



HAL
open science

A review on the Mullins effect

Julie Diani, Bruno Fayolle, Pierre Gilormini

► **To cite this version:**

Julie Diani, Bruno Fayolle, Pierre Gilormini. A review on the Mullins effect. European Polymer Journal, 2009, pp.601-612. 10.1016/j.eurpolymj.2008.11.017 . hal-00773015

HAL Id: hal-00773015

<https://hal.science/hal-00773015>

Submitted on 16 Jan 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

A review on the Mullins' effect

J. Diani*, B. Fayolle, P. Gilormini

Laboratoire d'Ingénierie des Matériaux, Arts et Métiers ParisTech - CNRS, 151 bd de l'hôpital, 75013 Paris

Abstract

The Mullins' effect remains a major challenge in order to provide good mechanical modeling of the complex behavior of industrial rubber materials. It's been forty years since Mullins [1] wrote his review on the phenomenon and still no general agreement has been found either on the physical source or on the mechanical modeling of this effect. Therefore, we reviewed the literature dedicated to this topic over the past six decades. We present the experimental evidences, which characterize the Mullins' softening. The phenomenon is observed in filled and crystallizing rubbers. Then, the phenomenological models dedicated to fit the mechanical behavior of rubbers undergoing some Mullins' softening are studied. To overcome the limit of a descriptive phenomenological modeling, several authors looked for a physical understanding of the phenomenon. Various theories have been exposed, but none of them has been supported unanimously. Nonetheless, these theories favor the emergence of physically based mechanical behavior laws. We tested some of these laws, which show little predictive abilities since the values of their parameters do not compare well with the physical quantities they are linked to.

1. Introduction

Rubber-like materials exhibit an appreciable change in their mechanical properties resulting from the first extension. This property, reported in filled and non-filled rubber-like materials, has been investigated intensively by Mullins and his co-workers and consequently is referred to as the "Mullins' effect." The objective of this contribution is to review and discuss this phenomenon, which remains a challenge in terms of physical understanding and mechanical modeling.

Although the Mullins' effect has been studied for more than six decades, it is still recognized as a major difficulty for rubber-like materials behavior. Stress-softening experimental evidences reported in the literature account for materials of distinct physical properties (unfilled rubbers, filled rubbers, thermoplastics...). In section 2, we tried to clarify the features of the Mullins' effect.

* Corresponding author: julie.diani@paris.ensam.fr
Fax: +33 1 44 24 62 90.

For the past three decades, in attempt to represent the mechanical behavior of rubbers depending on the strain history, specific efforts were accomplished to define new models. Due to the complexity of the mechanical behavior of rubbers, involving large deformations, nonlinear behavior and Mullins' softening, most models depend on phenomenological parameters. We report and test some of these models in section 3.

In order to provide a better understanding of the stress-softening resulting from the Mullins' effect, several physical interpretations were proposed, from chain breakage at the interface between the rubber and the fillers, slipping of molecules, rupture of the clusters of fillers, chain disentanglements, to more complex composite structure formation. These interpretations are presented and discussed in section 4. They provide materials for the emergence of physically motivated mechanical models. We present and discuss these models in section 5.

2. Experimental observations

2.1. Softening effect

In order to illustrate the material softening resulting from the Mullins' effect, cyclic uniaxial tension tests were performed on a sulfur-vulcanized SBR filled with 50 phr of N220 carbon black. Flat tensile samples were cut from SBR sheets. Uniaxial tension tests were performed on a G'Test 810 tensile machine operated in a local strain control mode through Appolor® video image analysis. Tests were run at a low constant strain rate of 10^{-3} s^{-1} . One sample was submitted to a simple uniaxial tension test, while another one was submitted to a cyclic uniaxial tension test with the maximum stretching increasing every 5 cycles. Fig. 1 presents the stress-strain responses of both samples. In Fig. 1, we observe a softening that is specific to materials exhibiting the Mullins' effect:

- Most of the softening, which is characterized by a lower resulting stress for the same applied strain, appears after the first load.
- After a few number of cycles (values up to 10 are reported in the literature depending on the material nature), the material responses coincide during the successive cycles.
- The softening appears for stretches lower or equal to the maximum stretch ever applied.
- When the extension exceeds the maximum extension previously applied, the material stress-strain response returns on the same path than the monotonous uniaxial tension test stress-strain response after a transition, which increases with the amount of strain.
- The softening increases progressively with the increasing maximum stretch.

The literature reports Mullins' effect for various materials, see table 1 for examples.

In his early work, Mullins [5] submitted filled and unfilled natural rubbers (NR) to the same amount of stretch and noticed a softening effect in the filled compounds only. He noted that the softening was increasing with the increasing stiffening ability of the fillers, and that for stretches of one-half of the pre-deformation, the filled NR stress-strain response approaches the pure NR. Mullins interpreted this by a disappearance of the reinforcing effect of the filler.

Later, by applying the same amount of stress to filled and unfilled NR, he and his co-authors [2] observed a softening in pure NR as well. Moreover, Harwood and Payne [3] noticed that a pure NR and a carbon-black filled NR experience a similar softening when both materials are stretched up to the same stress level. According to this result, it seemed more appropriate to relate the Mullins' softening to a stress level than to a strain level, and very often the Mullins' effect has been referred to as a stress-softening effect. Nevertheless, the mechanical quantity characterizing the Mullins' effect threshold has not yet been clearly defined. It would require applying various loading conditions consecutively. Although the Mullins' softening is reported in the literature for other states of deformation than uniaxial tension: Uniaxial compression [18], hydrostatic tension [19], simple shear [7], and equibiaxial tension [7,8,20,21], it is still not clear which mechanical quantity pilots the Mullins' effect.

Natural rubber is known to crystallize and Mullins' effect has been observed in such other pure crystallizing gums such as NBR [14]. It was reported also in filled gums that do not crystallize, such as SBR [2,10] or EPDM [11,22], in materials containing initially some crystallization like thermoplastics elastomers [23,24], and recently in polymer gels [25] and in living tissues that have a rubbery behavior [26-28]. But Mullins and Tobin [4] noted that pure gums that do not crystallize break before showing any softening effect. We observed similar break on polyurethane networks consisting of polyether diols reticulated by Toloante HDT triisocyanate. Hence, contrary to the general idea that the Mullins' effect takes place in filled and unfilled rubbers, it is necessary that unfilled rubbers crystallize to undergo this effect.

Applying cyclic uniaxial tension up to various stretch levels on several materials, we noted that there is no general stretching lower limit to observe some Mullins' softening, but rather it depends on the materials. Materials containing a fairly important amount of fillers may show some Mullins effect at very low stretch. As an example, Fig. 2 shows that our 50 phr carbon-black filled SBR undergoes some Mullins' effect after a 10 %-stretch, well before the upturn of the stress-strain curve.

2.2. Crystallization

As we mentioned earlier, in order to display some Mullins' softening, unfilled rubbers need either to initially contain crystallites like thermoplastic rubbers, or to crystallize during the deformation process. The strain-induced crystallization in natural rubber has been studied early [29,30]. Mullins and Tobin [4] studied the Mullins' effect in carbon-black filled and unfilled natural rubber vulcanizates, and noticed a decrease in the materials volume, which they relate to the occurrence of crystallization. More recently, Rault and his co-authors studied this phenomenon [31-34]. They measured the crystallinity in pure NR and filled NR during cyclic uniaxial tension loading conditions, and they showed that the hysteresis characterized by the difference between the loading and the unloading stress-strain responses results from crystallization [31]. They also observed that fillers act as a strain amplifier [34] like Mullins and Tobin proposed earlier [35]. Thus, crystallization, like the softening effect, appears at a lower strain level for filled NR than for pure NR. But most of all, Trabelsi et al. [32] measured the same amount of crystallinity during the first three cycles of uniaxial tension applied to a filled NR, whereas the stress-strain curves showed a conspicuous softening at the second cycle. Therefore, a similar crystallization appears at the second cycle, when the Mullins' effect is evacuated. Hence, we note that the presence of crystallites is necessary for the occurrence of the Mullins' softening in unfilled rubbers and the Mullins' softening does not affect the strain-induced crystallization.

