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 of 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[1], 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[2–5], chain orientation[6], kinetics of crystallization[7,8], non exhaustively.

Concerning the crystallinity measurement, Göritz and coworkers showed in the 1970s that strain-induced crystallinity could be quantified accurately with an alternative technique, based on "stretch calorimetry"[9]. Indeed, crystallization is strongly exothermal and the corresponding crystallinity can therefore be evaluated from the part of the total heat source[Note1] 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 crystallinity fields, typically at the crack tip of a notched specimen[10,11]. With the advent of non contact measurement techniques, it has been demonstrated that the calorimetric response could be directly obtained at the surface of a thin specimen as soon as the heat diffusion is characterized and that no temperature gradient occurs in the specimen thickness[12]. This technique has been successfully employed for characterizing the calorimetric signature of phenomena involved in the rubber deformation under homogeneous strain states[13,14] and at the crack tip where the mechanical and calorimetric fields are strongly heterogeneous[15,16]. Furthermore, such technique enables us to make energy balance and to identify the intrinsic dissipation[17–19].

Recently,[20] has proposed to couple the work by Göritz and co-workers and the IR thermography-based surface calorimetry approach to evaluate the strain-induced crystallinity. By this way, the author measured the crystallinity induced in an unfilled natural rubber submitted to one mechanical tensile cycle. Even though the crystallinity found seems to be in good agreement with the literature, no validation was done by comparing the result obtained with that obtained with XRD for the same material. This is the aim of the present study. In the first part of the paper, the framework for evaluating the strain-induced crystallinity from the two techniques is presented. The second part of the paper details the experiments carried out and compares the two measurements performed. Concluding remarks close the paper.

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 crystallite 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, a drawing velocity as high as 200 mm/min was only possible due to the high intensity beam delivered by a doubly-curved graphite monochromator that allowed exposure time of 0.2 s per frame. However, 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.

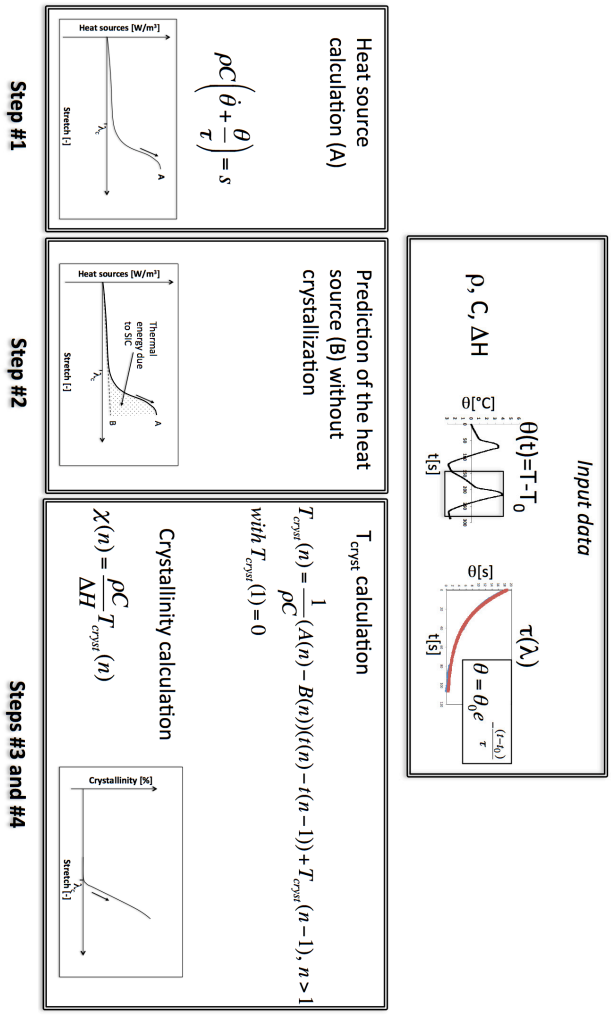


FIG. 1. Methodology for determining crystallinity from temperature variation measurement

