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Comparison between X-ray diffraction and quantitative surface calorimetry based on infrared thermography to evaluate strain-induced crystallinity in natural rubber

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The crystallinity of stretched crystallizable rubbers is classically evaluated using X-ray diffraction (XRD). As crystallization is a strongly exothermal phenomenon, quantitative surface calorimetry from infrared thermography (IRT-QSC) offers an interesting alternative to XRD for determining the crystallinity. In the present paper, the two measurement techniques have been used for evaluating the strain-induced crystallinity of the same unfilled natural rubber. This study provides the first comparison between the two techniques. Results obtained highlight a very satisfactory agreement between the two measurements, which opens a simple way for evaluating the strain-induced crystallinity from temperature measurements.

I. INTRODUCTION

Since the pioneering work by Katz in 1925, who obtained the first XRD pattern of a stretched natural rubber (NR), the strain-induced crystallization (SIC) of rubber is classically investigated using X-ray diffraction (XRD). XRD provides the crystallinity but also information of paramount importance on the crystalline phase structure, chain orientation, kinetics of crystallization, and at the crack tip where the mechanical and calorimetric fields are strongly heterogeneous.

Concerning the crystallinity measurement, Göritz and co-workers showed in the 1970s that strain-induced crystallinity could be quantified accurately with an alternative technique, based on "stretch calorimetry". Indeed, crystallization is strongly exothermal and the corresponding crystallinity can therefore be evaluated from the part of the total heat source that is produced by SIC only. This technique offered a simpler way than XRD to evaluate the crystallinity. Despite this, calorimetry under stretching was no longer used to measure crystallinity. A possible reason could be that the crystallinity obtained was averaged over all the specimen. Therefore, it is not possible to address heterogeneous zones if any. Much smaller beam spots can be reached with special optics and acquisition times as low as 0.2s per frame with good counting statistics are possible. The drawing speed can be selected between 1mm/min and 800 mm/min. However the necessity of collecting a sufficient number of frames (acquisition time: 0.2s) during the stretching phase limited the maximal drawing speed to 200mm/min. The incident beam diameter is ca. 1mm in that case, which precludes any detailed analysis of heterogeneous zones if any. Much smaller beam spots can be reached with special optics at the price of intensity loss and systematic mapping becomes highly time consuming.

II. XRD TECHNIQUE

Crystallinity indices reported here are derived from an analysis of angular scans centered on the amorphous halo as detailed in Ref.21. This method combines simplicity and direct access to the Herman orientation parameter for the amorphous phase. Further parameters provided by X-ray diffraction include the crystal dimensions and their orientation with respect to the draw axis (see the references cited in the introduction section). One main limitation for the use of XRD is that it requires the installation of a testing machine on a laboratory diffraction bench, which is out of the reach of many laboratories. In the present case the testing machine is installed on a rotating anode generator operated at medium power (copper anode, 40 kV, 40 mA, focus size: 0.2 × 0.2 mm²). The CuKα radiation is selected with a doubly curved graphite monochromator with a focalization distance of 24 cm. The sample is located at the focalization point which ensures optimized diffracted intensity. The set-up can be equipped with an indirect illumination CCD camera or a hybrid pixel detector. This last X-ray camera combines high efficiency and absence of noise and acquisition times as low as 0.2s per frame with good counting statistics are possible. The drawing speed can be selected between 1mm/min and 800 mm/min. However the necessity of collecting a sufficient number of frames (acquisition time: 0.2s) during the stretching phase limited the maximal drawing speed to 200mm/min. The incident beam diameter is ca. 1mm in that case, which precludes any detailed analysis of heterogeneous zones if any. Much smaller beam spots can be reached with special optics at the price of intensity loss and systematic mapping becomes highly time consuming.

III. QUANTITATIVE SURFACE CALORIMETRY FROM IR THERMOGRAPHY (IRT-QSC)

SIC is a strongly exothermal phenomenon, which explains why surface calorimetry is a relevant alternative to determine the crystallinity. Crystallinity can be evaluated from the part of the total heat source that is produced by SIC only, which gives access to the corresponding crystallization temperature T_cry. The crystallinity χ can then be deduced from T_cry by considering that the crystallization energy of natural rubber can be approximated nonlinearly.