2.3. Permanent set

The permanent set refers to the residual extension remaining after a material sample is stretched and released. Mullins [36] studied in parallel the permanent set and the softening of pure NR and filled NR. He noted that the permanent set is actually not exactly permanent and that part of it can even be recovered rapidly. Therefore, he fixed the release time to one hour, prior to any measurement of permanent set in order to allow the materials to recover from the residual deformation resulting from viscoelasticity. Similarly, after stretching a filled EPDM up to 200 %, Diani et al. [22] reported an instantaneous residual stretch of 31 %, which decreased to 13 % after 20 minutes and remained to 12 % after 48 hours. Mullins [36] noticed that materials showing little softening also show little residual deformations. Moreover, though the residual deformation depends on the type of fillers, it cannot be related simply to the stiffening effect of the fillers.

Dorfmann and Ogden [6] conducted cyclic uniaxial tension experiments on natural rubbers added of 1 phr, 20 phr and 60 phr of carbon black fillers. They reported a residual extension that increased with the amount of fillers and

with the amplitude of stretching applied to the materials. When submitted to uniaxial compressions, elastomers show a compressive residual strain increasing with the intensity of loading, like Boyce et al. [23] showed on EPDM-PP thermoplastic rubber. Finally, after cyclic uniaxial tension tests, rubbers show a permanent set in compression in the direction perpendicular to the direction of stretching, exhibiting an anisotropy of the permanent set [22,36].

2.4. Induced anisotropy

Mullins [5,36] noticed that stretching a reinforced rubber produces an uneven softening in all directions, and thus creates some anisotropy. Other authors showed experimental evidences of the Mullins induced anisotropy in carbon-black natural rubber [37], in silica filled PDMS [17] and in carbon black filled EPDM [22]. Nevertheless, we have not been able to find any study quantifying clearly the induced anisotropy according to the gum or filler nature, or to the applied strain history.

2.5. Recovery

Mullins [5] studied the stress-recovery of a filled NR previously stretched up to 420 %. For that, after various recovery periods, he measured the stress at an elongation of 200 % and compared it to the stress measured on the material stretched to the same elongation for the first time (virgin material). He showed a temperature-dependence of the recovery. At room temperature only a small recovery is observed (less than 20 %), while at 100 C, the material recovers 80 % of the softening after only two days. Mullins noted that exposing the material to such a high temperature changes its behavior due to aging. At high temperatures, Harwood and Payne [38] studied the stress-recovery in unfilled vulcanizates natural rubber depending of the type of crosslinking. After a first cyclic load, the materials were heated in vacuo at 100 C for 24 h. Then, the material was stretched for a second time and the stress-strain response was compared to the initial one. Results show that the recovery depends on the type of crosslinking and may be almost complete for monosulfide crosslinked and carbon to carbon crosslinked vulcanizates. Similarly, Laraba-Abbes et al. [37] showed a complete recovery of the softening (stress-strain response similar to the virgin material) of a carbon-black filled natural rubber exposed to a high temperature of 95 C in vacuo during 48 hours.

We tested the recovery at high temperature in vacuo on samples of SBR added of 50 phr of carbon black. Samples were submitted to cyclic uniaxial tensile tests up to 200%, after which, they were exposed to a temperature of 80 C in vacuo for up to 17 hours. Then, the samples were submitted for a second time to the same cyclic uniaxial tension

tests. After approximately 3 hours, we measured a full recovery of the residual strain but an incomplete recovery of the modulus. As shown in Fig. 3, the material stress-strain response was recovered after 17 hours of exposure to the heat.

At room temperature, Rigbi [39] showed that in a carbon black filled rubber, a long relaxation (4 weeks) leads to partial stress-recovery only, and Hanson et al. [17] mentions that in silica-filled PDMS, the stress softening produced during the first extension could not be recovered after 26 weeks.

Harwood and Payne [38] immersed their samples in a solvent and showed in some cases a complete recovery of the Mullins' effect by swelling.

Therefore, the physical phenomena taking place during the Mullins' softening are reversible but require a high temperature or a solvent exposure to heal. For this last reason, the Mullins' softening may be considered as the result of damage, and this is how it is introduced in the phenomenological models. Actually, due to the complexity of the stress-strain response of rubber-like materials, which involves large deformations, non-linearity and softening, most of the mechanical models are phenomenological.

3. Phenomenological models

In order to account for the Mullin's softening, Simo [40] proposed to penalize the classic elastic strain energy densities, $W_0(\mathbf{F})$, designed to fit the hyperelastic stress-strain responses of rubber-like materials submitted to the deformation gradient \mathbf{F} , by a reducing parameter of the Kachanov form [41],

$$W(\mathbf{F}) = (1 - d)W_0(\mathbf{F}). \quad (1)$$

The parameter d defines a damage, which is a priori unknown and may cover any physical phenomenon like chain and multichain damage, microstructural damage, microvoid formation.... During the past three decades, various models have been defined according to Eq. (1). They vary from each other by the damage criterion or/and by the damage evolution law. The damage criterion identifies when d changes, and so depends on the mechanical quantity characterizing d , while the evolution law expresses how d is changing.

As sketched in Fig. 4, we can file the models in two classes, according to whether or not the material stress-strain response at the second loading is identical to the unloading stress-strain response, as long as the maximum deformation is not reached. When both material responses superpose (Fig. 4a), damage is a function of a discontinuous quantity like the maximum applied stretch. For example, Simo [40] defines a discontinuous damage

variable that depends on the maximum of $\sqrt{2W_0(\mathbf{F})}$ over the past history. In the case of diverging unloading and reloading responses (Fig. 4b), damage depends not only on a discontinuous variable but also on a continuous one, with the latter accumulating continuously within the deformation process. In this way, Miehe [42] introduced a damage, which is partly governed by the arclength $\int_0^t |\dot{\mathbf{f}}|(s) ds$, where \mathbf{f} is the thermodynamic force which drives the

damage evolution. Several authors [43-45] adopted such a definition of damage. Another way to define a reloading response differing from the unloading one is to build a time-dependent constitutive law, which can be done by using rheological models with serial and parallel combinations of elastic and viscous elements, or by using Besdo and Ihlemann [46] model for which the stress-strain response is defined within two asymptotic curves. These asymptotic responses evolve according to the material history. Actually, rubber-like materials are viscoelastic materials since their stress-strain responses depend on the strain rate. But this topic is beyond the scope of this contribution, since it deals with viscohyperelastic modeling of the mechanical behavior of rubbers.

Albeit models of the first class show stress-strain responses which return to the primary (virgin material) stress-strain responses without any transition, they are usually preferred to the models of the second class for their simplicity. Among them, two different definitions of the evolution of d have been adopted. For the first approach, it is assumed that damage occurs during the first loading path, which can write as:

$$d = \begin{cases} d(x) & \text{when } \dot{x} \geq 0 \\ d(\text{Max}_{s \in [-\infty, t]} [x(s)]) & \text{otherwise} \end{cases} \quad (2)$$

This is for instance the case of the models proposed in [21,47-51].

For the second approach, damage stays zero when the material is virgin and evolves in the range of deformation yet seen by the material. This second definition writes as:

$$d = \begin{cases} 0 & \text{when } \dot{x} \geq 0 \\ d(x, \text{Max}_{s \in [-\infty, t]} [x(s)]) & \text{otherwise} \end{cases} \quad (3)$$

Such a definition of the damage variable has been largely adopted [6,52-56].

The quantity x , in Eqs. (2) and (3), defines the damage governing variable. It depends on the models, and we report some examples in table 2.

