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1                   **Elastocaloric effect: Impact of heat transfer on strain-induced**  
2                   **crystallization kinetics of natural rubber**

3  
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14   **Abstract:**

15   When natural rubber is rapidly loaded and unloaded there occurs a variation of its temperature  
16   called the elastocaloric effect. The objective of this work was to determine whether this  
17   temperature variation could be responsible for a delay in strain-induced crystallization (SIC)  
18   kinetics and stress relaxation. To this end, the SIC kinetics of cross-linked natural rubber  
19   samples with different thicknesses was studied at constant elongation after adiabatic stretching  
20   using thermal, mechanical and *in-situ* WAXS characterizations. The coupling of these  
21   techniques revealed that, at a fixed elongation  $\lambda$  (between 5 and 6), the crystallization kinetics  
22   and stress relaxation were faster in the thinner sample (with a short heat exchange time  
23   constant), thus providing evidence that heat transfer affected the SIC kinetics and should be  
24   considered when interpreting experimental results.

25  
26   Keywords: Natural rubber, Strain-induced crystallization, Crystallization kinetics, Latent heat,  
27   Infrared camera.

## 31 1. Introduction

32 The elastocaloric effect (eC) in elastomers can be used as an alternative cooling  
33 technology that has the potential to be cheap, efficient and environmentally friendly.[1–3] This  
34 effect is known as the change in temperature of a material when subjected to cyclic mechanical  
35 solicitation. It has been observed in different elastomers such as Natural Rubber (NR)[4–7] ,  
36 blends using recycled Natural Rubber[8], Polyurethanes [9,10], Silicone, Styrene-  
37 Butadiene[11] and poly(styrene-bethylene-co-butylene-b-styrene) (SEBS)[12]. In the following  
38 study, we focus on NR which has a large temperature variation up to  $\Delta T=12^{\circ}\text{C}$  and good fatigue  
39 resistance[3]. The origin of its eC effect is Strain-Induced Crystallization (SIC) and entropic  
40 elasticity.[7,8,11] Since the SIC is not an instantaneous phenomenon [13–15], its kinetics will  
41 necessarily have an impact on the choice of the operating frequency of the elastocaloric device,  
42 hence the need to study it. Among the first investigations carried out on the subject, one can  
43 cite that of Mitchell and Meier [16] who showed, using thermal measurements, that the  
44 crystallization of NR started less than 50 ms after the adiabatic deformation. More recently, this  
45 result was confirmed by Candau et al [17] and Albouy et al [18] based on *in-situ* WAXS  
46 measurements. The same technique was employed by several authors to demonstrate that at  
47 constant elongation, the crystallization kinetics could last several tens of seconds, [13–15,19–  
48 21] and this observation has been explained by mechanisms based on polymer chains diffusion,  
49 crystal nucleation and stress relaxation [13–15].

50 These results suggest that in order to maximize the phase transition at the origin of the  
51 elastocaloric effect, it would be preferable to perform long-period cycles (at least one hundred  
52 seconds). However, from an elastocaloric point of view, lowering the frequency would limit  
53 the power involved, which is why it would seem relevant to increase the frequency as much as  
54 possible. However, in this case, the material would partially crystallize and the heat that can be  
55 exchanged during the cycle between the system and the surroundings would be limited. In  
56 addition, the average temperature of the sample at high frequency can increase considerably  
57 due to self-heating (because of the viscoelasticity of the material) [17] and might reach  $50^{\circ}\text{C}$  at  
58 70Hz. According to the literature [7,10], with such an increase in temperature, the crystalline  
59 fraction developed at a given elongation would decrease considerably ( $\frac{d\chi_c}{dT} = -0.5\%/^{\circ}\text{C}$ ) [19]  
60 thus restraining the eC effect.

61 Crystallization kinetics is also temperature-dependent since it is controlled by the  
62 nucleation rate [15,23,24] which in turn is affected by the energy barrier that must be crossed

63 to create nuclei. In fact, when NR is stretched adiabatically at high elongations, crystallization  
64 is favored by the high elongations but the temperature rise induced by this phase transition (up  
65 to 12°C at  $\lambda=6$ ) [4,25] is likely to hinder the nucleation process as long as the generated heat  
66 has not been totally evacuated to the external environment. For a sample with an initial  
67 thickness equal to 1 mm that is stretched adiabatically at  $\lambda=6$ , the time required to reach thermal  
68 equilibrium with the air is of the order of a few tens of seconds [26,27]. This also corresponds  
69 to the duration of the fast relaxation induced by crystallization [28], and thus the following  
70 question arises: to what extent does heat transfer have an impact on the strain-induced  
71 crystallization kinetics?

