Strain-induced crystallization in rubber: A new measurement technique

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The crystallinity of stretched crystallizable rubbers is classically investigated using X-ray diffraction. In this study, we propose a new method based on temperature measurement and quantitative calorimetry to determine rubber crystallinity during mechanical tests. For that purpose, heat power density are first determined from temperature variation measurements and the heat diffu-sion equation. The increase in temperature due to strain-induced crystallization is then deduced from the heat power density by subtracting the part due to elastic couplings. The heat capacity, the density, and the enthalpy of fusion are finally used to calculate the crystallinity from the temperature variations due to strain-induced crystallization. The characterization of the stress–strain relationship and the non-entropic contributions to rubber elasticity is not required. This alternative crystallinity measurement method is therefore a user-friendly measurement technique, which is well adapted in most of the mechanical tests carried out with conventional testing machines. It opens numerous perspectives in terms of high speed and full crystallinity field measurements.

KEYWORDS

calorimetry, crystallinity, infrared thermography, natural rubber, strain-induced crystallization

1 | INTRODUCTION

The strain-induced crystallization (SIC) of rubber is classically investigated using X-ray diffraction (XRD). Since the pioneering work by Katz in 1925,[1] which provided the first XRD pattern of a stretched natural rubber (NR), numerous studies on SIC were carried out, dealing with the crystalline phase structure,[2–5] chain orientation,[6] and kinetics of crystallization,[7, 8] nonexhaustively.

On a practical point of view, specific equipments and tests conditions are required to measure crystallinity from the XRD technique. On a metrological point of view, quantifying small crystallinity changes is difficult, especially when crystallinity is inferior to about 2%.[8] Moreover, in case of heterogeneous fields, for instance in crack tip vicinity, each point of the crystallinity field are obtained successively, by scanning the zone under study.[9–11] Finally, the crystallinity is determined from relatively large measurement zones. As an example, the beam size in[10] was 300×200 μm, which is large compared to the stretch (crystallinity) gradient at the crack tip. In this context, developing an alternative measurement method providing

- the crystallinity field instantaneously,
- at higher resolutions (temporal, spatial and on the value of the crystallinity), and

- with a conventional testing machine

is an important issue to go further on the characterization of crystallization/melting process in crystallizing rubbers.

Change in the XRD is not the only effect of SIC. SIC is also well known to be strongly exothermal, and temperature or calorimetry measurements should be therefore a relevant alternative to determine the crystallinity. In the 1970s, Göritz and co-workers showed that crystallinity can be quantified accurately during stretching through calorimetric measurements and carried out numerous studies on the calorimetric response of stretched natural rubber (see for instance Göritz and Müller[12]).[1] This remarkable work on unfilled natural rubber provided the crystallinity in relation with the stretch during a mechanical loading and during stress relaxation tests carried out at different stretch levels. The authors showed that crystallinity deduced from quantitative calorimetry is measured with a higher accuracy than using XRD, especially at low stretches where XRD does no longer enable us to detect any change in crystallinity. Despite this, calorimetry under stretching was no longer used to measure crystallinity.

Recently, Spratte et al. have taken up the idea that crystallinity can be measured from the thermal activity at the surface of rubber specimens.[14] Authors used an infrared camera recording thermal field at the surface of crystallizing rubber, filled and unfilled, tested during cyclic mechanical loadings. The approach proposed by the authors is not a calorimetric one: Crystallinity was deduced from the temperature increase due to crystallization T_{cryst}. To do so, the authors invoked the kinetic theory due to Meyer and Ferri,[15] which considers that the whole work done on the system by the external force[2] is transferred into microscopic kinetic energy and is measurable as temperature. In other words, energetic effects are negligible. Therefore, only two contributions to temperature changes were distinguished by the authors: crystallinity change and entropy change. Authors measured the temperature variation and calculated the heat corresponding to the work done on the system. T_{cryst} was determined from the previous quantities by removing the effect of heat lost by convection at the specimen surface. The crystallinity χ was deduced from T_{cryst} by considering that the crystallization energy of natural rubber can be approximated by the enthalpy of fusion ΔH_{cryst}:

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

The authors assumed that the sample density ρ and heat capacity C_p were independent of strain and temperature. For filled materials, this ratio was weighted by a factor $\frac{1}{1-\Phi_{filler}}$, where Φ is the filler volume fraction. Results obtained enabled the authors to qualitatively compare the effects of the nature and surface treatment of fillers on the relationship between crystallinity and stretch. Nevertheless, a systematic deviation from the thermomechanical model was obtained in all the crystallinity measurements and led to a negative crystallinity at low stretches for which the material is not crystallizing. This was attributed by the authors themselves to the effect of nonentropic contributions (mainly rotation of carbon bonds, network bonds effects, and interactions between chains). The negative crystallinity they observed shifted therefore the onset of crystallization towards higher stretches and decreased the crystallinity.

Indeed, nonentropic contributions can be significant in rubber elasticity. Deviations to the classical kinetic theory of the rubber elasticity have already been experimentally evidenced by thermoelasticity studies by Allen et al.,[16–18] Shen,[19] and Le Cam.[20] As discussed in Treloar,[21] the nonentropic (energetic) contribution to rubber elasticity is due to not only changes in intermolecular internal energy but also to changes in the network chain conformational energies, that is, in intramolecular internal energy. This is confirmed by the fact that the energetic contribution to rubber elasticity does not change when diluents are incorporated.[22]

In this study, we propose to determine crystallinity from heat power density instead of temperature, by using infrared thermography during the mechanical tests. In practice, any temperature measurement technique can be used, typically a pyrometer. This method takes intrinsically into account both the nonentropic (energetic) and the entropic contributions to rubber elasticity. The measurement of the stress is therefore not required. Moreover, this technique provides a full thermal field, meaning that crystallinity heterogeneity can be characterized, at several thousands frames per second, each value of the field being obtained at the same time. Section 2 presents the methodology used to determine the crystallinity during rubber deformation. Section 3 presents the application of the methodology to experimental data available in the literature for unfilled NR. Concluding remarks close the paper.

2 | METHODOLOGY FOR CRYSTALLINITY MEASUREMENT

This section aims at presenting the thermomechanical framework of quantitative calorimetry, which enables us to define the heat power density from temperature measurements. Then, the methodology giving crystallinity from the heat power density evolution is detailed.

2.1 | Calorimetry under stretching: Thermodynamical framework

Most of mechanical tests are conducted under nonadiabatic 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, and the heat diffusion equation is used to determine the corresponding heat power density from temperature measurement. This quantity is intrinsic to the material deformation. In such conditions, any temperature measurement technique can be used as a calorimeter, an infrared camera in this study. To do so, any thermodynamical system out of equilibrium is considered as the sum of several homogeneous subsystems at equilibrium. The deformation is considered as a quasistatic 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 specific heat capacity, denoted C in the following, is the energy required to produce a unit temperature increase of a unit reference volume of a body while maintaining the deformation and internal variables fixed. It is defined by

$$C = -T\left(\frac{\partial^2 \Psi}{\partial T \partial T}\right)_{\mathbf{F},\xi_\alpha} > 0 \tag{2}$$

where Ψ is the free energy function. In unfilled natural rubber, volume changes are small[23, 24] and the specific heat does not vary significantly, even when crystallization occurs[25–27]; therefore, the product ρC can be assumed to be constant. The local form of the heat diffusion equation writes as follows:

$$\rho C\dot{T} - \mathrm{Div}(\boldsymbol{\kappa_0}\ \mathrm{Grad}\ T) = \underbrace{\mathcal{D}_{int} + T\frac{\partial \mathbf{P}}{\partial T} : \dot{\mathbf{F}} + T\sum_{\beta=1}^{m}\frac{\partial \boldsymbol{A}_\beta}{\partial T} : \dot{\boldsymbol{\xi}}_\beta}_{s} + R \tag{3}$$

where $\boldsymbol{\kappa_0}$ is a positive semidefinite tensor characterizing the thermal conductivity of the material and s denotes the overall heat power density induced by the deformation process. The term $\mathcal{D}_{int}$ corresponds to the intrinsic dissipation. The term $T\frac{\partial \mathbf{P}}{\partial T} : \dot{\mathbf{F}}$ is the heat power density 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. After some calculations, which are not detailed here, the heat diffusion equation can be rewritten in case of homogeneous heat power density field[28]:

$$\rho C\left(\dot{\theta} + \frac{\theta}{\tau}\right) = s \tag{4}$$

where τ is a parameter characterizing the heat exchanges between the specimen and its surroundings. 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, stretch level, etc.). For instance, in case where the material is beforehand heated, the exponential formulation of the temperature variation is used to determine parameter τ: $\theta = \theta_0 e^{\frac{-(t-t_0)}{\tau}}$. Further details are provided in Samaca Martinez et al.[29]