Models defined by Eqs. (1) and (2) have been scarcely confronted to experimental data. They do not seem to perform well when applied to fit a cyclic stress-strain response like the one presented in Fig. 1 [51]. Moreover, they show some theoretical issues. First, as sketched in Fig. 4, the level of the theoretical stress for the maximum stretch is the same for the first and the second loadings, which ignores the stress-softening at the maximum stretch. Second, considering a material uniaxially stretched up to two different strain levels, strains x and y , and calculating the ratio of the Cauchy stress corresponding to the two unloading responses vs. the material stretch \mathbf{F} , these models assume that the ratio remains constant:

$$\sigma(\mathbf{F}, d(x)) / \sigma(\mathbf{F}, d(y)) = (1 - d(x)) / (1 - d(y)), \quad \forall \mathbf{F}. \quad (4)$$

As reported by Chagnon et al. [51] and Diani et al. [10], actual rubber-like materials do not satisfy this theoretical property. We plotted in Fig. 5, values of the ratio wrote in Eq. (4) for $x=2$ and $y=3$, corresponding to the unloading responses of the 50 phr carbon-black filled SBR presented in Fig. 1. This ratio is obviously not constant.

Due to the definition of d depending on two variables (x and $\max(x)$), models defined by Eqs. (1) and (3) offer more flexibility and usually provide a better fit of the unloading responses. Good representations of experimental data are displayed in [52,55,56]. However, Kazakevičiūtė-Makovska [56] demonstrated a conflict between the theory and the experimental data. On one side, the Clausius-Duhem inequality imposes that:

$$-\frac{\partial W}{\partial d} \dot{d} \geq 0 \Rightarrow \dot{d} \geq 0. \quad (5)$$

Thus, the softening function d must increase monotonously with the deformation extent. On the other side, the experimental variations of d , estimated by calculating the ratio of the stress response of a material previously stretched (which is the unloading stress response) over the stress response of the virgin material, do not satisfy to this property. For instance, we show in Fig. 6, a non monotonous trend for the experimental values of d estimated on our 50 phr carbon-black filled SBR. Since rubbers do not satisfy to Eq. (5), which is a direct consequence of Eq. (1), other forms of the strain energy densities should be proposed in order to improve the mechanical modeling of rubber-like material softening,

Actually, very few other paths have been taken to suggest other forms of phenomenological models. Qi and Boyce [58] followed the early concept of Mullins and Tobin [4]. The material is described by a two-phase system containing a hard phase and a soft phase. The strain is sustained by the soft-phase, which percentage increases with the maximum stretch applied to the material. The main drawback of Qi and Boyce [58] model is a damage criterion

controlled by a scalar, which leads to an isotropic model with no residual strain and with a second loading response equal to the unloading one (Fig. 4a type of mechanical behaviour). Nonetheless, this model does not possess the theoretical limits reported for the constitutive laws following Eq. (1), and we tested it on the 50 phr carbon-black SBR. The 5 model parameters were fitted on the stress-stretch response (Fig. 1), and then the model estimates of the data plotted in Fig. 5 and Fig. 6 were calculated. The results are shown in Fig. 7. Although, the model is unable to accurately fit the data when presented like in Figs. 5 and 6, the stress-strain response is reproduced well. Actually, Figs. 5 and 6 emphasize the discrepancy between the model and the experimental data. When the induced anisotropy and the residual strains are neglected, this model seems to perform well. Moreover, although we used it as it is defined by its authors, some of the constitutive functions, like the evolution of the volume fraction of the soft domain or the strain amplifier function, can be modify to better fit one's specific materials.

As we discussed above, some phenomenological models can reasonably fit the mechanical behavior of rubberlike materials undergoing some stress-softening as long as the induced anisotropy and the permanent set is neglected. Nonetheless, they are limited by their descriptive abilities. An alternative to the phenomenological models may be provided by models grounded on physical interpretations of the Mullins' effect. For this purpose, several authors propounded various physical interpretations of the Mullins' effect; we present them in the next section.

4. Physical interpretations

In order to understand the pre-strain softening in rubbers, several physical interpretations have been proposed. The main physical interpretations and their representation are summarized in Table 3. They involve microstructural ruptures as well as microstructural changes, but they are mainly dedicated to filled rubbers and usually do not extend to the case of crystallizing pure gums. The various explanations suggested for the Mullin's effect show that there is still no general agreement on the origin of this effect at the microscopic or mesoscopic scale.

Blanchard and Parkinson [59] explained the Mullins' effect by bond ruptures. In their modeling, the shear modulus is related to the number of crosslinks, which are defined by the chemical crosslinks introduced by the vulcanization process added of the rubber-particle linkages. The pre-strain induces the rupture of the weaker bonds (physical bonds) at the rubber-particle interface. Further pre-strain breaks the stronger bonds (chemical bonds). Following the idea of Blanchard and Parkinson [59], Bueche [60] also interpreted the Mullins' softening by the rupture of chains linking two particles. He assumed an affine displacement between the centers of the particles, which highly

constrains the shorter chains in-between particles. When completely extended, these shorter chains break at the surface of the particles. Bueche [60] explained the difference between filled and unfilled rubbers by assuming that in unfilled rubbers, the junctions arrange so as not to over-stretch the shorter chains. Later, Suzuki et al. [64] used electron spin resonance to measure the chain scission in silica filled SBR. They observed a considerable number of carbon radicals corresponding to broken polymer chains and concluded that chain scission might contribute to the Mullins' effect, but they also observed chain scission in unfilled SBR, which does not exhibit any Mullins' softening. Since the reversibility of the softening was not studied in the filled SBR, it is difficult to assess if the chain scission is associated to either an unrecoverable softening or a recoverable Mullins' softening.

According to Houwink [61], the theory of physical bond rupture does not fit with the slow restoration of the Mullins' effect at room temperature. Moreover, if chemical filler-rubber bonds exist and break, this type of rupture would be permanent. Therefore, Houwink [61] proposed that during the first extension, molecules slip over the surface of the fillers and that new bonds are instantaneously created along the chains. The new bonds would be of the same physical nature as the original ones, but would appear at different places along the rubber molecules. This would result in a change of the material entropy, which could be restored by a temperature increase. The theory of chain slipping is equivalent to the mechanism of breaking and reforming adsorption bonds proposed earlier by Alexandrov and Lazurkin [65]. Dannenberg and Brennan [66], after measuring no significant change in the crosslink density of stretched networks, confuted the idea that the reversible part of the Mullins' effect results in bond breakage, and adhered to Houwink's theory [61]. According to them, only the irreversible, permanent, softening can be the consequence of the breakage of adsorption bonds. Later, Clément et al. [15] conducted uniaxial tension tests and atomic force microscopy observations on silica-filled PDMS. They attributed the stress-softening to bond rupture or chain slippage along the filler surface, of chains reaching their limit of extensibility. They observed more Mullins' effect in materials containing a non homogeneous distribution of silica, and explained it by larger local strains in regions with high silica concentrations, in relation with the high stiffness of silica.

Kraus et al. [62] carried out some swelling tests to ascertain the extent of bond rupture in prestretched filled rubbers. Like Dannenberg and Brennan [66], they measured a rather small change in the network density compared to the relatively large stress-softening observed. They concluded that the amount of bond ruptures at the rubber-particle interface is moderate and cannot be the main source of the Mullins' softening. Moreover, they looked at the volume expansion that could be caused by the separation of the polymer and the fillers creating vacuoles. While the

material is stretched up to 300%, the volume expands by a few percent only, which allowed the authors to reject the vacuole formation as the main cause of the pre-strain softening. As a consequence, while admitting that bond ruptures happen and vacuoles form in the material during the pre-strain, the authors proposed to attribute the main source of the stress-softening to the rupture of carbon black structure, especially for highly reinforced materials. Klüppel and Schramm [12] used the same interpretation of the Mullins' softening. The main contradiction about this idea is mentioned in [12]. Such a process would be almost irreversible. Moreover, this theory is difficult to extend to the case of unfilled crystallizing rubbers.

Harwood and Payne [2,38] studied the Mullins' recovery in pure NR according to the nature of the crosslinks. They observed an incomplete recovery of the stress-softening for rubbers with polysulfidic crosslinks. In such a case, they attributed the major part of the stress-softening to a rearrangement of the network due to local nonaffine deformation resulting from completely extended short chains. Roland [67] confuted this hypothesis by observing similar Mullins' softening in several crosslinked networks with different structures. He proposed that Mullins' softening arose from adjustments of local imbalances in segment density and contraction of primitive path of network chain ends. To further study the possible effect of dangling chains on the Mullins' softening, Santangelo and Roland [68] carried out some tests on natural rubber with various chain-end fractions. Their results demonstrated that the stress-softening is unrelated to the presence of dangling chains, or to the dispersion in the network strands. The contraction of chain ends cannot contribute to the stress-softening.