72 In this work, the crystallization of an industrial crosslinked NR was characterized by *in-*  
73 *situ* Wide-angle X-ray Scattering (WAXS) and Infra-Red (IR) thermography at different  
74 elongations in order to study the correlation between the duration of the crystallization process  
75 and the time needed to exchange the generated heat with the surroundings. We prepared  
76 crosslinked NR samples with different thicknesses (between 0.13 mm and 1.15 mm) but  
77 identical intrinsic properties, so that only their form factor varied and thus also their heat  
78 exchange time constant  $\tau$  (a parameter characterizing the heat exchange between the sample  
79 and its surroundings [29]). In order to maximize the potential influence of the increase in  
80 temperature during the test on the crystallization, samples were stretched under adiabatic  
81 conditions. Finally, the impact of heat transfer on the crystallization kinetics was discussed.

## 82 **2. Experimental setup**

### 83 **2.1 Materials and specimen geometry**

84 Two types of unfilled crosslinked natural rubber samples were studied in this work. The  
85 first one, denoted NR<sub>1.53</sub>, was purchased from Xinyinte Rubber Products Co., Ltd., China and  
86 the second, named NR<sub>1.46</sub>, was prepared in the laboratory using the recipe detailed in Table 1.  
87 The densities of the elastically active chains (EAC) of these materials were estimated from the  
88 swelling ratio in toluene and from the Flory-Rehner equation [30] and were found to be  
89  $1.53 \times 10^{-4} \text{ mol. cm}^{-3}$  and  $1.46 \times 10^{-4} \text{ mol. cm}^{-3}$ , respectively. This EAC density was  
90 high enough to avoid undesirable phenomena (inverse yield, stable crystals at room temperature  
91 after retraction[31–33], ...) and close to the optimal EAC density that would allow a maximum  
92 crystallization rate [34].

93

94 Table 1: Chemical composition of the studied material in phr (parts per hundred, i.e., g per 100g  
95 of rubber)

Components	NR <sub>1.46</sub>
NR	100
6PPD*	3
SA**	2
ZnO	1.5
CBS***	1.9
Sulfur	1.2

96 \*N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine), \*\*Stearic acid, \*\*\* N-cyclohexyl-2-  
97 benzothiazole sulfenamide.

98 Regarding the geometry of the samples, the original length was 40 mm with an initial distance  
99 between the jaws of 20 mm, and a width of 20 mm. The thickness of NR<sub>1.53</sub> was 0.63 mm, and  
100 those of NR<sub>1.46</sub> were 0.19 mm and 1.15 mm.

## 101 2.2 Mechanical measurements

102 The tensile testing machine was similar to the one used by Yoshida et al. [35]. It is a  
103 single axis robot RSDG212 (MISUMI Corporation, Japan) with an analog force sensor  
104 XFTC300-200N (Measurement Specialties, France). The displacement was measured via a  
105 Laser optical displacement sensor ILD1420-200 (micro-epsilon, France). The signals recovered  
106 from both sensors were simultaneously recorded via an oscilloscope.

107 In order to avoid residual elongation due to Mullin's effect [36] and to ensure  
108 reproducibility of thermomechanical properties, the material was subjected to cyclic strain  
109 (between  $\lambda = 1$  and  $\lambda = 6.8$ ) ten times. The initial length was then adjusted in order for the  
110 sample to be taut. The samples were tested at least 5 minutes after this procedure, and the same  
111 waiting time was applied between each test at room temperature (i.e. T=22°C). It was indeed  
112 checked that 5 min was enough for the materials to show the same mechanical response as a  
113 material having rested during 30 min (cf. supporting information Fig.S1; note that 5 minutes  
114 would be likely insufficient in the case of a filled elastomer). The distance between the jaws  
115 was taken as the initial length  $l_0$  and the elongation was defined as  $\lambda = \frac{l(t)}{l_0}$ .

