



Mechanisms of deformation in crystallizable natural rubber. Part 2: Quantitative calorimetric analysis

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ABSTRACT

This paper deals with the calorimetric analysis of deformation processes in natural rubber. Infrared thermography is first used to measure the temperature evolution of specimens under quasi-static uniaxial loading at ambient temperature (see Part 1). Then the heat sources produced or absorbed by the material due to deformation processes are deduced from the temperature variations by using the heat diffusion equation. Different main results are obtained from cyclic and relaxation tests. First, no mechanical dissipation (intrinsic dissipation) is detected during the material deformation. Second, strain-induced crystallization leads to significant heat production, whereas the melting of crystallites absorbs the same heat quantity with different kinetics. This difference in kinetics explains the mechanical hysteresis. Finally, relaxation tests show that crystallite melting does not systematically occur instantaneously.

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1. Introduction

The physical mechanisms involved in the deformation of natural rubber are numerous and are still the object of keen scientific debate, among them viscosity, strain-induced crystallization and crystallite melting, cavitation and energetic and entropic effects on the thermomechanical response. To investigate these physical deformation processes, several experimental techniques have been used, including X-ray diffraction [1–3], X-ray microtomography [4], dilatometry [5,6] and classic mechanical tests such as stress relaxation and cyclic tests. Any deformation process induces heat production or absorption that can be detectable or analyzable with the abovementioned techniques. For this purpose, infrared (IR) thermography seems to be an appropriate technique to detect heat sources from measured temperature variations. Indeed, IR thermography has proved over the last twenty years to be a relevant technique to provide information of importance on the deformation processes in materials such as steels, aluminium alloys and composites. Moreover, various studies previously carried out by Chrysochoos and co-workers [7] have shown that heat sources produced

by the material itself were more relevant than temperatures when analyzing various phenomena such as **Lüders** bands [8], fatigue [9] or strain localization [10]. The main reason is that the temperature field is influenced by heat conduction as well as heat exchanges with the ambient air and the grips of the testing machine used.

In rubbery materials, which undergo large deformations, only two studies have recently been carried out to develop motion compensation techniques in the case of heterogeneous tests [11,12]. These studies focused on the numerical post-treatment of temperature fields, and were not dedicated to the analysis of the deformation processes. The present paper aims therefore at applying quantitative calorimetry to characterize and to analyze the thermomechanical behaviour of natural rubber under homogeneous uniaxial tensile tests, at ambient temperature. More particularly, the paper focuses on the calorimetric effects accompanying stress-induced crystallization and crystallite melting, which offers a new route to study such phenomena and their kinetics [13–15].

The first section describes the thermomechanical framework used to assess heat sources from temperature fields measured at the specimen surface. The second section describes the experimental setup, in terms of the material used, loading conditions and IR measurement technique. The third section presents the results obtained and discussion on the deformation processes.

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2. Thermomechanical framework

Temperature fields measured at the flat surface of a specimen by an IR camera are 2D, *i.e.* bidimensional. As the tests performed are assumed to be homogeneous in terms of strain and stress, the fact that rubbers have a very low thermal diffusivity leads to nearly homogeneous temperature fields. So a ‘0D’ approach can be developed. This approach is detailed below.

Let us start from the 3D formulation of the heat diffusion equation. In a thermomechanical framework [16], the local state axiom is assumed [17]. Any thermodynamic system out of equilibrium is considered as the sum of several homogeneous subsystems at equilibrium. The thermodynamic process is considered as a quasi-static phenomenon.

The state of any material volume element is defined by N state variables: temperature T , a strain tensor denoted E and internal variables V_1, V_2, \dots, V_{N-2} which can correspond to plastic strain or volume fractions of some phases. The specific free energy potential is denoted $\Psi(T, E, V_k)$, $k(1, 2, \dots, N-2)$. Considering the first and second principles of thermodynamics and assuming Fourier’s law to model heat conduction, the heat diffusion equation is written:

$$\rho C_{E, V_k} \dot{T} - \text{div}(K \text{grad}T) - r = \underbrace{d_1 + \rho T \frac{\partial^2 \Psi}{\partial T \partial E} \dot{E} + \rho T \frac{\partial^2 \Psi}{\partial T \partial V_k} \dot{V}_k}_s \quad (1)$$

where ρ is the density, C_{E, V_k} is the specific heat at constant E and V_k , K is the thermal conductivity tensor and r is the external heat source (*e.g.* by radiation). The right-hand side of equation (1) represents the heat sources s produced by the material itself. It can be divided into two terms that differ in nature:

- *mechanical dissipation* d_1 (or *intrinsic dissipation*): this positive quantity corresponds to the heat production due to the mechanical irreversibilities during any mechanical process;
- *thermomechanical couplings*: these correspond to the couplings between the temperature and the other state variables.