1 The term 'heat source' is used in this paper to mean the heat power density in W/m³, which is produced or absorbed by the material.
by the enthalpy of fusion $\Delta H_{\text{cryst}}$ (in J/dm$^3$)$^{20,23}$:

$$\chi(t) = \frac{\rho C T_{\text{cryst}}(t)}{\Delta H_{\text{cryst}}}$$  \hspace{1em} (1)

$\rho$ and $C$ are respectively the material’s density (in kg/dm$^3$) and the heat capacity (in J/(kg K)). The material’s density and heat capacity are assumed to be independent of strain and temperature.

Determining strain-induced crystallinity from infrared (IR) thermography has several advantages:

- the crystallinity field is measured instantaneously, which is of paramount importance in case of heterogeneous crystallinity field;
- IR thermography provides high resolution thermal measurements (temporal, spatial and on the value of the crystallinity itself through the thermal resolution of 20 mK in the temperature range of the present experiment);
- the measurement can be performed in any lab equipped with a conventional testing machine;
- the heat source produced by SIC can be directly linked with constitutive equations through the thermomechanical couplings. Therefore, this technique is all the more interesting that it enables us to validate and to improve thermomechanical SIC models.

Nevertheless, this technique does not provide information on the crystalline phase structure and chain orientation. In the next section, the thermomechanical framework used to determine the heat source and the crystallization temperature due to SIC is presented.

IV. HEAT SOURCE RECONSTRUCTION

Most of mechanical tests are conducted under non-adiabatic. The temperature measured is therefore affected by heat diffusion within the specimen and with the specimen outside. Therefore, changes in temperature are not only due to the material deformation itself, and the heat diffusion equation is used to determine the corresponding heat source from temperature measurement. This quantity is intrinsic to the material deformation and can be directly compared with constitutive model predictions. Thus, any temperature measurement technique can be used as a calorimeter, an IR camera in the present study, as soon as the heat diffusion by conduction and convection is characterized. In the thermodynamic framework applied, any thermodynamical system out of equilibrium is considered as the sum of several homogeneous subsystems at equilibrium. The deformation is considered as a quasi-static thermodynamic process. The equilibrium state of each volume material element is defined by $n$ state variables: the absolute temperature $T$, the deformation gradient tensor $F$ and $m (= n - 2)$ internal tensorial variables $\xi_\alpha$. The local form of the heat diffusion equation writes as follows in the Lagrangian configuration:

$$\rho CT - \text{Div} (\kappa_0 \text{Grad} T) = R + \mathcal{D}_{\text{int}} + T \frac{\partial \mathbf{P}}{\partial T} \cdot \mathbf{F} + T \sum_{\beta=1}^{m} \frac{\partial A_\beta}{\partial T} \cdot \xi_\beta$$  \hspace{1em} (2)

where $\kappa_0$ is a positive semi-definite tensor characterizing the thermal conductivity of the material. $R$ stands for the external heat source due to radiation. $S$ denotes the overall heat source induced by the deformation process. The term $\mathcal{D}_{\text{int}}$ corresponds to the intrinsic dissipation. The term $T \frac{\partial A_\beta}{\partial T} : \xi_\beta$ corresponds to the other thermomechanical couplings (for instance related to phase change in the material). Let us denote $\theta$ the temperature variation with respect to the equilibrium temperature $T_{\text{ref}}$ in the reference state, corresponding to the undeformed state ($T_{\text{ref}}$ is constant and equal to the ambient temperature). In case where changes in ambient temperature occur, $T_{\text{ref}}$ has to be corrected accordingly with the measurement of ambient temperature variations. Moreover, in the case where the heat conduction in the specimen plane is neglected, the tri-dimensional formulation of the heat diffusion equation can be simplified and written in case of homogeneous heat source field. After some calculations that are not detailed here, the heat diffusion equation can be rewritten in case of homogeneous heat source field$^{12}$:

$$\rho C \left( \frac{\theta}{\tau} + \frac{\theta}{\tau} \right) = S$$  \hspace{1em} (3)

