



New elements concerning the Mullins effect: A thermomechanical analysis

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ABSTRACT

This paper investigates thermomechanical effects in carbon black-filled rubbers under cyclic uniaxial tensile loading at ambient temperature. More especially, it focuses on the calorimetric response of rubbers during stress softening, which occurs during the first mechanical cycles. Two materials were studied, natural rubber (NR) and styrene butadiene rubber (SBR), which are respectively crystallizable and non-crystallizable under stress. Temperature changes were first measured by infrared thermography. Then heat sources produced or absorbed by the material due to deformation processes were deduced from these temperature changes by using the heat equation. Heat source variations during each mechanical cycle were analyzed. In particular, the mechanical dissipation produced in each cycle was deduced. For both materials, the relative contribution to mechanical dissipation of dissipative mechanisms involved in stress softening and viscosity was determined. One of the main results is that, for both materials, the mechanical dissipation due to the Mullins effect is not produced only during the first cycle. In the second cycle, the mechanical dissipation due to the Mullins effect is not negligible: it corresponds to up to 35% (compared to the first cycle) for the highest stretch ratio tested in the present study. Moreover, mechanical dissipation due to the Mullins effect increases less significantly at high maximum stretch ratios.

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1. Introduction

One of the main phenomena in the mechanics of rubber-like materials dates from the observation by Bouasse in 1903 (see Ref. [1]) of stress softening after the first mechanical load. Later, this phenomenon was studied more precisely by Mullins in 1948 (see Ref. [2]) and was then referred to as “the Mullins effect”. Considering a

cyclic uniaxial tensile test, this effect can be defined by five main features (see Ref. [3]):

- most of the softening is obtained after the first load;
- a few cycles are necessary to stabilize the mechanical response;
- softening appears for stretch ratios lower than or equal to the maximum stretch ratio previously applied;
- when the stretch ratio exceeds the maximum stretch ratio previously applied, the material stress–strain

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response returns on the same path as the monotonous uniaxial tension test stress–strain response after a transition, which increases with the amount of strain;

- softening increases progressively with the increasing maximum stretch ratio.

Despite the numerous studies reported in the literature since the work of these pioneers, no consensus has been found on the physical origin of the Mullins effect. Among the phenomena described, one can cite bond rupture (see Ref. [4]), chain rupture (see Ref. [5]), chain slipping (see Ref. [6]), chain disentanglement (see Ref. [7]), filler-cluster breakdown (see Refs. [8,9]) and network rearrangement (see Refs. [10,11]).

Up to now, the Mullins effect has only been investigated from a mechanical point of view, while its thermal and calorimetric signatures might provide information of paramount importance. In this study, we propose to measure the temperature changes during the deformation of rubbers by using infrared thermography (IRT). IRT is a full thermal field measurement technique that provides accurate information about temperature variations at the surface of a specimen subjected to influences that can differ in nature (mechanical, thermal, chemical). It can be noted that in the tests performed in the present study, stress softening in rubbers is accompanied by heat production and heat exchanges with the outside. Moreover, during the first cycles, the temperature evolution is not stabilized. Consequently, the analysis of the temperature does not provide a clear understanding of the thermomechanical phenomena. For this reason, temperature variation cannot easily be used to study the thermal effects accompanying stress softening. This is the reason why we use the framework of the thermodynamics of irreversible processes (TIP) and the heat diffusion equation to measure the total heat source produced or absorbed by the material. The heat source is composed of several terms. Under certain hypotheses, the part due to thermomechanical cosoftened filled styrene–butadiene rubber (see Ref. [12]) for further information. This approach is applied in the present study in order to identify the calorimetric signature of the Mullins effect, i.e. the mechanical dissipation due to stress softening.

The paper is divided into two parts. The first part presents the experimental set-up and the second presents the results, analysis and discussion. Concluding remarks close the paper.

2. Experimental setup

2.1. Material and specimen geometry

The materials considered here were natural rubber (NR) and styrene–butadiene rubber (SBR), both filled with the same amount of carbon black 50 phr.¹ They are respectively denoted NR50 and SBR50 in the following. Apart from the macromolecules themselves, the compounds had the same

Table 1

Chemical composition in parts per hundred rubber (phr).

Ingredient	NR50	SBR50
NR	100	
SBR		100
Carbon black N347	50	50
Antioxidant 6PPD	1.9	1.9
Stearic acid	2	2
Zinc oxide ZnO	2.5	2.5
Accelerator CBS	1.6	1.6
Sulfur solution 2H	1.6	1.6

chemical composition (see Table 1). The degree of cross-linking density is $6.5 \times 10^{-5} \text{ mol cm}^{-3}$ for NR50 and $8.3 \times 10^{-5} \text{ mol cm}^{-3}$ for SBR50. It should be noted that only the NR50 formulation is subject to stress-induced crystallization: the characteristic stretch ratios at which crystallization and crystallite melting occur are denoted by λ_c and λ_m and are close to 1.8 and 1.6, respectively. Thin dumbbell-shaped specimens were used. They were 5 mm in width, 10 mm in length and 1.4 mm in thickness. The width was chosen to ensure the homogeneity of the mechanical fields during uniaxial tensile tests, i.e. a uniaxial tension state.

2.2. Loading conditions

The mechanical tests corresponded to cyclic uniaxial tensile loadings. They were applied under prescribed displacement using an INSTRON 5543 testing machine with a load cell capacity of 500 N. The signal shape was triangular in order to ensure a constant strain rate during loading and unloading. Indeed, most filled rubbers exhibit viscosity; it is therefore more relevant not to change the strain rate during material deformation. The loading rate and the nominal strain rate ($\dot{\lambda}$) were equal to $\pm 300 \text{ mm/min}$ and $\pm 0.5 \text{ s}^{-1}$, respectively. The tests corresponded to 4 series composed of uniaxial mechanical cycles, at four different maximum stretch ratios. The number of cycles for each maximum stretch ratio was chosen in such a way that the mechanical response was stabilized for the last cycle. This number was equal to 5 for NR50 and 3 for SBR50. The following maximum stretch ratios were chosen (see Fig. 1):

- for NR50, the four maximum stretch ratios denoted by $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ were chosen equal to 1.4, 2, 4 and 6, respectively. λ_1 was chosen as lower than λ_c . λ_2 was close to λ_c . λ_3 and λ_4 were higher than λ_c (λ_4 was close to the failure stretch ratio).
- for SBR50, the four maximum stretch ratios $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ were chosen equal to 2, 3, 4 and 4.5, respectively.

Note that, for the two formulations, the maximum stretch ratios $\lambda_i, i = 1, \dots, 4$ chosen were different, due to the fact that the stretches at failure of the materials were different (6.3 for NR50 and 4.8 for SBR50).

Temperature field measurements were performed using a Cedip Jade III-MWIR infrared camera. The principal features of this camera are presented in Table 2. The calibration of the camera detectors was performed using a black body and a Non-Uniformity Correction (NUC) procedure.

¹ Part per hundred of rubber in weight.

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