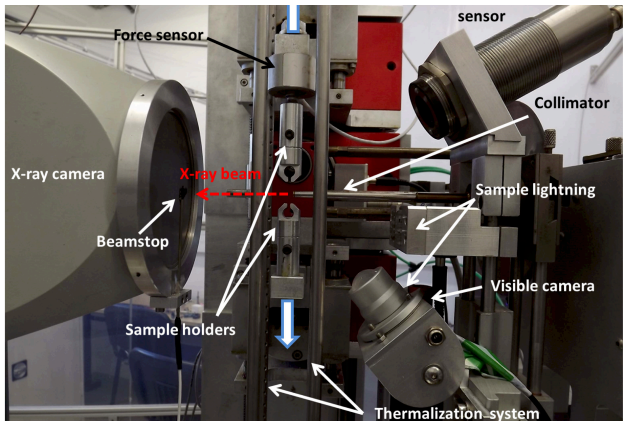


FIG. 2. Experimental setup for the XRD technique

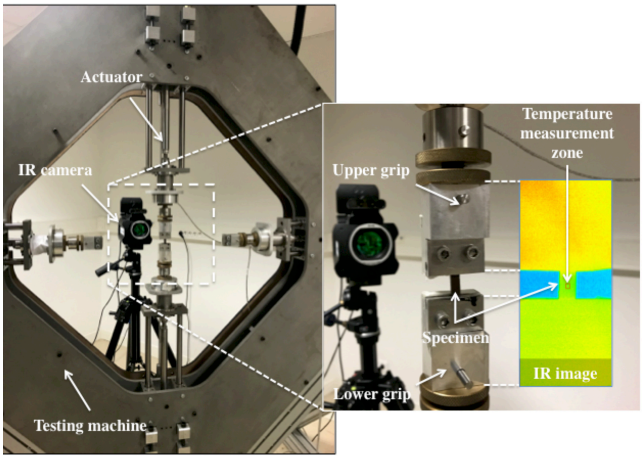


FIG. 3. Experimental setup for the temperature measurement

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_{cryst}. The crystallinity χ can then be deduced from T_{cryst} by considering that the crystallization energy of natural rubber can be approximated by the enthalpy of fusion ΔH_{cryst}:

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

ρ and C are respectively the specimen density and the heat capacity.

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

- the crystallinity field is measured instantaneously, which is of paramount importance in case of heterogeneous crystallinity field;
- infrared 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 conditions. The temperature measured is therefore affected by heat diffusion during the tests, possible temperature gradients at the surface of the undeformed specimen and external heat sources (for instance radiations). 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 infrared camera in the present study, as soon as the heat diffusion 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 $\mathbf{F}$ and m $(= n-2)$ internal tensorial variables $\boldsymbol{\xi_\alpha}$. The local form of the heat diffusion equation writes as follows in the Lagrangian configuration:

$$\rho C\dot{T} - \mathrm{Div}(\boldsymbol{\kappa_0}\,\mathrm{Grad}\,T) = R + \underbrace{\mathscr{D}_{int} + T\frac{\partial \mathbf{P}}{\partial T} : \dot{\mathbf{F}} + T\sum_{\beta=1}^{m}\frac{\partial \boldsymbol{A_\beta}}{\partial T} : \dot{\boldsymbol{\xi}_\beta}}_{S} \tag{2}$$

where $\boldsymbol{\kappa_0}$ is a positive semi-definite tensor characterizing the thermal conductivity of the material. S denotes the overall heat source induced by the deformation process. The term $\mathscr{D}_{int}$ corresponds to the intrinsic dissipation. The term $T\frac{\partial \mathbf{P}}{\partial T} : \dot{\mathbf{F}}$ is the heat source due couplings between temperature and strain, where $\mathbf{P}$ is the nominal stress tensor. The term $T\frac{\partial \boldsymbol{A_\beta}}{\partial T} : \dot{\boldsymbol{\xi}_\beta}$ corresponds to the other thermomechanical couplings (for instance related to phase change in the material). Let us denote θ the temperature variation with respect to the equilibrium temperature T^{ref} in the reference state, corresponding to the undeformed state (T^{ref} is constant and equal to the ambient temperature). In case where changes in ambient temperature occur, T^{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]:

$$\rho C\left(\dot{\theta} + \frac{\theta}{\tau}\right) = S \tag{3}$$

where τ is a parameter characterizing the heat exchanges between the specimen and its surroundings[Note2]. 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 τ: $\theta = \theta_0 e^{\frac{-(t-t_0)}{\tau}}$. In case of large deformations, τ depends on the stretch. Either a measurement is performed at different stretches, further details are provided in Ref.[13], or the value of τ is corrected according to its dependency to the stretch in case of incompressible materials. In the former case, the determination of τ for stretches higher than that at which crystallization starts is affected by the fact that additional heat is produced due to additional crystallization (or melting if the material is cooled) occurs during the natural return to ambient temperature. This is the reason why in the present study $\tau(\lambda)$ has been determined for the undeformed state (it is denoted τ_0) and the effect of the stretch is given by by the following equation:

$$\tau = \frac{\tau_0}{\sqrt{\lambda}} \tag{4}$$

A. Determination of the crystallinity

Figure 1 illustrates the methodology proposed. It requires the temperature variation θ, parameter τ and the thermophysical parameters ρ, C and ΔH as input data, and is composed of four steps:

