch, the stress on II' is lower than the stress on I'. Repeating this process, the loading path corresponding to the increase of stretch from 0 to λ_{II} is the path that joins II' and the part III of the virgin curve. Finally, the corresponding unloading follows the path III'. These observations illustrate Mullins' remarks, as accommodation occurs only from strain lower than the maximum strain obtained in the material history, and when strain reaches the maximum strain ever attained, the behaviour becomes the one of an undamaged material.

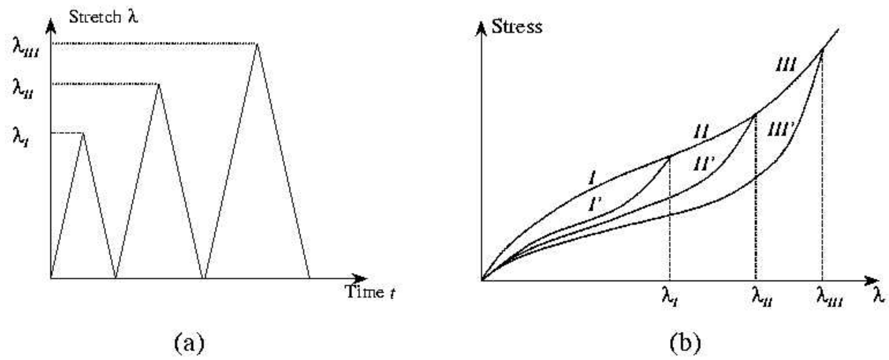

Figure 2. Mullins effect under quasi-static conditions

Different approaches have been proposed to model the Mullins effect, and there is no unanimous explanation of the physical causes of it. Mullins and Tobin (1947) proposed a model in which the rubber could exist in either one of two possible phases, so-called hard and soft phases. They consider that the rubber is initially in its hard phase, and that it would degrade into soft phase as it deforms. A damage parameter is introduced to measure the transition between the two phases. This parameter is related to the strain amplification in the remaining hard phase of the rubber. Mullins (1969) suggested that this stress-softening is due to disentanglements of the network chains produced by the breakdown of filler particles/ rubber interactions. The same idea was suggested by Bueche (1960, 1961) that developed a probabilistic model of contact between chains and fillers.

More recently, Chagnon *et al.* (2001) analysed the Mullins effect from an experimental point of view. They studied the stiffness decrease under deformation during tensile tests in order to determine a damage evolution law. Following this experimental work, Marckmann *et al.* (2002) considers that the Mullins effect is mainly due to the breakage of links between rubber chains. During stretching, they observed the evolution of chains length between two junction points and concluded that the number of monomers between two junctions points increases. As a consequence, the chain density decreases. The evolution of these two parameters, said the number of monomers per chains and the chain density, are introduced in the eight-chains model. Constitutive parameters of the original eight chains model are replaced by functions of the maximum strain and a phenomenological law is proposed to simulate the increasing number of monomers between two junction points:

$$N = N_0 \exp\left(N_1 \lambda_{chain\,\max}\right) \tag{3}$$

The conservation of the number of monomers per unit of volume implies that the two parameters of the eight-chains model must be related by:

$$N\,C_r = Cte \tag{4}$$

For details on this model, the reader can refer to Marckmann *et al*. (2002).

2.3. HYSTERESIS

Under cyclic loading conditions, elastomers reveal their viscoelastic nature. Two different viscous phenomena can be identified. The first one is the hysteretic behaviour: after accommodation to the Mullins effect, loading and unloading curves do not follow the same path, as shown in Figure 3. The second phenomena is the well-known long-term relaxation. Both phenomena are due to viscoelasticity but we can say that they do not take place at the same time scale. Consequently, hysteresis and long-term relaxation can not be modelled by the same method. In the present work, our study is restricted to the hysteretic behaviour.