where $\tau$ is a parameter characterizing the heat exchanges between the specimen and its surroundings$^2$. It can be easily identified from a natural return to room temperature after a heating (or a cooling) for each testing configuration (machine used, environment, etc.). For instance in case where the material is beforehand heated, the exponential formulation of the temperature variation is used to determine parameter $\tau$: $\theta = \theta_0 \exp\left(-\left(t - t_0\right)/\tau\right)$. In case of large deformations, $\tau$ depends on the stretch. Either $\tau$ is determined at different increasing stretches, further details are provided in Ref.$^1$, or the value of $\tau$ is corrected according to its dependency to the stretch in case of incompressible materials. In the former case, the determination of $\tau$ during the natural return to ambient temperature for stretches higher than that at which crystallization starts is affected by the fact that additional heat is produced (absorbed) due to crystallization (melting) during the material cooling (heating). This is the reason why in the present study $\tau(\lambda)$ has been determined from its value in the undeformed state (denoted $\tau_0$) and the link between the thickness and the stretch. This link depends on the biaxiality ratio $B$, defined as the ratio between the logarithm of $\lambda_2$ and the logarithm of $\lambda_1$. $\lambda_1$ and $\lambda_2$ are the maximum and minimum principal stretches in the specimen plane, respectively. By assuming the material to be incompressible, $\tau$ writes:

$$\tau = \tau(\lambda, B) = \frac{\tau_0 \lambda^{-B-1}}{\sqrt{\lambda}}.$$  \hspace{1em} (4)

In the present case of the uniaxial tension, $B$ is equal to $-0.5$ and $\tau$ writes finally:

$$\tau(\lambda) = \frac{\tau_0}{\sqrt{\lambda}}.$$  \hspace{1em} (5)

A. Determination of the crystallinity

Figure 1 illustrates the methodology proposed. It requires the temperature variation $\theta$, parameter $\tau$ and the thermophysical parameters $\rho$, $C$ and $\Delta H$ as input data, and is composed of four steps:

$^2$ In this case, only a one-point temperature measurement is required, meaning that the crystallinity can be evaluated with a pyrometer.
Comparison between X-ray diffraction and quantitative surface calorimetry

This method is very simple and does not require measuring the variation of the nominal stress variations or characterizing possible non-entropic effects, because they are included in the calorimetric response.

V. EXPERIMENTS

The material considered here is an unfilled natural rubber of grade SMR 5L vulcanized by sulfur (1.5 phr) in the presence of conventional activators and antioxidant agents. The average molecular weight between cross-links is 6330 g mol$^{-1}$ (86 isoprene units) based on mechanical measurements. For the calculations, the density, specific heat and fusion enthalpy values for the calculations were chosen equal to 0.936 kg/dm$^3$, 1768 J/(kg K) and $62 \times 10^3$ J/dm$^3$, respectively. The mechanical loading is applied symmetrically at a stretch equal to 7.2 and two different loading rates: 100 and 200 mm/min. The averaged specimen dimensions were 19.3 mm in height, 7.2 mm in width and 1.4 in thickness. The experimental set-up used for the XRD technique is depicted in Figure 2.

The experimental setup used from the temperature measurement is presented in Figure 3. Tests were conducted with a home-made biaxial testing machine. Four independent electrical actuators enable us to stretch symmetrically the specimens in two perpendicular directions. Actuators are driven by means of a home-made LabVIEW program. The cell load capacity is 1094 N. In the present case, the testing machine is used to stretch symmetrically the specimen in one direction only. Therefore, the zone where the thermal measurement is performed remains in the...
Comparison between X-ray diffraction and quantitative surface calorimetry

same place, which enables us to obtain the temperature variation by subtracting the current measurement zone to the initial one, without any motion compensation technique. In order to reduce the external radiation, the grips were covered with a black body leaf (see the IR image in Fig. 3).

VI. RESULTS

Figure 4 presents the mechanical responses obtained in terms of the nominal stress, defined as the force per unit surface, in relation to the stretch for the two loading rates during the two types of measurement. The continuous and dotted lines are the mechanical response obtained with the tensile machine used for IR thermography and XRD measurements, respectively.