2.2 | Determination of the crystallinity

Figure1 illustrates the methodology proposed. It is composed of four steps. Input data are the temperature variation θ, parameter τ, and the thermophysical parameters ρ, C, and ΔH.

- The first step consists in calculating the heat power density by using Equation 4. The diagram illustrates the typical calorific response of unfilled NR, which exhibits a strong increase in the heat power density when crystallization starts.[12, 29] Here, λ_c and λ_m stand for the stretches at which SIC starts and melting is complete, respectively. It should be noted that all the work done by the system may not systematically increase the specimen temperature.[16–22] Therefore,

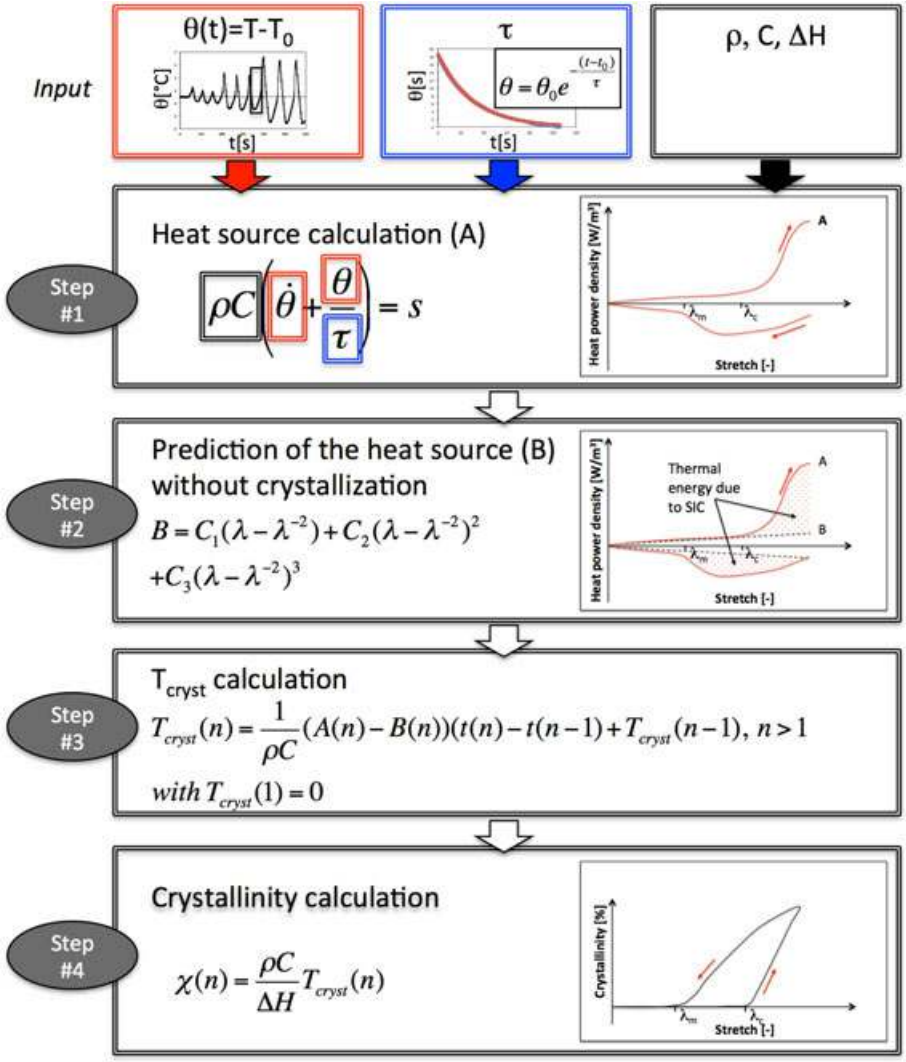


FIGURE 1 Methodology summary

the strain power density and the heat power density are not systematically superimposed, whatever the material is crystallizing or not;[3]

