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Material behaviour

Filler effects on the thermomechanical response of stretched rubbers

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ABSTRACT

This paper deals with the calorimetric analysis of deformation processes in filled styrene-butadiene rubbers. More especially, the study focuses on the effects of the addition of carbon black fillers on the calorimetric response of "demullinized" SBR. Temperature variations are measured by infrared thermography during cyclic uniaxial tensile tests at ambient temperature. Heat sources[1] produced or absorbed by the material due to deformation processes are deduced from temperature fields by using the heat diffusion equation. First, the results show that no mechanical (intrinsic) dissipation is detected for weakly filled SBR, meaning that the heat produced and absorbed over one mechanical cycle is the same whatever the stretch ratio reached. Second, the mechanical dissipation in highly filled SBR is significant. The quantitative analysis carried out highlights the fact that it increases quasi-linearly with the stretch ratio. Finally, a simplified framework is proposed to discuss the identification of the heat sources, in particular the mechanical dissipation.

1. Introduction

Elastomers are widely used in industrial and research applications, mainly due to their ability to undergo large deformations without any damage, and to their damping properties. Nevertheless, due to their poor thermal conductivity, such materials are subject to significant self-heating during stretching, all the more so if they are reinforced by fillers.

In this study, infrared thermography (IRT) is used to investigate the effects of fillers on the thermomechanical response of styrene-butadiene rubber (SBR). 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…). The temperature changes are due to the material response (heat source due to thermoelasticity, viscosity, phase changes, strain-induced crystallization, damage…) as well as structure effects (heat conduction and heat exchanges with the environment outside the specimen under study). Thus, due to heat conduction and heat exchanges, temperature is not a relevant quantity (see for example [1,2]). For instance, temperature variation does not allow us to determine the characteristic strains at which strong exo- or endothermal phenomena occur, typically chain crystallization and crystallite melting (see for example [3]).

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[1] The term heat source is used in this paper to mean the heat power being produced or absorbed.

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This is the reason why thermal analysis has widely been extended to quantitative calorimetry (see for instance [4]). For this purpose, the framework of the thermodynamics of irreversible processes (TIP) and the heat diffusion equation are used. This approach enables us to measure the total heat source produced or absorbed by the material. Under certain hypotheses, it is also possible to distinguish the part due to thermomechanical couplings, including thermoelastic couplings, from the part due to mechanical dissipation. This approach is used in the present study in order to determine the variation in mechanical dissipation due to filler effects in a SBR whose mechanical behaviour is stabilized, *i.e.* "demullinized". The mechanical dissipation here is only due to viscosity, not to the Mullins effect.

The paper is composed of two parts. The first presents the experimental set-up while 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 SBR filled with two different amounts of N347 carbon black, 5 and 50 phr (part per hundred of rubber in weight), they are denoted SBR5 and SBR50, respectively. As shown in Table 1, apart from the filler quantity, their formulations were the same. The molar mass and the glass transition temperature of the SBR used were respectively 120,000 g/mol and −48 °C. It should be noted that these material formulations do not lead to stress-induced crystallization, unlike natural rubber, for instance. SBR5 and SBR50 were cured for 35 and 22 min, respectively. The mould temperature was set to 150 °C.

The non-standard specimen geometry is presented in Fig. 1. It was a thin dumbbell-shaped specimen, with width, length and thickness equal to 5 mm, 10 mm and 1.4 mm, respectively. It can be noted that 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 loading corresponded to uniaxial cyclic loading. It was applied under prescribed displacement using an INSTRON 5543 testing machine. The signal shape was triangular in order to ensure a constant strain rate during loading and unloading. The loading and nominal strain rates were equal to ±300 mm/min and ±0.5 s^{-1}, respectively. The test corresponded to series of three cycles at four increasing maximum stretch ratios, defined as the ratios between the current and the initial length of the specimen. The maximum stretch ratio levels were chosen as follows:

- For the SBR5, the four maximum stretch ratios were $\lambda_1 = 2$, $\lambda_2 = 3$, $\lambda_3 = 3.5$ and $\lambda_4 = 4$, as shown in Fig. 2(a).
- For the SBR50, the four maximum stretch ratios were $\lambda_1 = 2$, $\lambda_2 = 3$, $\lambda_3 = 4$ and $\lambda_4 = 4.5$, as shown in Fig. 2(b).

λ_3 and λ_4 slightly differed from one formulation to the other, due to the fact that the elongations at failure were different (4.2 for SBR5 and 4.8 for SBR50).

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

Ingredient	SBR5	SBR50
Styrene–Butadiene rubber (SBR)	100	100
Carbon black	5	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

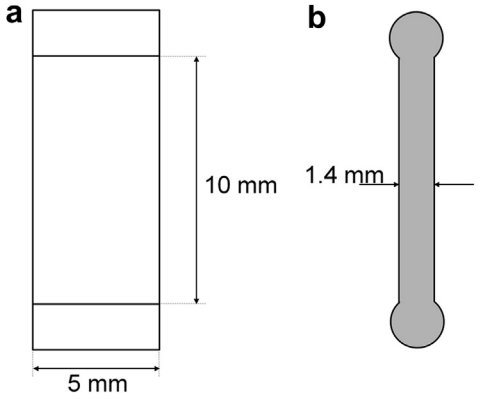

Fig. 1. Specimen geometry: (a) front view; (b) side view.

2.3. Temperature field measurement

Temperature field measurements were performed using a Cedip Jade III-MWIR infrared camera, which features a local plane array of 320 × 240 pixels and detectors with a wavelength range of 3.5–5 μm. Integration time was equal to 1500 μs. The acquisition frequency f_a was 147 Hz. The thermal resolution, namely the noise-equivalent temperature difference, was equal to 20 mK for a temperature range of 5–40 °C. The calibration of the camera detectors was performed with a black body using a Non-Uniformity Correction (NUC) procedure. During the measurement, the external heat sources were reduced by using a black box surrounding the specimen, featuring a small window for the IR camera to be able to observe the gauge zone of the specimen. The thermal quantity considered in the present study was the mean temperature variation of a small zone at the centre of the specimen. This quantity was obtained by subtracting the initial temperature from the current one, after applying a suitable movement compensation technique [3] to track this small zone during the test.

2.4. Heat source calculation

The heat sources produced or absorbed by the material itself were studied within the framework of the thermodynamics of irreversible processes. Considering the first and second principles of thermodynamics and assuming