Hanson et al. [17] proposed another interpretation of the Mullins' softening, which accommodates the induced anisotropy. Using Hamed and Hatfield [69] configuration of chain entanglements between particles, they assumed that the removal of entanglements associated with the strain axis causes the stress-softening. The number of active chains is assumed to remain constant; only the entanglement density changes with respect to the extension. The recovery is supplied by thermal motions, which could produce new entanglements.

Looking at the larger picture of the carbon black reinforcement of elastomers, Fukahori [63,70] proposed an interface model to explain the mechanics and mechanisms of reinforcement and softening. In this model, the material is represented by aggregates of particles, which are regarded as spherical, surrounded by a double-layer structure of bound rubber embedded in a crosslinked rubbery matrix. The inner layer consists of polymer in the glassy state (GH, glassy hard) with strictly constrained molecular motions, while the outer layer (SH, sticky hard) is made of highly constrained polymer compared to the unfilled rubber vulcanizate. When the particles are well dispersed the SH layer

is discontinuous. During the first loading, SH layers orient and extend, and finally connect with others SH layers to create a super-network structure. When unloading, it is assumed that the bundles of the super-network cannot hold the stress and, instead, the matrix of vulcanized rubber supports the stress. In the second loading, as long as the stretch remains below the maximum stretch ever applied, the matrix sustains the load. When the stretch exceeds the extension previously applied, the super-network structure returns to its previously extended state and support the stress. The entropic forces in the super-network structure are believed to be the source of the Mullins' effect recovery. Unfortunately, this model cannot be extended to the pure crystallizing gums, since, as shown by Trabelsi et al. [31], the crystallites melt down when the material is unloaded and, therefore, the persistence of a super-network structure is unlikely.

Besdo and Ihlemann [71] wrote a computer program to simulate the deformation of a macromolecular network. The network is represented by a number of connections which are linked by strings with specific features. The strings behave like springs. They can break or form according to the distance between the connections. Rigid strings are introduced to represent chemical crosslinks. Moreover, some randomly picked connections are assumed fixed to simulate the presence of crystallites or fillers. During an applied deformation, the system self-organizes. This self-organization leads to a hysteretic behavior including Mullins' softening during cyclic loading conditions. The model seems to capture well the main features of the cyclic uniaxial stress-strain response of rubber-like materials. Moreover, it shows that the assumption of fixed connections is crucial to observe a Mullins' effect. Further investigation testing the resulting anisotropy of the simulated model material would be interesting.

An alternative to the phenomenological models is to write the physical interpretations exposed so far into equations. This leads to macromolecular models, which parameters are related to physical properties of the materials. Although these models are based on physical interpretations of the Mullins' softening, they do not show particularly good predictive abilities, because the values of their fitted parameters are unrealistic. Nonetheless, they are sometimes a convenient alternative to introduce the induced anisotropy as will be shown in the next section.

5. Macromolecular models

Pursuing the concept of Bueche [60], Govindjee and Simo [72] modeled the softening of virgin materials by the rupture of chains linking particles. The strain energy density decomposes into the sum of a contribution of chains stretched between two crosslinks and a contribution of chains attached to two particles. The model is based on the

isotropic macromolecular three-chain model [73], and the damage parameter depends on the largest eigenvalue of the deformation gradient. Although, the model is physically based, its parameters are phenomenological. Moreover, it depends on integrals, which makes it more difficult to compute. Finally, this isotropic model is unable to account for the residual strain and for the difference between the material unloading and reloading responses. In order to account for the induced anisotropy and for the residual strain, Göktepe and Miehe [74] improved the model of Govindjee and Simo [72] by employing 21 material directions instead of the three chain directions parallel to the principal directions of the deformation gradient. The induced anisotropy results from an account of the damage history by one scalar for each material direction.

Killian et al. [75] proposed a physical model that defines the Mullins' softening as irreversible chain slippages. The model is based on the extension of chains parted into those located on the surface of the particle and those going from the filler to the matrix. The model depends on 12 parameters, which have to be fitted and which are difficult to interpret.

Klüppel and Schramm [12] adhered to Kraus et al. [62] theory of the filler cluster breakdown. As we mentioned earlier, the adjunction of fillers is recognized as a local strain amplifier, which is modelled by a strain amplification factor. Although this factor has an understandable physical source, it cannot be related quantitatively to a measurable physical quantity. In Klüppel and Schramm model [12], this factor decreases linearly with the maximum strain applied to the material. The model is isotropic and depends on 8 parameters, we tried it on our experimental data. Results are plotted in Fig. 8. The model reproduces fairly well the stress-strain response of the SBR, but not as well as the phenomenological model of Qi and Boyce [58].

Marckmann et al. [76] defined another alteration network model, assuming that the Mullins' softening is caused by the breakage of network crosslinks. The network alteration results into longer but also fewer chains sustaining the stress. The damage is actuated when the chains are stretched above the maximum stretch ever applied. In Fig. 9, we propose a comparison of the model with our experimental data. The experimental stress-strain response is well replicated by the model, but like Qi and Boyce model [58], the model shows some discrepancies with the experimental data when these last ones are shown like in Figs. 5 and 6. The model is based on the Arruda and Boyce [77] 8-chain macromolecular model, for which all chains are equally stretched and thus equally damaged. Therefore, the model is unable to reproduce the induced anisotropy and the resulting residual strain. For this reason, like Göktepe and Miehe [74] extended Govindjee and Simo [72] model, Diani et al. [22] adapted the model of

Marckmann et al. [76] to a set of material directions. Each material direction softens according to the maximum stretch applied in this specific direction. The material is then unevenly damaged, which induces some residual strain and anisotropy.

Let us mention that Meissner and Matějka [78] proposed earlier a semi-phenomenological model which is close to the model of Marckmann et al. [76]. Based on a macromolecular energy density, they assumed that the finite extensibility of the chains increases progressively with the level of deformation. They defined the limit extensibility of the chains as a phenomenological function of the maximum stretch undergone by the chains. This idea is equivalent to increasing the length of the chains, since the limit of extension of a chain is directly related to its length. Finally, Horgan et al. [54] applied the Marckmann et al. [76] softening to the phenomenological hyperelastic law of Gent [79]. This leads to a tensorial phenomenological model, which is potentially anisotropic but this aspect has not been tested.

Although based on a physical understanding of the Mullins' effect, not all the previously cited models depend on parameters that can be compared to measurable physical quantities. The models [12,54,72,74,75,78] depend on phenomenological parameters. Moreover, when the model parameters are clearly related to physical quantities, the fitted values do not often coincide with the physical properties they are related to. For instance, one of the parameters of the Marckmann et al. [76] model is the number of monomers per chain. In their paper, the fitted value of this parameter increases with the maximum applied stretch from 2 to 5, which is unrealistic for the SBR and the NR they considered. For the model estimate plotted in Fig. 9, the same parameter varied from 2 to 6. As a consequence, the range of applicability of the macromolecular models is limited to the description of the mechanical behaviour of rubberlike materials and further efforts are required to define predictive models, which would estimate the expected Mullins' softening of a material from some of its physical parameters.

6. Conclusions

We have reviewed the literature on the Mullins' effect. The Mullins' effect is a softening that occurs in rubbers when first stretched above the ever applied level of deformation. It goes with residual strain and induced anisotropy. Contrary to the commonly reported allegation that Mullins' softening is observed in filled and unfilled rubbers, only filled rubbers and pure gums that crystallize show some Mullins' softening. The phenomenon is reversible, since materials heal when exposed to high temperature in vacuo or to solvent swelling.

The mechanical behavior of rubbers undergoing Mullins' softening has been often modeled by adopting a damage continuum mechanics approach. The hyperelastic strain energy density is penalized by a damage parameter, which is defined by a scalar quantity. This leads to constitutive laws that neglect the residual strain and the induced anisotropy. Such a definition of the softening has been challenged by the evaluation of the damage evolution. Experimental estimates of the damage evolution do not agree with the thermodynamics laws which impose damage to increase monotonously with deformation. Nonetheless, some phenomenological models show a fairly good estimate of the cyclic uniaxial tension stress-strain response of rubberlike materials, as long as the induced anisotropy and the residual strain are neglected.