- Step 2 deals with the prediction of the heat power density due to elastic couplings only. The thermal energy due to SIC is indeed the area located between the heat power density (curve A) and the part of the heat power density due to elastic couplings (curve B). The latter is not known once crystallization starts but is known before. In this study, we assume that the elastic couplings evolve in a similar way after crystallization starts. The corresponding heat power density is predicted by using a polynomial form such as $C_1(\lambda-\lambda^{-2})+C_2(\lambda-\lambda^{-2})^2+C_3(\lambda-\lambda^{-2})^3$, which parameters are identified from the experimental heat power density before SIC starts. It should be noted that the heat power density can be different from zero at the lowest stretches (typically inferior to 1.1), due to energetic effects, but this does not affect the prediction of the heat power density due to elastic couplings at higher stretches;
- The heat power density due to SIC (A–B) is then computed in Step 3 for determining the temperature variation due to SIC T_{cryst}. In practice, T_{cryst} is calculated as the primitive of the heat power density due to SIC. The integration constant is determined considering that T_{cryst} is equal to zero before crystallization starts (see the numerical scheme provided in Figure 1, Step #3). It should be noted that the numerical scheme presented is not centered, but another numerical scheme can be used;
- The fourth step consists in calculating the crystallinity by applying Equation 1.

This method is very simple and does not require measuring the nominal stress variations nor characterizing possible nonentropic effects.

3 | APPLICATION TO AN UNFILLED NATURAL RUBBER

The methodology proposed for measuring crystallinity is now applied to experimental data issued from the literature. Here, data given in other literature[29, 30] are used. They were obtained with an unfilled natural rubber submitted to cyclic uniaxial tensile loading. The mechanical loading applied corresponded to four sets of three cycles at a maximum stretch of 2, 5, 6, and 7.5 at ±100 mm/min. The stretch is defined as the ratio of the current length over the initial length. ρ and C are equal to 936 kg/dm^3 and 1768 J/(kg.K). τ depends on the stretch and is defined as $\tau(\lambda) = 40.48 - 3.25\lambda$.

3.1 | Mechanical and calorimetric responses

Figure 2 presents the mechanical response obtained in terms of the nominal stress in relation to the stretch. As expected, no stress softening is observed, and all the curves are superimposed for cycles at the same maximum stretch.

A significant hysteresis loop is observed for cycles at $\lambda > 5$, that is, at stretch superior to the stretch at which crystallization starts (about 4). These results are in good agreement with those reported in the literature for unfilled natural rubber. The size of the hysteresis loop increases when the maximum stretch is increased. This is consistent with an increase in the crystallinity with the maximum applied stretch. As assumed by Flory[31] and widely highlighted experimentally, once crystallization occurs, relaxation is induced in the amorphous phase, and a plateau is observed in the stress–strain curve.[7, 8]

Figure 3 depicts the heat power density in relation to the stretch. During loading, the heat power density is positive and increases with the stretch. During unloading, the heat power density is negative. This highlights preponderant entropic

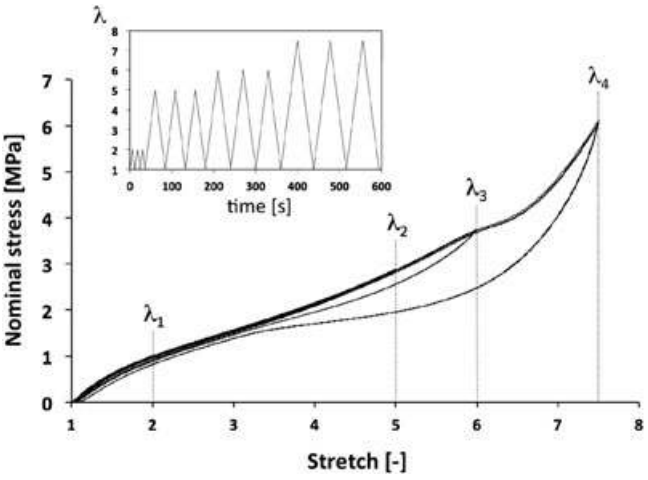


FIGURE 2 Mechanical response obtained during cyclic loading of unfilled NR in terms of the stress-stretch relationship