116

117

### 2.3 Thermal measurements

118 While stretching the material, an infrared camera, Optris PI450 (Optris, Germany) with  
119 a 29° optic simultaneously recorded the temperature variation of its surface. The frequency  
120 chosen to acquire the signal was  $f=80$  Hz and the surface of measurement was about 15  
121  $\text{mm}^2$ . This surface was chosen to be in the center of the material in the stretched state to  
122 minimize the effect of the edges (both mechanically and thermally). A second area was used to  
123 measure the temperature in the center of the material at  $\lambda=1$ . (see Supporting Information  
124 Fig.S.2)

125 During the test, there were three possibilities for the sample to evacuate thermal energy:  
126 thermal radiation, heat conduction with a clamping system, and convection. The former was  
127 neglected since the temperature variation between the sample and the environment remained  
128 small (up to 13K at most). The second was also neglected since the thermal conductivity of NR  
129 is small ( $\sim 0.146 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) [37], and also because the jaws were covered with strips of natural  
130 rubber acting as thermal insulators. An emissivity of 0.95 was used during our experiments  
131 [38], in accordance with a comparison between direct measurements using a thermocouple and  
132 the information retrieved by the IR measurements. Convection was considered to be the most  
133 important mechanism of heat exchange.

134

### 2.4 *In-situ* WAXS measurements

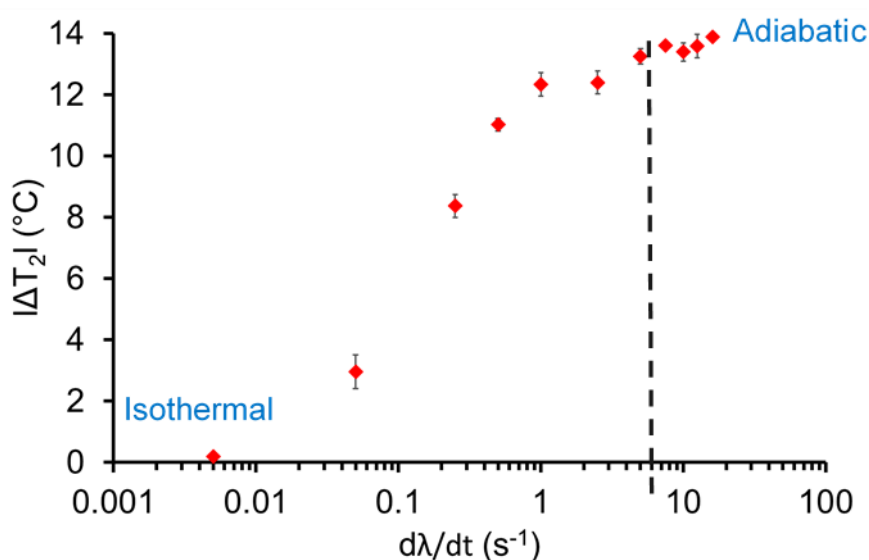
135 The *in-situ* WAXS measurements were carried out on the D2AM beam-line of the  
136 European Synchrotron Radiation Facility (ESRF). The X-ray wavelength was 1.54 Å. The  
137 irradiation area was about  $150*150 \mu\text{m}^2$ . The acquisition times were fixed at 500 ms for the  
138 part of the study dedicated to the characterization of the crystallization right after deformation,  
139 and this time was then extended to 5 s to study the evolution of the crystallinity index during  
140 200 s after adiabatic stretching. Each pattern was integrated as a function of the scattering angle  
141 ( $2\theta$ ), cleaned of air scattering, and then normalized by sample thickness and transmission.

142 In this study, the evolution of the crystallinity was followed via the intensity of the (200)  
143 plane's reflection after the deconvolution of the curve  $I=f(2\theta)$  (denoted  $I_{200}$  and proportional to  
144 the crystallinity index as shown in Supporting Information, Fig.S3). This intensity will be called  
145 crystallinity index since it does not correspond to the real value of crystallinity.