In order to propose physically motivated models, several authors have developed theories to explain the Mullins' effect. These theories include bond ruptures, molecules slipping, filler clusters rupture, chain disentanglement, chain retraction, network rearrangement, and composite microstructure formation. One major problem is that most of these theories are built for filled rubbers and do not extend to pure gums, which crystallize. For the moment, none has gained a general agreement, and more work is necessary to reach a consensus on the actual physical source of the Mullins' effect. Nevertheless, the physical interpretations have inspired authors to propose physically motivated mechanical models. Some of these models can fit the rubberlike materials stress-softening but, although their parameters are in principle related to physical quantities, when fitted, their values do not correspond to the physical parameters they are related to. Therefore, the models have limited predictive abilities and have the same range of application as the phenomenological ones.

Acknowledgments

This work was supported by grant JC05_43403 from the French Agence Nationale de la Recherche.

References

- [1] Mullins L. Softening of rubber by deformation. *Rubber Chem Technol* 1969;42:339-362.
- [2] Harwood JAC, Mullins L., Payne AR. Stress softening in natural rubber vulcanizates. Part II. Stress softening effects in pure gum and filler loaded rubbers. *Rubber Chem Technol* 1966;39:814-822.
- [3] Harwood JAC, Payne AR. Stress softening in natural rubber vulcanizates III. Carbon black filled vulcanizates. *J Appl Polymer Sci* 1966;10:315-323.

- [4] Mullins, L, Tobin, NR. Theoretical model for the elastic behavior of filler reinforced vulcanized rubbers. *Rubber Chem Technol* 1957;30:555-571.
- [5] Mullins L. Effect of stretching on the properties of rubber. *J Rubber Res* 1948;16:275-282.
- [6] Dorfmann A, Ogden RW. A constitutive model for the Mullins effect with permanent set in particle-reinforced rubber. *Int J Solids Struct* 2004;41:1855-1878.
- [7] Mars WV, Fatemi A. Observations of the constitutive response and characterization of filled natural rubber under monotonic and cyclic multiaxial stress states. *J Engng Mat Technol* 2004;126:19-28.
- [8] Németh I, Schleinzer G., Ogden RW, Holzapfel GA. On the modelling of amplitude and frequency-dependent properties in rubberlike solids. In *Constitutive models for rubber IV*, editor. Balkema, 2005. p. 285-292.
- [9] Dall'Asta A, Ragni L. Experimental tests and analytical model of high damping rubber dissipating devices. *Engng Struct* 2006;28:1874-1884.
- [10] Diani J, Brieu M, Vacherand JM. A damage directional constitutive model for Mullins effect with permanent set and induced anisotropy. *Eur J Mech Solids/A* 2006;25:483-496.
- [11] Flamm M, Steinweger T, Spreckels J, Brüger T. In *Mechanical properties of EPDM In Constitutive models for rubber V*, editor. Balkema, 2008. p233-242.
- [12] Klüppel M, Schramm M. A generalized tube model of rubber elasticity and stress softening of filler reinforced elastomer systems. *Macromol Theory Simul* 2000;9:742-754.
- [13] Heinrich G, Klüppel M, Vilgis TA. Reinforcement of elastomers. *Curr Opinion Solids St Mat Sci* 2002;6:195-203.
- [14] Kakavas, P.A., 1996. Mechanical properties of bonded elastomer discs subjected to triaxial stress, *J. Appl. Polym. Sci.*, 59, 251-261.
- [15] Clément F, Bokobza L, Monnerie L. On the Mullins effect in silica-filled polydimethylsiloxane networks. *Rubber Chem Technol* 2001;74:846-870.
- [16] Stevenson I, David L, Gauthier C, Arambourg L, Davenas J, Vigier G. Influence of SiO₂ fillers on the radiation ageing of silicone rubbers. *Polymer* 2001;42:9287-9292.
- [17] Hanson DE, Hawley M, Houlton R, Chitanvis K, Rae P, Orlor EB, Wroblewski DA. Stress softening experiments in silica-filled polydimethylsiloxane provide insight into a mechanism for the Mullins effect. *Polymer* 2005;46:10989-10995.

- [18] Amin AFMS, Alam MS, Oku Y. An improved hyperelasticity relation in modelling viscoelasticity response of natural and high damping rubbers in compression: experiments, parameter identification and numerical verification. *Mech Mater* 2002;34:75-95.
- [19] Dorfmann A. Stress softening of elastomers in hydrostatic tension. *Acta Mech* 2003;165:117-137.
- [20] Johnson MA, Beatty MF. The Mullins effect in equibiaxial extension and its influence on the inflation of a balloon. *Int J Engng Sci* 1995;33:223-245.
- [21] Li J, Mayau D, Lagarrigue V. A constitutive model dealing with damage due to cavity growth and the Mullins effect in rubber-like materials under triaxial loading. *J Mech Phys Solids*, 2008;56:953-973.
- [22] Diani J, Brieu M, Gilormini P. Observation and modeling of anisotropic visco-hyperelastic behavior of a rubberlike material, *Int J Solids Struct* 2006;43:3044-3056.
- [23] Boyce MC, Kear K, Socrate S, Shaw K. Deformation of thermoplastic vulcanizates. *J Mech Phys Solids* 2001;49:1073-1098.
- [24] Qi HJ, Boyce MC. Stress-strain behavior of thermoplastic polyurethanes. *Mech Mat* 2005;37:817-839.
- [25] Webber AE, Creton, C, Brown HR, Gong, JP. Large strain hysteresis and Mullins effect of tough double-network hydrogels, *Macromolecules* 2007;40:2919-2927.
- [26] Dorfmann AL, Woods WA, Trimmer BA. Muscle performance in a soft-bodied terrestrial crawler: constitutive modeling of strain-rate dependency. *J R Soc Interface* 2008;5:349-36.
- [27] Muñoz MJ, Bea JA, Rodríguez JF, Ochoa I, Grasa J, Pérez del Palomar A, Zaragoza P, Osta R, Doblaré M. An experimental study of the Mouse skin behaviour: Damage and inelastic aspects. *J Biomech* 2008;41:93-99.
- [28] Rubod C, Boukerrou M, Brieu M, Clay JC, Dubois P, Cosson M. Biomechanical properties of vaginal tissue preliminary results. *Int Urogynecol J*, 2008;19:811-816.
- [29] Treloar LRG. Crystallization phenomena in raw rubber. *Trans Faraday Soc* 1941;37:84-97.
- [30] Gent AN. Crystallization and the relaxation of stress in stretched natural-rubber vulcanizates. *Trans Faraday Soc* 1955;50:521-533.
- [31] Trabelsi S, Albouy PA, Rault J. Crystallization and melting processes in vulcanized stretched natural rubber. *Macromolecules* 2003;36:7624-7639.
- [32] Trabelsi S, Albouy PA, Rault J. Effective local deformation in stretched filled rubber. *Macromolecules* 2003;36:9093-9099.