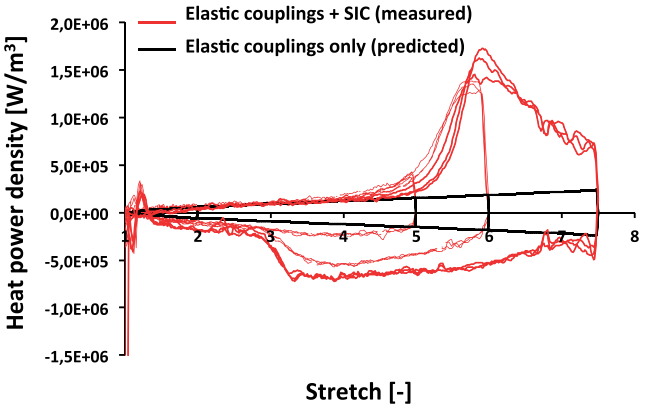


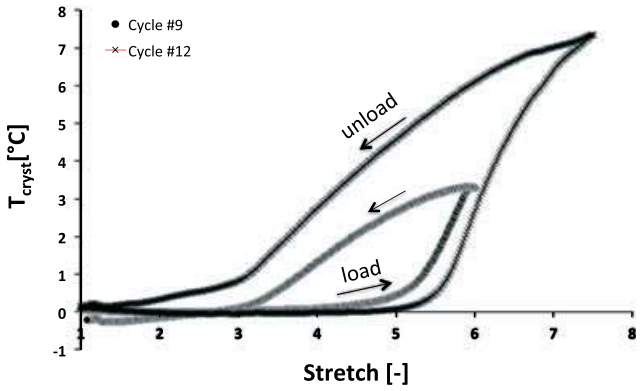
FIGURE 3 Measured heat power density (in red) and predicted heat power density due to elastic couplings (in black) in relation to the stretch (see Steps #1 and #2)

effects in the thermal response. Before SIC starts, the load–unload curves are symmetrical, meaning that the heat produced during the loading phase is equal to the heat absorbed during the unloading phase. Once SIC starts, the heat power density evolution for loading and unloading are no longer symmetrical. During loading, the heat power density evolves in a quasilinear manner until a stretch close to 4 is reached. A dissymmetry is observed for stretches higher than 4; the stretch level at which SIC starts. During unloading, the heat power density rate first increases in absolute value until reaching a stretch equal to 4, is constant until a stretch equal to 3.5 is reached, and then decreases. Hence, crystallization continues during unloading. It should be noted that no intrinsic dissipation was detected in Samaca Martinez et al.[29] The hysteresis loop is therefore due to SIC without any viscous effects (in the range of the low stretch rates applied).

