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Review article

A review on the Mullins effect

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A B S T R A C T

The Mullins effect remains a major challenge in order to provide good mechanical modeling of the complex behavior of industrial rubber materials. It has been forty years since Mullins [Mullins L. Softening of rubber by deformation. Rubber Chem Technol 1969;42:339–62.] 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 rubbers and crystallizing pure gum. 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 proposed, 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 either cannot be measured experimentally or do not compare well with the physical quantities they are linked to.

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1. Introduction

Rubber-like materials exhibit an appreciable change in their mechanical properties resulting from the first extension. This property, first observed by Bouasse and Carrière [2], 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 etc.). In Section 2, we tried to clarify the features of the Mullins effect.

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, non-linear 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 compression molded sheets. Uniaxial tension tests were performed on a GTest 810 tensile machine operated in a local strain control mode through VideoTraction® 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.

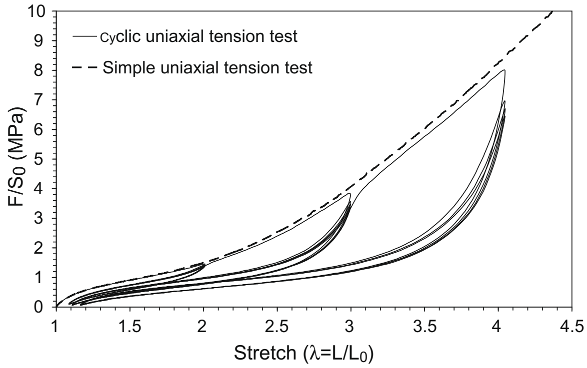

Fig. 1. Stress–strain responses of a 50 phr carbon-black filled SBR submitted to a simple uniaxial tension and to a cyclic uniaxial tension with increasing maximum stretch every 5 cycles.

- After a few cycles (values up to 10 are reported in the literature depending on the material nature), the material responses coincide during the following cycles, aside from a fatigue effect.
- 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 example).

In his early work, Mullins [6] 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 [3] observed a softening in pure NR as well. Moreover, Harwood and Payne [4] 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 re-

Table 1
Examples of materials showing some Mullins softening.

Gum nature	No filler	Carbon-black fillers	Silica fillers	Other fillers
NR	[3–5]	[3–12]	[6]	[6]
SBR		[3,11,13,14]	[14]	
NBR	[15]			
EPDM		[11–13]		
PDMS			[16–18]	
Neoprene		[11]		