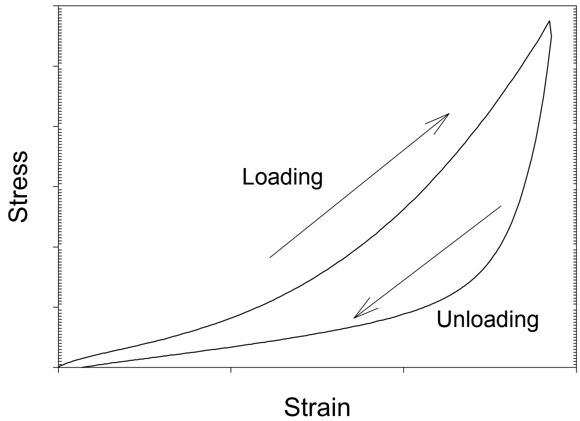

Figure 3. Hystereric behaviour

In the last few years, several studies attempted to model the hysteretic nature of rubber-like material both experimentally and theoretically (Lion, 1996; Bergström and Boyce, 1998; Banks *et al*., 1999; Miehe and Keck, 2000). These models are based on the same approach: the superposition of a rate-dependent response on an equilibrium elastic response. They only differ in the details of the stress-strain relationships.

Here, we adopt the model developed by Bergström and Boyce (1998). As mentioned above, their model is based on the decomposition of the elastomeric behaviour into two responses, an elastic one and a rate-dependent one. The elastic part of the behaviour is described by the eight chains model, presented above. The non-equilibrium part reproduces the chains slippage phenomenon which ensures that the material behaviour is similar under loading and unloading conditions. This slippage of the chains is modelled by a classical tube approach. This constitutive equation is schematised in Figure 4.

More precisely, the model is governed by three major equations; the two eight-chains models stress-strain relationships (presented above) and the slippage law given by:

$$\dot{\gamma}_B = C_1\left[\lambda_{chain}^{Bp} - 1\right]^{C_2} \tau_B{}^m \tag{5}$$

where τ_B and λ_{chain}^{Bp} are respectively the stress and the chain length of the rate-dependent part of the model, and C_1, C_2 and m are three parameters to be determined.

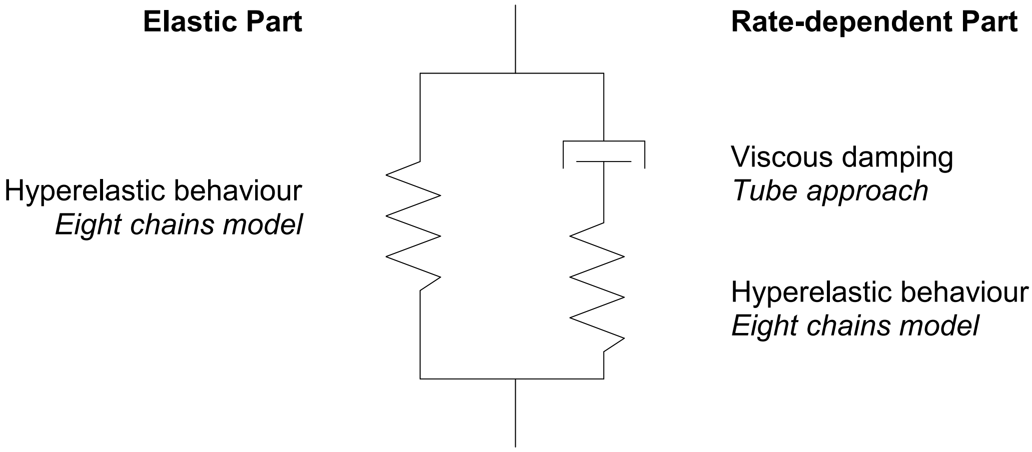

Figure 4. The Bergström and Boyce model.

2.4. PRESENTATION OF THE FINAL CONSTITUTIVE EQUATION

In order to consider both Mullins effect and hysteresis simultaneously, it is necessary to combine the different models described in the previous paragraphs. The key point is that these models are based on the same physical approach. As we considered that the Mullins effect is the stiffness decrease between the first and the second loadings curves, it only affects the material behaviour for loading paths. The elastic part of Bergström and Boyce model corresponds to loading paths and the rate-dependent part to unloading paths, so that our modelling of the Mullins effect, detailed in Marckmann *et al*. (2000), is only introduced in the elastic part of the Bergström and Boyce constitutive equation. Finally, this final assembled model can be represented schematically as shown in Figure 5. Note that it depends on eight parameters.