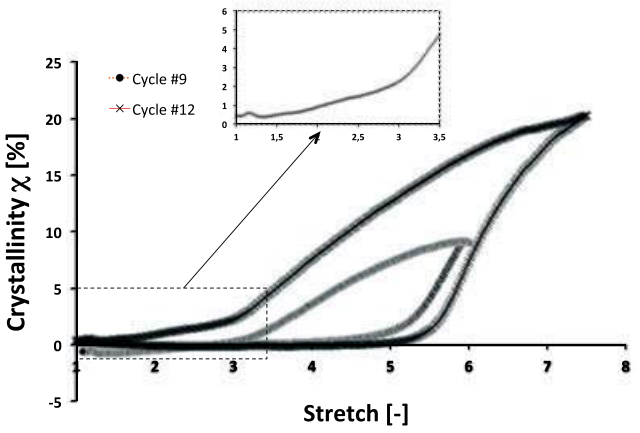
3.2 | Determining crystallinity

As explained in Section 2.2, the thermal energy due to SIC is the area located between the heat power density measured (curve A in Figure 1) and the predicted part of the heat power density curve due to elastic couplings (curve B). Figure 3 gives the heat power density measured (Step #1) and the predicted heat power density due to elastic couplings (Step #2). The difference between the two curves, that is, the heat power density due to SIC, is processed to determine the corresponding temperature variation T_{cryst} (see Figure 4(a)). In practice, a primitive calculation of the heat power due to SIC is carried out. The integration constant is determined considering that T_{cryst} before crystallization starts is equal to zero. Only cycles at a maximum stretch applied equal to 6 and 7.5 for which a significant hysteresis loop is observed are considered. The results being the same for cycles conducted at the same maximum stretch, only cycles #9 and #12 are presented.

The crystallinity is obtained by dividing T_{cryst} by the enthalpy of crystallite fusion ΔH_{cryst} and multiplying by ρC. The crystallization energy of natural rubber is approximated by the enthalpy of fusion, which is assumed to be independent of temperature and stretch.[31] Here, as a first approach, we use the value determined by,[32] that is, 15,3 cal. per gram of poly-



(a)



(b)

FIGURE 4 Temperature change due to (a) crystallization and melting (see Step #3) and (b) crystallinity (see Step #4) in relation to the stretch

mer, which corresponds to 59,9 J.cm^{-3}. The crystallinity versus stretch is given in Figure 4(b). For cycle #9 at $\lambda = 6$, SIC starts approximately at $\lambda = 4.5$, slightly increases before increasing linearly with the stretch. The maximum crystallinity reached is about 9%, which is consistent with XRD measurements performed at lower stretch rates.[8] During unloading, crystallinity is higher than during loading at any stretch, meaning that crystallization continues during unloading. Crystallite melting seems to be complete at $\lambda = 3$. Before $\lambda = 3$ is reached, the slope curve decreases. For cycle #12 at $\lambda = 7.5$, SIC starts at a higher stretch ($\lambda = 5$). This slight shift in the stretch at which SIC starts is explained by a slight accommodation effect due to previous mechanical cycles. Taking into account the residual strain in the calculation of the initial length will decrease the level of the characteristic stretches λ_c and λ_m. Crystallinity increases linearly with the stretch until reaching about 9%, then its rate decreases. This is consistent with the decrease in the heat power density rate observed in Figure 3 from $\lambda = 6$ on. The maximum crystallinity reached is about 20%. During the unloading, the same evolution as for the lower stretch is observed except for the end of the unloading. Indeed, from $\lambda = 3$ on, the crystallinity does not return to zero. The magnification in the boxed zone shows that the curve slope decreases and the crystallinity decreases linearly with the stretch until reaching a value close to zero. This questions a possible melting kinetics and echoes previous work by Müller[33] and Samaca Martinez et al.[29] This is currently studied by the author, and no further discussion is provided in this paper.

4 | CONCLUSION

This study proposes a new measurement technique to determine the crystallinity in stretched crystallizing rubber using IR thermography. For this purpose, a methodology based on quantitative calorimetry is proposed. This methodology enables us to define the temperature variation due to SIC from the corresponding heat power density. The characterization of the stress–strain relationship and the nonentropic contributions to rubber elasticity is not required. It is therefore well adapted to characterize heterogeneous crystallinity field. Crystallinity obtained as a function of the stretch provides comparable results as those obtained by XRD measurements. The method proposed is therefore a realistic alternative to measure crystallinity of stretched crystallizing rubbers from any temperature measurement technique and quantitative calorimetry. It is a user-friendly measurement technique, accurate, and well adapted to most of the mechanical tests performed with conventional testing machine. Measuring temperature from infrared thermography should open numerous perspectives in terms of high speed and full crystallinity field measurements.

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ENDNOTES

[1] It should be noted that Boonstra was the first who suggested that crystallinity could be determined from the induced change in internal energy and the heat of fusion per repeating unit.[13] Using calorimetry is in the same line, because change in the internal energy can be taken into account with a "stretch calorimeter."

[2] $\sigma d\epsilon$ under uniaxial loading, with $\sigma$the Cauchy stress and ϵ the engineering strain.

[3] This might explain why negative crystallinity was found in Spratte et al.[14] when the material was not crystallizing;

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