The thermal response is shown in the red curves in Figure 5. This figure shows the typical response of a crystallizing rubber, i.e. a strong temperature increase occurs once the crystallization stretch onset is exceeded. It should noted that the temperature increases at the end of the unloading. This is due to non-adiabatic effects that are all the more significant that the loading rate is low. Further explanations on non-adiabatic effects on the temperature variation are provided in Ref. (pages 2721-2722).

The corresponding adiabatic temperature variations (curves in black color in Figure 5) are deduced from the heat source. The fact that \( \tau(\lambda) \) enables us to retrieve a temperature equal to zero at the end of each cycle validates the characterization of the non-adiabatic effects, i.e. the value of \( \tau \), as the material does not produce heat at each mechanical cycle.

Figure 6 depicts the heat source in relation to the stretch (curve A), obtained from Equation 3 (Step #1). During loading, the heat source is positive and increases with the stretch. Once SIC starts, a strong increase in the heat produced is observed. The polynomial form in (Step #2) is used to predict the heat source due to elastic couplings and to determine the area between the two curves, i.e. the thermal energy, due to SIC only. Then, the crystallization temperature is obtained from the primitive calculation of the heat source due to SIC.

The integration constant is determined considering that \( T_{\text{cryst}} \) before crystallization starts is equal to zero. It should be noted that without any crystallization, i.e. below the strain at which crystallization starts during the loading, \( T_{\text{cryst}} \) is equal to zero, i.e. no temperature variation is due to SIC. Indeed, for this un-
filled NR formulation the XRD measurements have shown that the crystallinity returns to zero at the end of each cycle. The crystallinity is calculated by using the fusion enthalpy. The crystallinity obtained for the two loading rates applied corresponds to continuous lines in Figure 7. The XRD measurement, which was performed during the first loading, corresponds to lines with cross symbol in the figure. This comparison clearly shows the relevancy of evaluating strain-induced crystallization from IR thermography measurements.

VII. CONCLUSION
In the present study, the crystallinity of an unfilled natural rubber has been evaluated by two different techniques: the IR thermography based quantitative surface calorimetry (IRT-QSC) and the X-ray diffraction (XRD) techniques. Results obtained highlight a very satisfactory agreement between the two measurements, which validate the IR-QSC technique proposed in Le Cam (2018) to measure the strain-induced crystallinity. Further investigations are currently carried out by coupling the two techniques for a better characterization of the thermo-physical properties and their evolution with the stretch. It is to note that X-ray diffraction is also complementary of temperature measurements at low drawing velocity where calorific effects become hardly detectable.

VIII. AUTHOR’S CONTRIBUTIONS
All authors contributed equally to this work.

IX. DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

FIG. 7. Crystallinity in % during the loading #2 (-) surface calorimetry (x) XRD (a) 100 mm/min (b) 200 mm/min