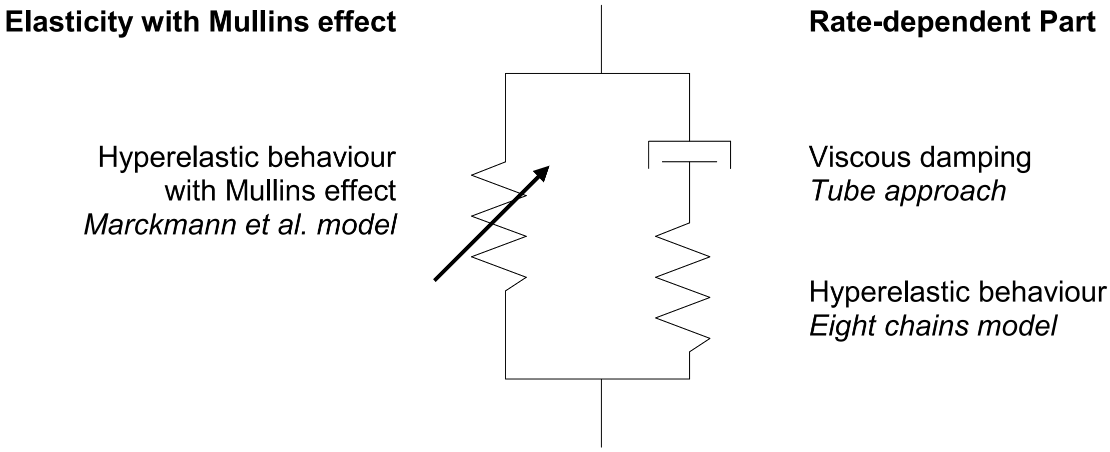

Figure 5. Final constitutive equation including large strains, hysteresis and Mullins effect.

3. PARAMETERS IDENTIFICATION AND SIMULATION

Uniaxial tension and pure shear cyclic experiments were conducted on a carbon black filled natural rubber. These tests were performed at different maximum strains. A global identification of the parameters, said using uniaxial tensile and pure shear data, leads to the values of the material parameters presented in Table 1.

	Parameters	**Values**
Mullins effect model	N_A^0	1.787
	N_A^1	0.3277
	$N_A.Cr_A$	0.6250
8 chains model of the hysteresis part	Cr_B	1.999
	N_B	5.6351
Slippage function	C_1	1
	C_2	-0.9999
	m	2.3867

Table 1. Material parameters

To verify these results, the experiments are simulated. Comparisons between numerical results and experimental data are presented in Figure 6 for uniaxial tensile tests and in Figure 7 for pure shear tests. The numerical results show that our model is able to simulate both Mullins effect and hysteresis.

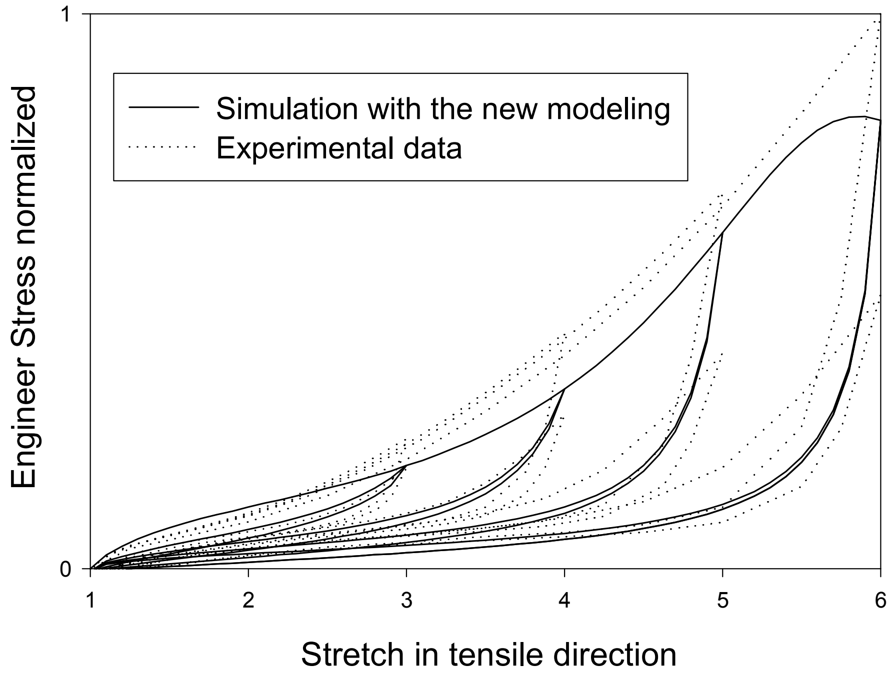

Figure 6. Tensile test simulation using the global model.

