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Experimental characterization and modelling of the cyclic softening of carbon-black filled rubbers

Yannick Merckel[a], Julie Diani[b,*], Mathias Brieu[a], Daniel Berghezan[c]

[a] LML, Ecole Centrale de Lille, bd Paul Langevin, 59650 Villeneuve d'Ascq, France
[b] Laboratoire PIMM, CNRS, Arts et Métiers ParisTech, 151 bd de l'Hôpital, 75013 Paris, France
[c] Manufacture Française des Pneumatiques Michelin, CERL, Ladoux, 63040 Clermont-Ferrand, France

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ABSTRACT

Several carbon-black filled styrene-butadiene rubbers (SBRs) were submitted to uniaxial tension cyclic tests at large strain for investigating filled rubbers cyclic softening. In order to study the effect of the material composition (amount of fillers and crosslink density) and of the stretch intensity, an original method for cyclic softening characterization is proposed. The softening is seen as an amplification of the stretch in the rubber gum, and a stretch amplification factor is then introduced as the softening parameter. The latter is evaluated for various materials and several levels of cyclic stretch intensity. Material softening is shown to increase with the loading intensity, the amount of carbon-black fillers and the decrease of the crosslink density. In terms of modelling, the introduced softening parameter provides access to the entire stress-stretch responses of the softened material for any cycle. Therefore, a model is written for the description and the prediction of the stress-stretch responses of filled rubbers during proportional cyclic tests.

1. Introduction

Rubber-like materials are used in various industrial applications. Elastomeric parts are particularly suitable for engineering applications designed to be submitted to cyclic loading conditions, like tires or vibration isolators. In order to increase their stiffness [1,2] and delay crack propagation [3–5], fillers are added to rubber compounds. Resulting from this adjunction, rubbers show an undesired stress softening known as the Mullins effect [6] when first loaded. Considering proportional cyclic loadings, the Mullins softening may be linked to the maximum stretch applied to the material along the loading history. Once the latter softening occurred, the material softening evolves so slowly with respect to the number of cycles [7,8] that the changes of the mechanical behavior between two successive cycles may rapidly become unnoticeable. The stress softening occurring during the first cycle and attributed to the Mullins effect has been the focus of numerous contributions over the past decades (see [9] for a review) while contributions on rubbers submitted to a large number of cycles usually aim at studying lifetime (see [10] for a review). Actually, only few papers have been drawing their attention to the evolving mechanical behavior of rubbers during cyclic loading conditions [7,8,11,12], and yet, when used as structural parts submitted to cyclic loadings, one may be interested in rubber cumulative stress-softening induced by large number of cycles.

Moderate (few percent of strain) cyclic uniaxial tests on notched samples reveal that close to the crack, strains may reach several hundred percent [5]. In this highly strained local region, the material undergoes a relatively low number of cycles (typically 1000) before the crack propagates through the highly strained region. Therefore, the study of rubber softening at large strain during a moderately large number of cycles, may be a key ingredient in the crack propagation understanding. In the current study, we will focus on the secondary stress-softening that begins after the first cycle when the major part of the Mullins effect had happened, at large strain and for a moderately large number of cycles. For this purpose, an original approach for rubber softening characterization is proposed based on the concept of stretch amplification due to material softening. Unlike the standard softening characterization method based on the observation of the maximum stress change (resp. strain) with respect to the number of applied cycles at constant maximum strain (resp. stress), this original approach introduces a softening parameter identified on the entire material stress-stretch responses. Such an approach provides an effective parameter for the comparison of the softening of materials of different compositions and for the prediction of the stress-stretch responses for any number of cycles. Hence, we will first compare the softening of styrene-butadiene rubbers (SBR) according to the amount of fillers and the crosslink density, and second we will write

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* Corresponding author. Tel.: +33 1 44 24 61 92; fax: +33 1 44 24 62 90.
E-mail addresses: yannick.merckel@gmail.com (Y. Merckel), julie.diani@ensam.eu (J. Diani).

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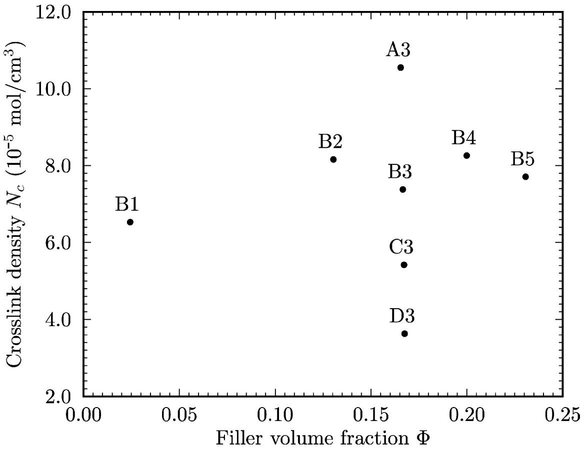

Fig. 1. Material strategy.

constitutive equations for modelling the cyclic softening of filled rubbers.