- **Step** #1**:** the heat source is calculated by applying Equation 3. The diagram illustrates the typical increase in the heat source produced in unfilled NR once crystallization starts[9,13]. Here, λ_c stands for the stretch at which SIC starts;
- **Step** #2**:** The thermal energy due to SIC is deduced from the area located between the heat source measured (curve A) and the part of the heat source that would be due to the elastic coupling only (curve B). The latter is predicted by using a polynomial form, which parameters are identified by fitting the heat source measured before SIC starts ($\lambda < \lambda_c$): $C_1(\lambda - \lambda^{-2}) + C_2(\lambda - \lambda^{-2})^2 + C_3(\lambda - \lambda^{-2})^3$. It is inspired from the Yeoh's model[22]. As the tests are performed under controlled displacement, the strain rate effect is accounting by a constant that is multiplied with the C_i parameters;
- **Step** #3**:** the temperature variation due to SIC T_{cryst} is computed from the heat source due to SIC, i.e. the area between curves A and B. See for instance the not centered numerical scheme given in the figure;
- **Step** #4**:** the crystallinity is calculated by applying Equation 1.

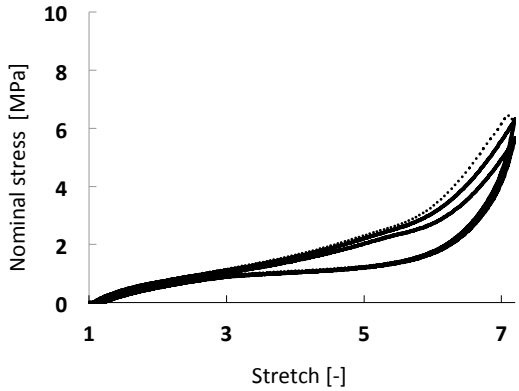
This method is very simple and does not require measuring the nominal stress variations nor characterizing possible non-entropic effects[23], because they are included in the calorimetric response.

V. EXPERIMENTS

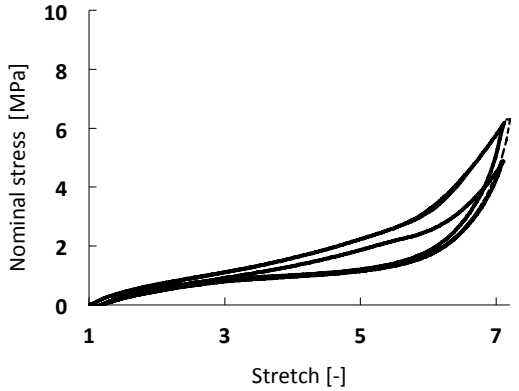
The material considered here is an unfilled natural rubber of grade SMR 5L vulcanized by sulfur ($1.5phr$) in the presence of conventional activators and antioxidant agents. The average molecular weight between cross-links is 6330 $g.mol^{-1}$ (86 isoprene units) based on mechanical measurements. For the calculations, the density, specific heat and fusion enthalpy values for the calculations were chosen equal to 936 kg/dm^3, 1768 $J/(kg.m)$ and 62 J/cm^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 enables 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 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[24]. In order to reduce the external radiation, the grips were covered with a black body leaf (see the infrared image in Fig. 3).

It should be noted that two mechanical cycles were performed for the infrared measurement in order to validate the expression of $\tau(\lambda)$ as the second cycles is a thermodynamic cycle.



(a) 100 mm/min



(b) 200 mm/min

FIG. 4. Mechanical response obtained: XRD experiments in dotted line, IRT experiments in continuous line

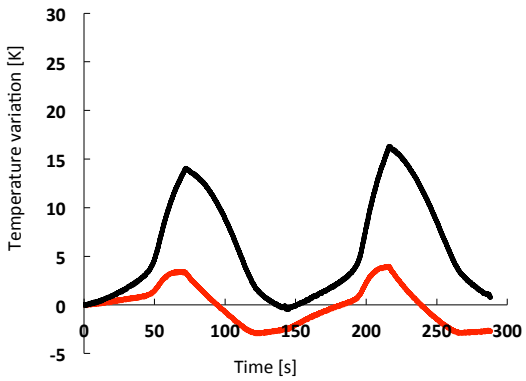
A. Results

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 hysteresis loop are induced by

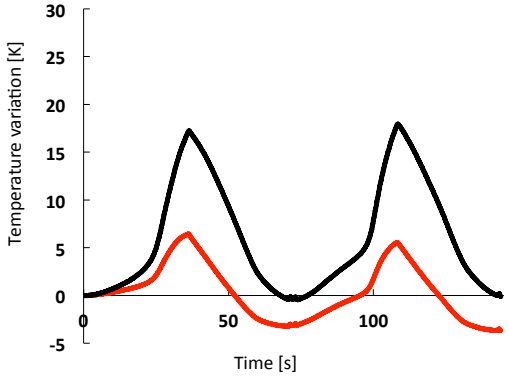
The thermal response is shown in the red curves in Figure 5. This figure shows the typical response of a crystallizing rubber, i.e. a strong temperature occurs once the crystallization stretch onset is exceeded.