- [33] Albouy PA, Marchal J, Rault J. Chain orientation in natural rubber, Part I: The inverse yielding effect. *Eur Phys J* 2005;17:247-259.
- [34] Rault J, Marchal J, Judeinstein P, Albouy PA. Stress-induced crystallization and reinforcement in filled natural rubbers: ^2H NMR Study. *Macromolecules* 2006;39:8356-8368.
- [35] Mullins L, Tobin NR. Stress softening in rubber vulcanizates. Part I. Use of a strain amplification factor to describe elastic behavior of filler-reinforced vulcanized rubber. *J Appl Polymer Sci* 1965;9:2993-3007.
- [36] Mullins L. Permanent set in vulcanized rubber. *India Rubber World* 1949;120:63-66.
- [37] Laraba-Abbes F, Ienny P, Piques R. A new 'Taylor-made' methodology for the mechanical behaviour analysis of rubber-like materials: II. Application to the hyperelastic behaviour characterization of a carbon-black filled natural rubber vulcanizate. *Polymer* 2003;44:821-840.
- [38] Harwood JAC, Payne AR. Stress softening in natural rubber vulcanizates. IV. Unfilled vulcanizates. *J Appl Polymer Sci* 1966;10:1203-1211.
- [39] Rigbi Z. Reinforcement of rubber by carbon black. *Adv Polym Sci*, 1980;36:21-68.
- [40] Simo JC. On a fully three-dimensional finite-strain viscoelastic damage model: Formulation and computational aspects. *Comput Methods Appl Mech Engrg* 1987;60:153-173.
- [41] Kachanov LM. Time of the rupture process under creep conditions. *Izvestiya Akad Nauk SSR Otd Tekh Nauk* 1958;58:26-31.
- [42] Miehe C. Discontinuous and continuous damage evolution in Ogden-type large-strain elastic materials. *Eur J Mech A/Solids* 1995;14:697-720.
- [43] Miehe C, Keck J. Superimposed finite elastic-viscoelastic-plastoelastic stress response with damage in filled rubbery polymers. Experiments, modeling and algorithmic implementation. *J Mech Phys Solids* 2000;48:323-365.
- [44] Kaliske M, Nasdala L, Rothert H. On damage modeling for elastic and viscoelastic materials at large strain, *Comput. Structures* 2001;79:2133-2141.
- [45] Lin RC, Schomburg U. A finite elastic-viscoelastic-elastoplastic material law with damage: theoretical and numerical aspects. *Comput Methods Appl Mech Engrg* 2003;192:1591-1627.
- [46] Besdo D, Ihlemann J. A phenomenological constitutive model for rubberlike materials and its numerical applications. *Int J Plast* 2003;19:1019-1036.

- [47] Lion A. A constitutive model for carbon black filled rubber: Experimental investigations and mathematical representation. *Continuum Mech Thermodyn* 1996;8:153-169.
- [48] Ernst LJ, Septanika, EG. Hysteresis and time-dependent constitutive modeling of filled vulcanized rubber. *J Phys IV France* 1999;9: 63-72.
- [49] Beatty MF, Krishnaswamy S. A theory of stress-softening in incompressible isotropic materials. *J Mech Phys Solids* 2000;48:1931-1965.
- [50] Laiarinandrasana L, Piques R, Robisson A. Visco-hyperelastic model with internal state variable coupled with discontinuous damage concept under total Lagrangian formulation. *Int J Plast* 2003;19:977-1000.
- [51] Chagnon G, Verron E, Gornet L, Marckmann G, Charrier P. On the relevance of continuum damage mechanics as applied to the Mullins effect in elastomers. *J Mech Mater Phys Solids* 2004;52:1627-1650.
- [52] Ogden RW, Roxburgh DG. A pseudo-elastic model for the Mullins effect in filled rubber. *Proc R Soc Lond A* 1999;455:2861-2877.
- [53] Zúñiga AE, Beatty MF. A new phenomenological model for stress-softening in elastomers. *Z Angew Math Phys* 2002;53:794-814.
- [54] Horgan CO, Ogden RW, Saccomandi G. A theory of stress softening of elastomers based on finite chain extensibility. *Proc R Soc Lond A*, 2004;A460:1737-1754.
- [55] Elías-Zúñiga A. A phenomenological energy-based model to characterize stress-softening effect in elastomers. *Polymer* 2006;46:3496-3506.
- [56] Kazakevičiūtė-Makovska R. Experimentally determined properties of softening functions in pseudo-elastic models of the Mullins effect. *Int J Solids Struct* 2007;44:4145-4157.
- [57] Krishnaswamy S, Beatty MF. The Mullins effect in compressible solids. *Int J Engng Sci* 2000;38:1397-1414.
- [58] Qi HJ, Boyce MC. Constitutive model for stretch-induced softening of the stress-stretch behavior of elastomeric materials. *J Mech Phys Solids* 2004;52:2187-2205.
- [59] Blanchard AF, Parkinson D. Breakage of carbon-rubber networks by applied stress. *Ind Eng Chem* 1952;44:799-812.
- [60] Bueche F. Molecular basis for the Mullins effect. *J Appl Polym Sci* 1960;4:107-114.
- [61] Houwink R. Slipping of molecules during the deformation of reinforced rubber. *Rubber Chem Technol* 1956;29:888-893.

- [62] Kraus G, Childers CW, Rollman KW. Stress softening in carbon black reinforced vulcanizates. Strain rate and temperature effects. *J Appl Polym Sci* 1966;10:229-240.
- [63] Fukahori Y. New progress in the theory and model of carbon black reinforcement of elastomers. *J Appl Polym Sci* 2005; 95:60-67.
- [64] Suzuki N, Ito M, Yatsuyanagi F. Effects of rubber/filler interactions on deformation behavior of silica filled SBR systems. *Polymer* 2005;46:193-201.
- [65] Alexendrov AP, Lazurkin JS. Strength of amorphous and crystallizing rubber polymers. *Doklady Akad Nauk SSSR* 1944;45:291-294.
- [66] Dannenberg EM, Brennan JJ. Strain-energy as a criterion for stress softening in carbon-black-filled vulcanizates. *Rubber Chem Technol* 1965;39:597-608.
- [67] Roland CM. Network recovery from uniaxial extension: The origin of the Mullins effect. *Rubber Chem Technol* 1989;62:880-895.
- [68] Santangelo PG, Roland CM. Chain ends and the Mullins effect in rubber. *Rubber Chem Technol* 1992;65:965-972.
- [69] Hamed GR, Hatfield S. On the role of bound rubber in carbon-black reinforcement. *Rubber Chem Technol* 1989;62:143-156.
- [70] Fukahori Y. Generalized concept of the reinforcement of elastomers. Part 1: Carbon black reinforcement of rubbers. *Rubber Chem Technol* 2007;80:701-725.
- [71] Besdo D, Ihlemann J. Properties of rubberlike materials under large deformations explained by self organizing linkage patterns. *Int J Plast* 2003;19:1001-1018.
- [72] Govindjee S, Simo J. A micro-mechanical continuum mechanical model for carbon black filled rubbers incorporating Mullins' effect. *J Mech Phys Solids* 1991;39:87-112.
- [73] James HM, Guth E. Theory of the elastic properties of rubbers. *J Chem Phys* 1943;11:455-481.
- [74] Göktepe S, Miehe C. A micro-macro approach to rubber-like materials. Part III: The micro-sphere model of anisotropic Mullins-type damage. *J Mech Phys Solids* 2005;53:2259-2283.
- [75] Killian HG, Strauss M, Hamm W. Universal properties in filler-loaded rubbers. *Rubber Chem Technol* 1994;67:1-16.

- [76] Marckmann G, Verron E, Gornet L, Chagnon G, Charrier P, Fort P. A theory of network alteration for the Mullins effect. *J Mech Phys Solids* 2002;50:2011-2028.
- [77] Arruda EM, Boyce MC. A three-dimensional constitutive model for the large deformation stretch behavior of rubber elastic materials. *J Mech.Phys Solids* 1993;41:389-412.
- [78] Meissner B, Matějka L. Description of the tensile stress-strain behavior of filler-reinforced rubber-like networks using a Langevin-theory-based approach. Part I. *Polymer* 2000;41:7749-7760.
- [79] Gent AN. A new constitutive relation for rubber. *Rubber Chem Technol* 1996;69:59-61.