This equation applies both in reference configuration as well as in current configuration, provided that we give the suitable definition of symbols ρ , div , K , grad and s . However, only in lagrangian variables the total derivative \dot{T} can be calculated as a partial derivative.

2.1. Usual assumptions to calculate heat sources

The approach classically used to assess heat sources from the temperature fields obtained by an IR camera [18,19] is shortly described in this section.

By using thin specimens, the problem can be considered as bidimensional. At a given point (x, y) on the surface, the temperature is thus nearly homogeneous through the thickness. In fact, a small temperature gradient exists close to the specimen faces due to the heat exchange by convection with the air, but the surface temperature can be considered as very close to the mean temperature in the thickness. Then, by integrating the heat diffusion equation (1) over the specimen thickness [20] and defining the mean thermal disequilibrium through the thickness between the specimen and its surroundings by $\theta(x, y)$ the following bidimensional formulation of the heat diffusion equation is obtained:

$$\rho C_{E, V_k} \left(\dot{\theta} + \frac{\theta}{\tau_{2D}} \right) - \text{div}_{2D}(K_{2D} \text{grad}_{2D} \theta) = s \quad (2)$$

where div_{2D} , K_{2D} and grad_{2D} are the restrictions of div , K and grad to the (x, y) plane, respectively. τ_{2D} is a time constant characterizing

the heat exchanges by convection with the air at the specimen surface. It is assumed to be the same at any point (x, y) of the specimen. It can be defined as follows (see Ref. [20]):

$$\tau_{2D} = \frac{e \rho C_{E, V_k}}{2h} \quad (3)$$

where e is the specimen thickness and h a convection coefficient. In practice, the constant τ_{2D} is experimentally assessed by identification from a simple test of natural return to room temperature.

Considering that the stress state is everywhere plane, it can be shown by explicit calculation that the expression (3) applies whatever the configuration considered, as it should after the remark preceding. Indeed, going from reference to the current configuration, we have $e \rightarrow e \lambda_z$, $\rightarrow \rho J^{-1}$, $h \rightarrow h / (J \sqrt{C_{zz}^{-1}}) = J^{-1} \lambda_z h$, so that the combination $e \rho / h$ remains unchanged.

The 2D equation (2) can be reduced to a ‘0D’ formulation in the case of heat source fields which are homogeneous in the specimen [21]. In the present study, this approach is relevant because the tests are assumed to be homogeneous in terms of strain and stress. Moreover, rubbers have a very low thermal diffusivity, which leads to nearly homogeneous temperature fields. In such a case, the heat diffusion equation can be rewritten [21]:

$$\rho C_{E, V_k} \left(\dot{\theta} + \frac{\theta}{\tau} \right) = s \quad (4)$$

where τ ($=\tau_{0D} \approx \tau_{2D}$) is a time constant characterizing the heat exchanges between the specimen and its environment, *i.e.* the ambient air and the jaws of the testing machine. It can be noted that τ must be measured for each testing configuration (material, specimen geometry, environment in terms of ambient air and jaws of the testing machine).

Some comments can be added concerning tests that are performed on rubber materials. Because of large displacements, the convection conditions with the ambient air depend on the velocity of the material point. Moreover, large deformations lead to a variation in the specimen thickness, leading also to a change in the value of τ (see equation (3)). Thus the situation is much more complex than with metallic materials subjected to small displacements and deformations. The experimental procedure to measure θ is more precisely detailed in subsection (3.3).

Let us conclude with some considerations on units. The heat source s is expressed in $[\text{W m}^{-3}]$. However, it is generally useful to divide this quantity by $\rho C_{E, V_k}$:

$$\dot{\theta} + \frac{\theta}{\tau} = \frac{s}{\rho C_{E, V_k}} \quad (5)$$

The quantity $s / \rho C_{E, V_k}$ is expressed in $^{\circ}\text{C s}^{-1}$ (corresponding to the temperature rate that would be obtained in an adiabatic case). In the rest of the paper, the term ‘heat source’ will also be used for this quantity $s / \rho C_{E, V_k}$.

Note finally that throughout the document, the term ‘heat’ must be distinguished from ‘heat source’. The heat is the temporal integration of the heat sources. It is expressed in J m^{-3} (in $^{\circ}\text{C}$ when divided by $\rho C_{E, V_k}$).

3. Experimental setup

3.1. Material and specimens

The material considered here is an unfilled natural rubber. Its formulation is given in the companion paper denoted Part 1 in the following [22]. The specimen denoted NR in the following, was obtained by sulphur vulcanization, and was cured for 22 min at 150°C .

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