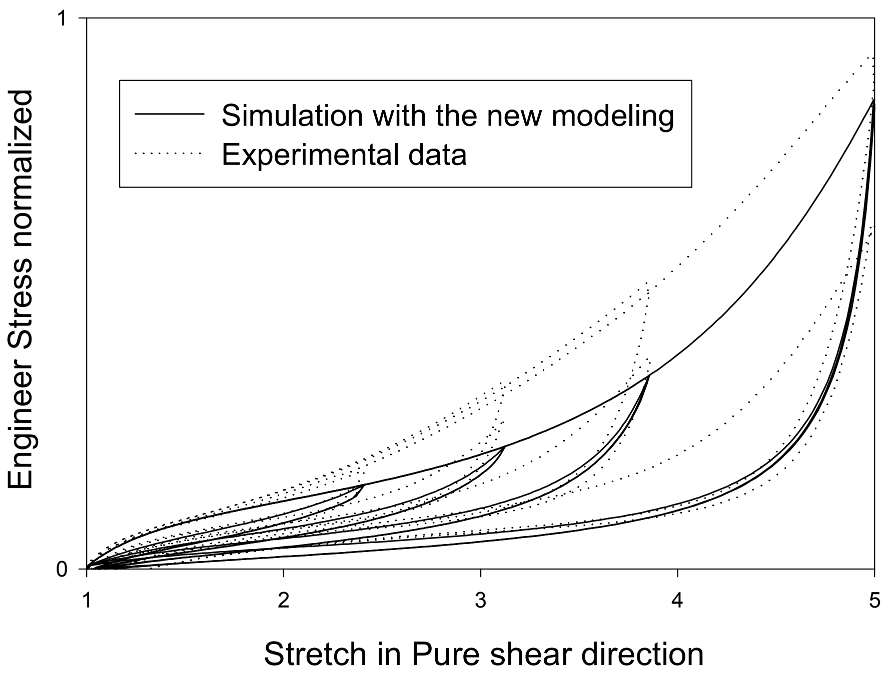

Figure 7. Pure shear test simulation using the global model

It can be said that the present model is in a good qualitative agreement with experiments. Nevertheless, the quantitative results are not as good as expected. In our model, the Mullins effect highly dominates the hysteretic effect of stress-strain curves. For a given loading stretch, the first cycle is well reproduced by the model. But the second cycle exhibits a too small amount of hysteresis, said the cycle is flattened. This difficulty can be explained by the fact that the first cycle includes both the Mullins effect and the hysteresis, so that the stiffness decreases between loading and unloading paths is well reproduced. For the second cycle, the material is accommodated to the Mullins effect and the hysteresis is underestimated. This might be a consequence of the fitting methodology that was performed globally. It might be more appropriate to identify various effects separately.

Finally, note that the relaxation behaviour is not taken into account in the present model: the stiffness decreases after each successive loop due to viscoelasticity is not considered. In order to improve this approach, it is necessary to add long-term time dependent phenomena. Indeed, the relaxation highly influences the stress-strain curve during the first loading cycles and can be neglected for next cycles. Addition of relaxation parameters in the model would reduce the influence of the Mullins effect that is overestimated for the first cycles. Moreover, the shape and the size of stress-strain loops would be reproduced in a more precise manner.

4. CONCLUDING REMARKS

The different phenomena that constitute the behaviour of elastomers are classically studied separately. In order to model the global behaviour of these materials, it is necessary to combine these separated approaches. A major problem induced by the addition of models is the large number of material parameters to be determined, so that these parameters can not be simply calculated. That is the reason why the choice of efficient models with few numbers of parameters for each phenomenon is highly important. Moreover, in order to be assemble these sub-models into a single global constitutive equations, the approaches adopted must be compatible.

The present study is based on a physical approach that focus on the chains behaviour under loading conditions. The hyperelastic basis of our model is the eight-chains constitutive equation. The Mullins effect modelling considers the breakage of secondary links between elastomeric chains. And finally, the hysteretic part of the behaviour is based on the slippage of chains. Consequently, all these approaches can be mixed together in order to define a global model.

This final model successfully describes the hysteresis and Mullins effect of elastomers. It can be improved by adding the other characteristic phenomena observed in elastomeric materials, the most important being the long-term viscoelasticity.

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