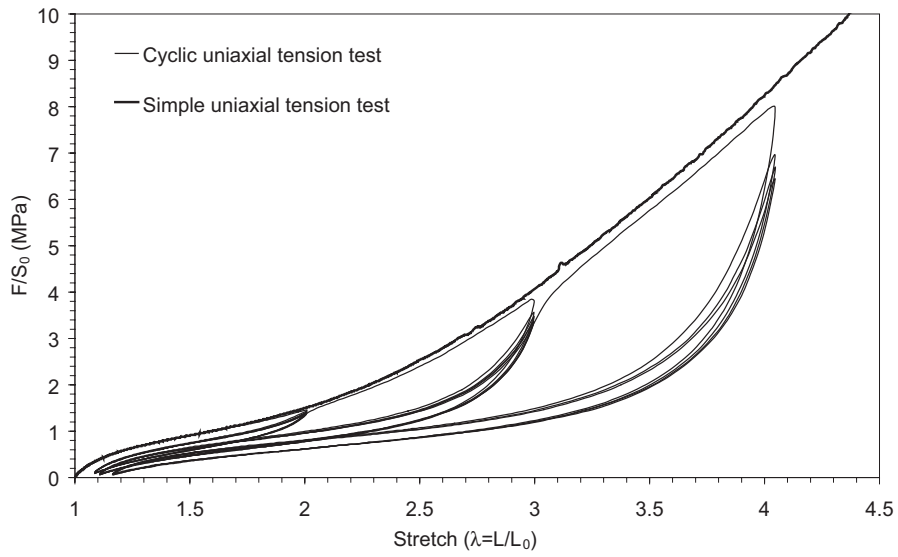


Fig. 1. Stress-strain responses of a 50 phr carbon-black filled SBR submitted to a simple uniaxial tension and to a cyclic uniaxial tension with increasing maximum stretch every 5 cycles.

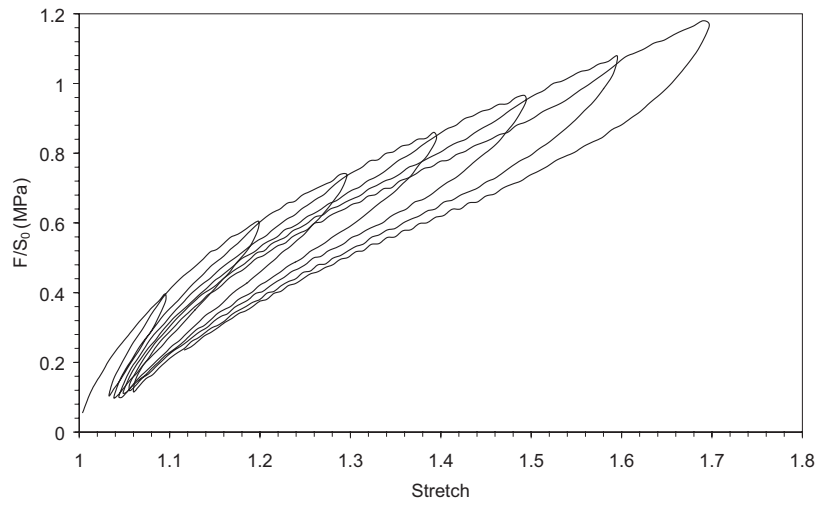


Fig. 2. Mullins' effect at small and moderate deformation observed on a 50 phr carbon-black filled SBR submitted to cyclic uniaxial tension.

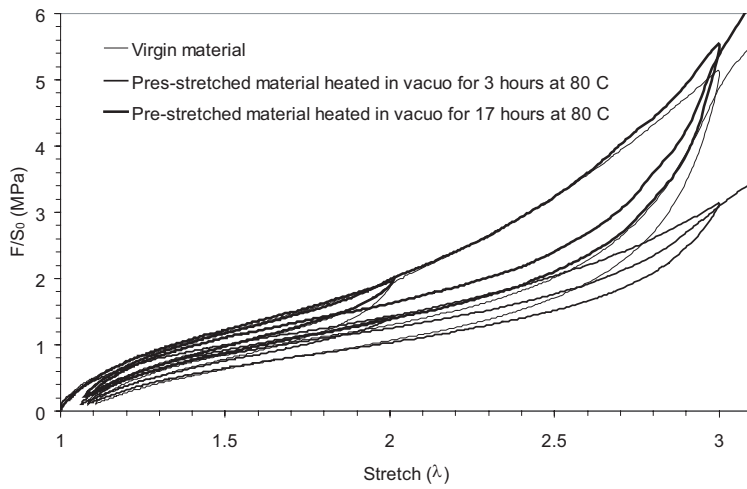


Fig. 3. Recovery of pre-stretch softening by in vacuo heating. Stress-strain responses of 50 phr carbon black filled SBR submitted to cyclic uniaxial tension in virgin state, and in pre-stretched state after 3 hours and 17 hours exposure to 80 C.

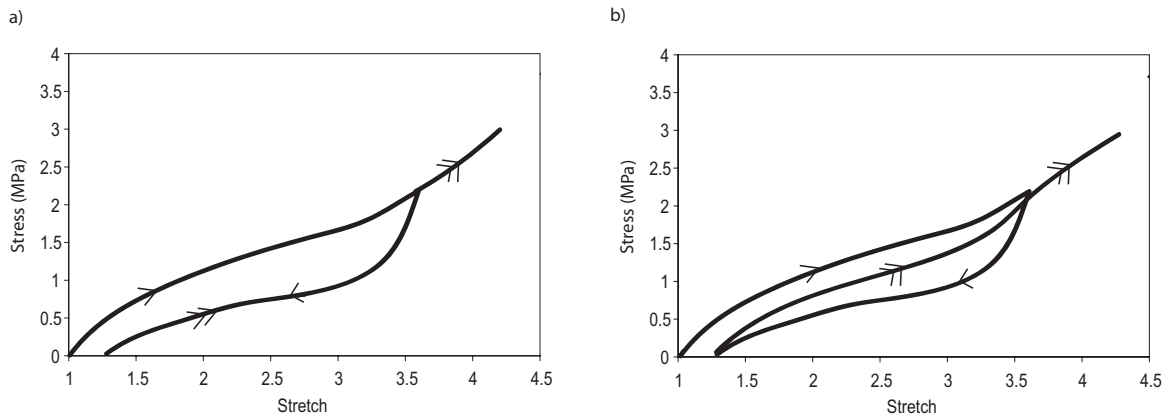


Fig. 4. Model representation of the mechanical behavior of rubbers undergoing Mullins' softening. a) First class of models: reloading response coincides with the unloading response, b) Second class of models: the reloading and the unloading responses differ.

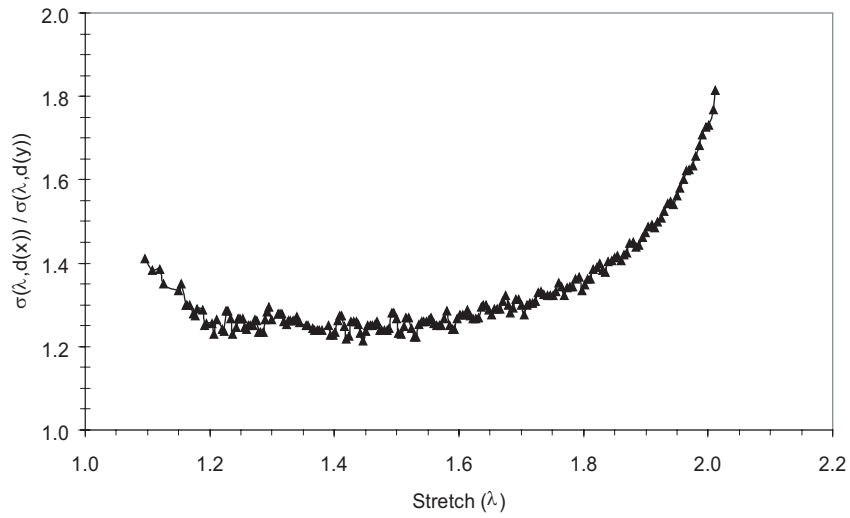


Fig. 5. For the 50 phr carbon-black filled SBR, ratio of the stress unloading response of the material stretched to 100 % ($x=2$) over the stress unloading response of the material stretched to 200% ($y=3$), vs. stretch λ .