- [3] Y. Takahashi and T. Kumano, “Crystal structure of natural rubber,” Macromolecules 37, 4860 (2004)
- [4] A. Immirzi, C. Tedesco, G. Monaco, and A. Tonelli, “Crystal structure and melting entropy of natural rubber,” Macromolecules 38, 1223 (2005)
- [5] G. Rajkumar, J. Squire, and S. Arnott, “A new structure for crystalline natural rubber,” Macromolecules 39, 7004 (2006)
- [6] S. Toki, I. Sics, S. Rani, L. Liu, B. Hsiao, S. Murakami, M. Tosaaka, S. Kojihya, S. Poopradth, Y. Ikeda, and A. Tsu, “Structural developments in synthetic rubbers during uniaxial deformation by in situ synchrotron x-ray diffraction,” Journal of Polymer Science Part B: Polymer Physics 42, 956–964 (2004)
- [7] S. Toki, T. Fujimaki, and M. Okuyama, “Strain-induced crystallization of natural rubber as detected real-time by wide-angle x-ray diffraction technique,” Polymer 41, 5423–5429 (2000)
- [8] S. Trabelsi, P.-A. Alzoubi, and J. Rault, “Effective local deformation in stretched filled rubber,” Macromolecules 36, 9093–9099 (2003)
- [9] D. Göritz and F. Müller, “Die kalorimetrische erfassung der dehnungs-krystallisation polymeren,” Kolloid-Zeitschrift und Zeitschrift für Polymere 241, 1075–1079 (1970)
- [10] S. Trabelsi, P.-A. Alzoubi, and J. Rault, “Stress-induced crystallization around a crack tip in natural rubber,” Macromolecules 35, 10054–10061 (2002)
- [11] P. Rubin, B. Huneau, E. Verron, N. Saintier, S. Beurrot, A. Leygue, C. Mocuta, D. Thiaudière, and D. Bergehezan, “Multiaxial deformation and strain-induced crystallization around a fatigue crack in natural rubber,” Engineering Fracture Mechanics 123, 59–69 (2014)
- [12] A. Chryschoos, “Analyse du comportement des matériaux par thermographie infra rouge,” in Colloque Photomécanique, Vol. 95 (1995) pp. 201–211
- [13] J. Samaca Martínez, J.-B. Le Cam, X. Balandraud, E. Toussaint, and J. Caillard, “Mechanisms of deformation in crystallizable natural rubber. part 2: Quantitative calorimetric analysis,” Polymer 54, 2727–2736 (2013)
- [14] J.-B. Le Cam, J. Samaca Martínez, X. Balandraud, E. Toussaint, and J. Caillard, “Thermomechanical analysis of the singular behavior of rubber: Entropic elasticity, reinforcement by fillers, strain-induced crystallization and the multiaxial effect,” Experimental Mechanics 55, 771–782 (2015)
- [15] J. Samaca Martínez, X. Balandraud, E. Toussaint, J.-B. Le Cam, and D. Bergehezan, “Thermomechanical analysis of the crack tip zone in stretched crystallizable natural rubber by using infrared thermography and digital image correlation,” Polymer 55, 6345–6353 (2014)
- [16] J. R. Samaca Martínez, E. Toussaint, X. Balandraud, J.-B. Le Cam, and D. Bergehezan, “Heat and strain measurements at the crack tip of filled rubber under cyclic loadings using full-field techniques,” Mechanics of Materials 81, 62–71 (2015)
- [17] J.-B. Le Cam, “Energy storage due to strain-induced crystallization in natural rubber: the physical origin of the mechanical hysteresis,” Polymer 127, 166–173 (2017)
- [18] A. Lachhab, E. Robin, J.-B. Le Cam, F. Mortier, Y. Trel, and F. Canivet, “Energy stored during deformation of crystallizing tpu foams,” Strain e12271 (2018), 10.1111/str.12271
- [19] M. Loukil, G. Corvec, E. Robin, M. Miroir, J.-B. Le Cam, and P. Garnier, “Stored energy accompanying cyclic deformation of filled rubber,” European Polymer Journal 55, 2727–2736 (2013)
- [20] J.-B. Le Cam, “Strain-induced crystallization in rubber: A new measurement technique,” Strain 54, e12256 (2018)
- [21] P.-A. Alzoubi, A. Vieyres, R. Perez-Aparicio, O. Sanseau, and P. Sotta, “The impact of strain-induced crystallization on strain during mechanical cycling of cross-linked natural rubber,” Polymer 55, 4022–4031 (2014)
- [22] P.-A. Alzoubi and P. Sotta, “Draw ratio at the onset of strain-induced crystallization in cross-linked natural rubber,” Macromolecules 53, 992–1000 (2020)
- [23] T. Spratte, J. Plagge, M. Wunde, and M. Klpple, “Investigation of strain-induced crystallization of carbon black and silica filled natural rubber composites based on mechanical and temperature measurements,” Polymer 115, 12–20 (2007)
- [24] L. Treloar, “The elasticity and related properties of rubbers,” Reports on Progress in Physics 36, 755 (1973)
- [25] E. Toussaint, X. Balandraud, J.-B. Le Cam, and M. Grediac, “Combining displacement, strain, temperature and heat source fields to investigate the thermomechanical response of an elastomeric specimen subjected to large deformations,” Polymer Testing 31, 916–925 (2012)
- [26] J. Samaca Martínez, J.-B. Le Cam, X. Balandraud, E. Toussaint, and J. Caillard, “Mechanisms of deformation in crystallizable natural rubber. part 1: Thermal characterization,” Polymer 54, 2717–2726 (2013)