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 τ, 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[Note3] due to SIC. The integration constant is determined considering that T_{cryst}

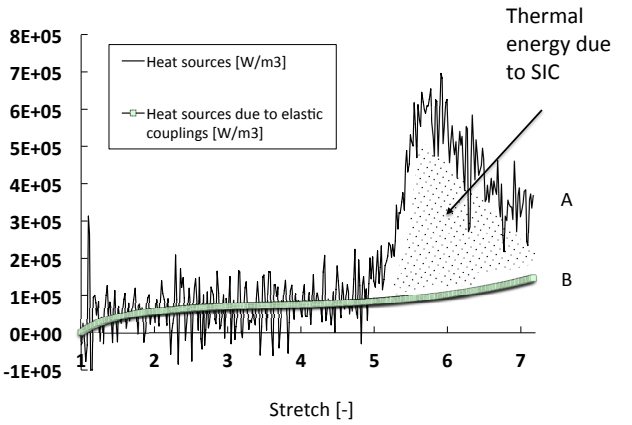


(a) 100 mm/min

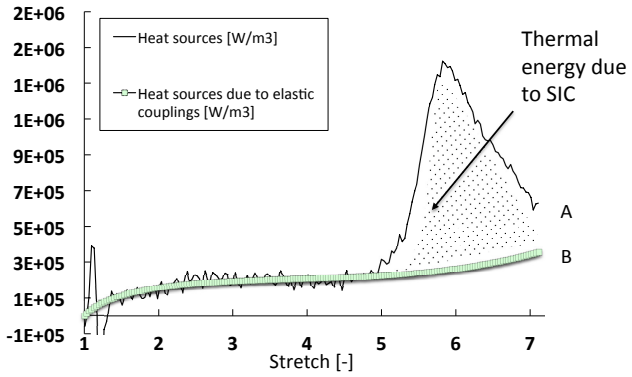


(b) 200 mm/min

FIG. 5. Temperature variation measured (in red) and the corresponding adiabatic one (in black) during the first two cycles.



(a) 100 mm/min



(b) 200 mm/min

FIG. 6. Heat source, strain power density and heat source due to elastic couplings during the loading #2

before crystallization starts is equal to zero. 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.

VI. CONCLUSION

In the present study, the crystallinity of an unfilled natural rubber has been evaluated by two different techniques: the infrared 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 validates the infrared thermography based quantitative surface calorimetry 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.

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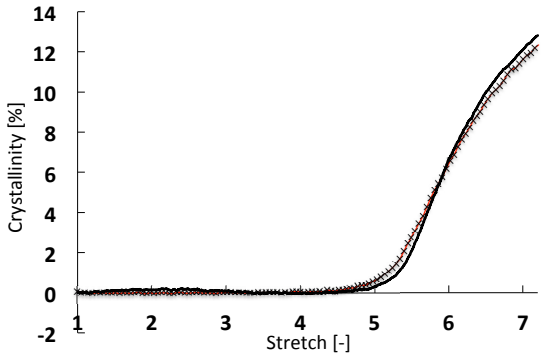
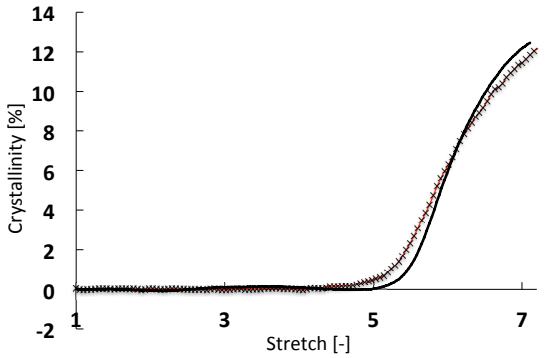


(a) 100 mm/min



(b) 200 mm/min

FIG. 7. Crystallinity in % during the loading #2 (-) surface calorimetry (x) XRD

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[Note1]The term 'heat source' is used in this paper to mean the heat power density in W/m^3, which is produced or absorbed by the material.

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[Note2]In this case, only a one-point temperature measurement is required, meaning that the crystallinity can be evaluated with a pyrometer

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[Note3]Here the heat source is expressed in $/s$, i.e. $\frac{S}{\rho C}$