In the following section, the material strategy and the experimental procedure are presented. Then in Section 3, we introduce the original softening parameter and highlight its interest. Section 4 shows the effect of mechanical and material parameters like the loading intensity, the amount of fillers and the crosslink density on the softening of SBR materials. In Section 5, we show how the introduced softening parameter provides a simple tool for modelling the softened stress-stretch responses of rubbers for large strain proportional loadings. Finally, concluding remarks close the paper.

2. Materials and experiments

2.1. Materials

For this study, several filled SBRs were manufactured by Michelin company in order to investigate the relation between the material composition and the material cyclic softening. The SBR gum is a random copolymer with a 15% styrene molar fraction. N347 carbon-black fillers were used, which morphologies were characterized by the fineness of the elementary particles and by the aggregate structure. The fineness corresponds to the specific surface area of fillers, it was found close to 90 m^2/g by nitrogen absorption using the Brunner Emmet Teller (BET) analysis. The aggregate structure characterizing the branching of the aggregates, was measured at 120 ml/100 g by dibutyl-phthalate absorption (DBP absorption). The crosslink density was measured by Michelin by swelling using the Flory–Rehner theory. The material strategy was to vary the filler volume fraction Φ and the crosslink density N_c. From a reference material B3, materials B1, B2, B4 and B5 were obtained by varying the filler amount from 40 phr to 5, 30, 50 and 60 phr respectively. Materials A3, C3 and D3 contain the same amount of fillers than material B3 but their crosslink densities vary. Fig. 1 illustrates how each material compares to others. Details of the compositions of materials A3, B3, C3 and D3 are listed in Table 1. The lists of the filler volume fractions and of the crosslink densities appears in Table 2.

Table 1
Material composition in parts per hundred rubber (phr).

Ingredient	A3	B3	C3	D3
SBR	100	100	100	100
Carbon-black (N347)	40	40	40	40
Antioxidant (6PPD)	1.9	1.9	1.0	1.9
Stearic acid	2.0	2.0	2.0	2.0
Zinc oxide	2.5	2.5	2.5	2.5
Accelerator (CBS)	2.3	1.6	1.2	1.0
Sulfur	2.3	1.6	1.2	1.0

2.2. Experiments

Mechanical tests were conducted on an Instron 5882 uniaxial testing machine operating at room temperature. The samples were normalized flat dumbbell geometry with an initial cross section of $S_0 = 4 \times 2.5$ mm^2 and a 30 mm length. The force, F, was measured by a 2 kN load cell. The local strain in the stretched direction was measured by video extensometry. All tests were run at a constant crosshead speed of 3 mm/s, which according to the sample dimensions is equivalent to an average strain rate close to 10^{-1} s^{-1}. For each test, a fresh sample was submitted to 1000 cycles from null force to a chosen maximum stretch measured locally.

Throughout the paper the material responses will be plotted as stress vs. stretch $\lambda = l/l_0$. The stress is defined by $F\lambda/S_0$, which stands for the Cauchy stress when incompressibility is assumed. The latter assumption is commonly made for filled rubbers submitted to uniaxial tension tests. In order to illustrate the effect of the material compositions on their mechanical behavior, the material responses during the first cycle are shown in Fig. 2. One notices the strong effect on the mechanical behavior of both the amount of fillers and the crosslink density.

2.3. Decoupling the Mullins effect from the cyclic softening

Performing a cyclic loading with increasing the maximum stretch at each cycle highlights the strong stress-softening occurring at the first cycle when reaching a level of stretch never undergone by the material (Fig. 3, left). This softening is attributed to the Mullins effect. Then, performing cyclic loadings by repeating cycles with set constant maximum stretch, provides evidences of a secondary cyclic softening that depends on the number of cycles (Fig. 3, right). In order to isolate the cyclic softening, we limit our study to the mechanical responses after the first cycle. Therefore, in the sequel, we designate the second loading-unloading as the cycle ($N = 1$).

The following section presents an original characterization of cyclic softening for proportional cyclic loadings.

3. Original characterization of cyclic softening

3.1. Softening standard parameter

Commonly used in continuum mechanics for metallic materials [13], the concept of continuum damage variable [14], was extended to rubber-like materials by Simo [15]. In order to account for the

Table 2
Crosslink density N_c and filler volume fraction Φ for each materials.

Material	B1	B2	B3	B4	B5	A3	C3	D3
N_c (10^{-5} mol/cm^3)	6.53	8.16	7.38	8.26	7.71	10.55	5.42	3.63
Φ (%)	2.43	13.03	16.65	19.98	23.06	16.54	16.72	16.75