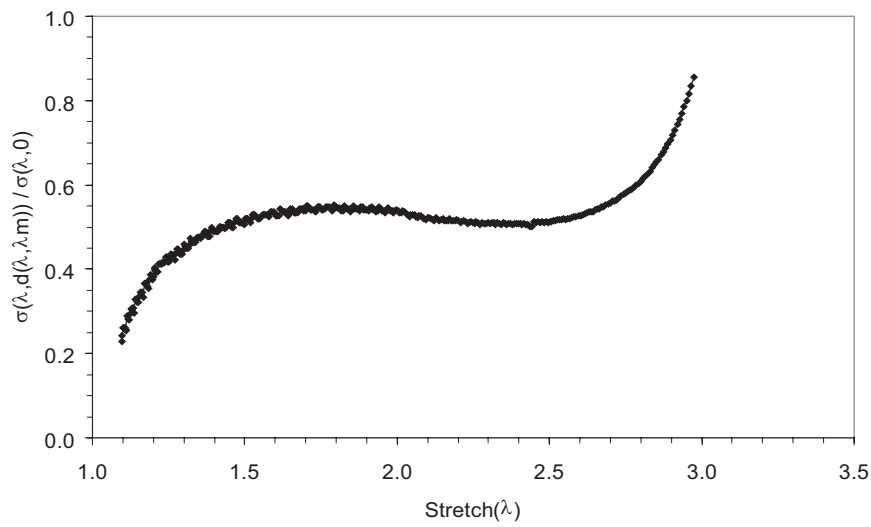


Fig.6. Experimental estimate of the damage function defined by Eqs. (1) and (3), $d(\lambda, \lambda_m=3)$ vs. stretch λ , for a 50 phr carbon-black filled SBR stretched up to 200 % ($\lambda_m=3$), which stress-strain response is plotted in Fig. 1.

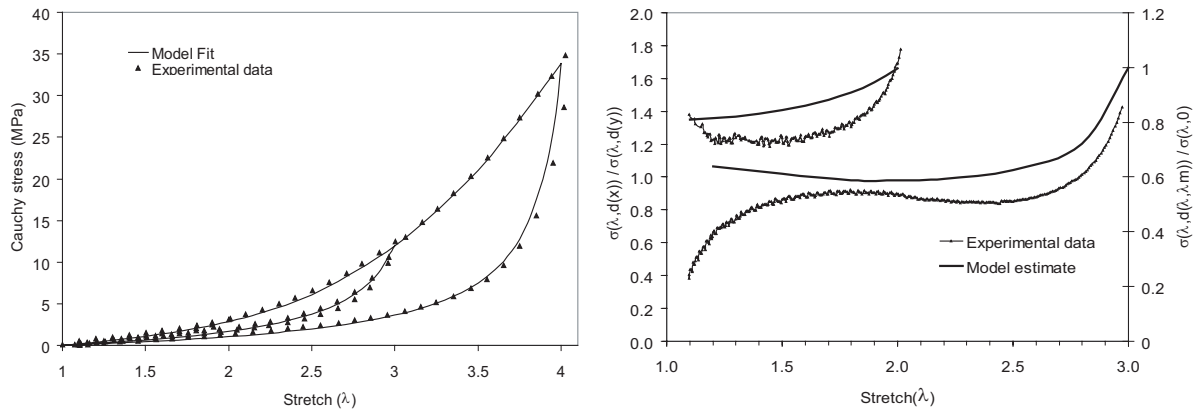


Fig. 7. Comparison of Qi and Boyce model [58] with experimental data. Left: Fit of the material stress-strain response presented in Fig. 1. Right: Model estimate of the data presented in Figs. 5 and 6.

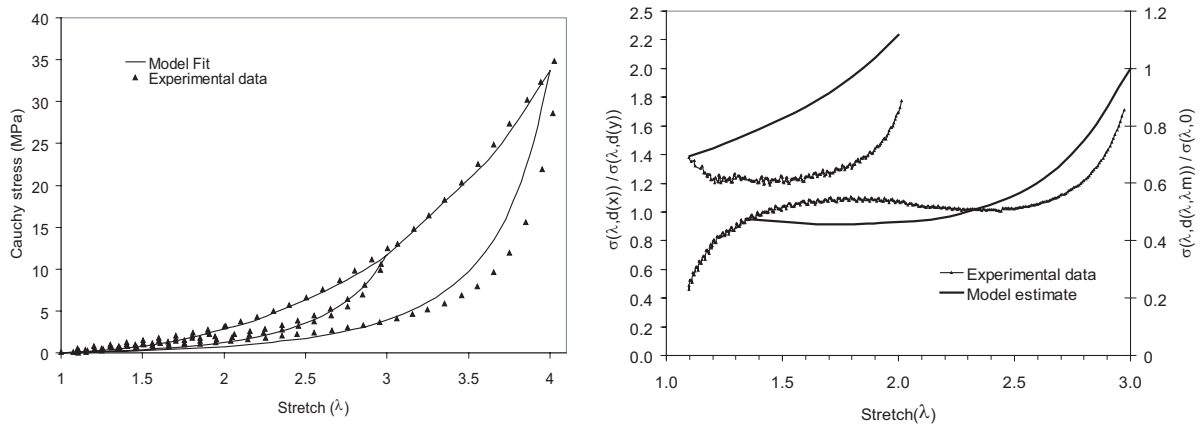


Fig. 8. Comparison of Klüppel and Schramm model [12] with experimental data. Left: Fit of the material stress-strain response presented in Fig. 1. Right: Model estimate of the data presented in Figs. 5 and 6.

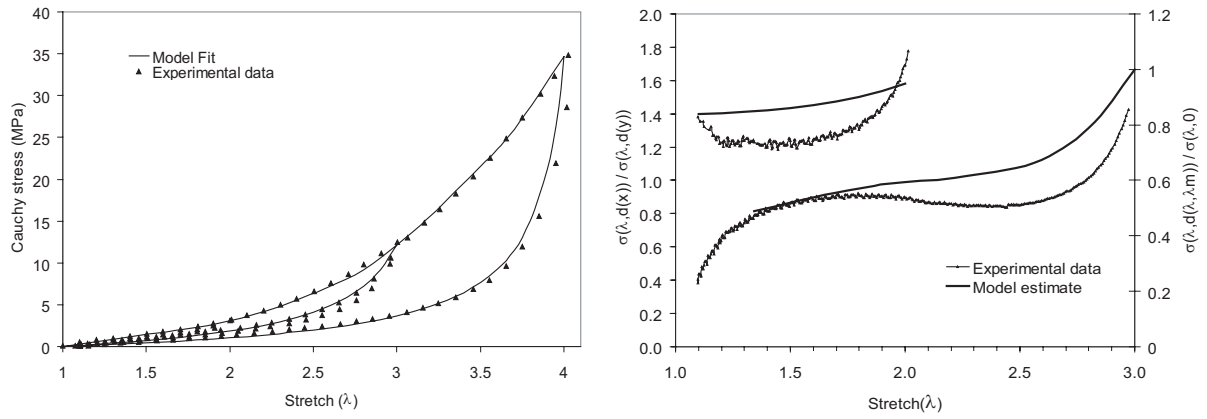


Fig. 9. Comparison of Marckmann et al. model [76] with experimental data. Left: Fit of the material stress-strain response presented in Fig. 1. Right: Model estimate of the data presented in Figs. 5 and 6.

Table 1

Examples of materials showing some Mullins' softening

Gum nature	No filler	Carbon-black fillers	Silica fillers	Other fillers
NR	[2-4]	[2-11]	[5]	[5]
SBR		[2,10,12,13]	[13]	
NBR	[14]			
EPDM		[10-12]		
PDMS			[15-17]	
Neoprene		[10]		

Table 2

Variable driving the discontinuous damage d for some phenomenological models defined by Eq. (1)

Variable x	Reference
$\sqrt{2W_0(\mathbf{F})}$	[42]
$W_0(\mathbf{F})$	[6,21,52,54]
Largest eigenvalue of \mathbf{F}	[50]
$\sqrt{I_1/3 - 1}$	[51]
$trace(\boldsymbol{\epsilon}^2)$	[47]
$\sqrt{\mathbf{B} \cdot \mathbf{B} - \sqrt{3}}$ where $\mathbf{B} = \mathbf{F}^T \mathbf{F}$	[55,56]
$\sqrt{trace(\frac{1}{2}(1 - \mathbf{B}^{-1}))^2}$	[57]

Table 3

Physical explanations of the Mullins' effect

Physical source	Sketch
Bond rupture [59,60]	
Molecules slipping [61]	
Filler rupture [62]	
Disentanglement [17]	
Double-layer model [63]	