146

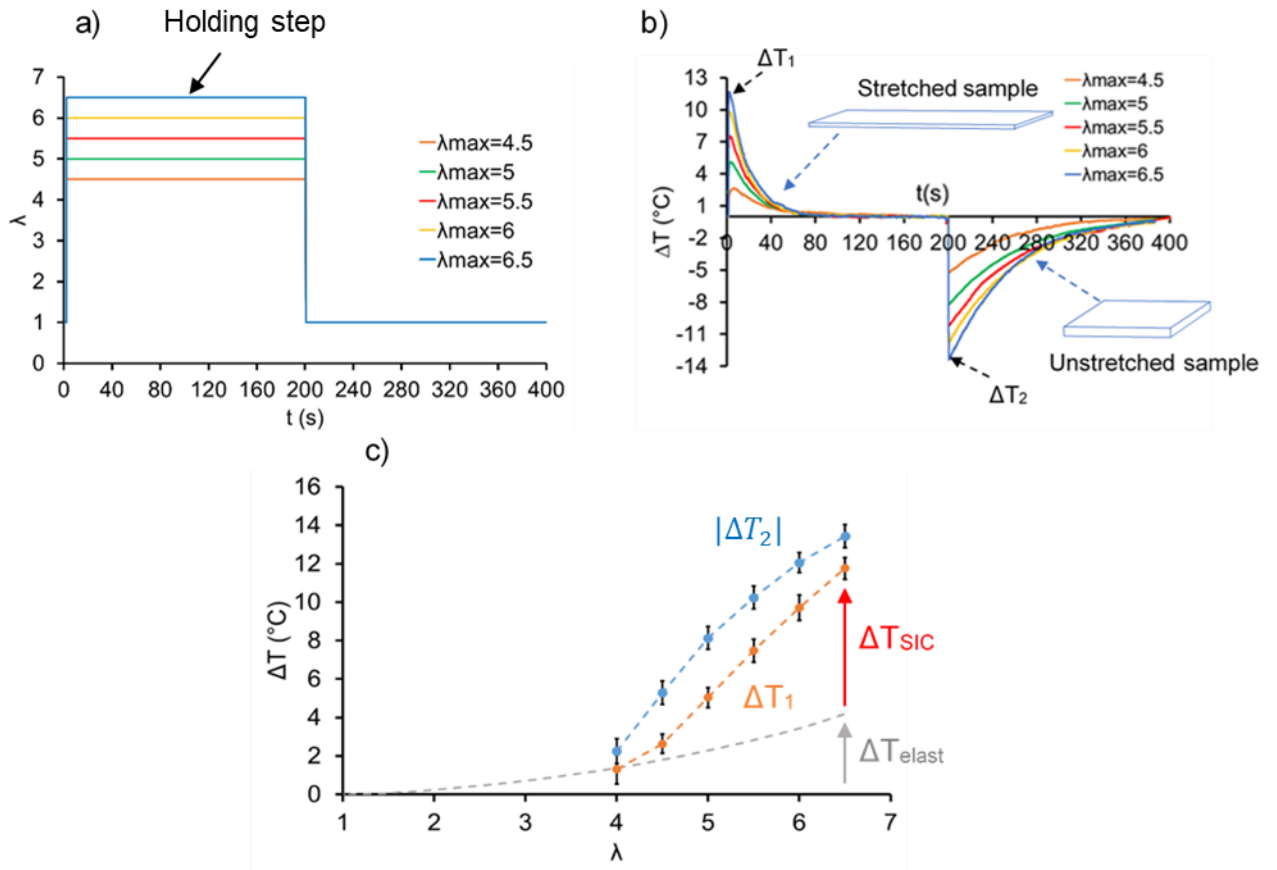
147 **3. Results and discussion**

148 The impact of heat transfer on strain induced crystallization kinetics is expected to be  
 149 maximal when sample is stretched adiabatically. Therefore, to determine the adiabatic and  
 150 isothermal deformation domains, NR<sub>1.53</sub> sample was deformed at different strain rates ranging  
 151 from 0.005 s<sup>-1</sup> to 16 s<sup>-1</sup> between  $\lambda=1$  and  $\lambda=7$ . The maximum temperature variation measured  
 152 after discharge  $|\Delta T_2|$  are plotted in Fig. 1 as a function of the strain rate ( $d\lambda/dt$ ). The results  
 153 suggest that at high rates of deformation ( $d\lambda/dt > 8$  s<sup>-1</sup>) the temperature change is almost  
 154 constant ( $\approx 13^\circ\text{C}$ ) (adiabatic domain). Once this strain rate is lowered, the sample exchanges  
 155 heat with the external environment, therefore the values of  $|\Delta T_2|$  gradually decrease until  
 156 reaching 0°C at  $d\lambda/dt = 0.005$  s<sup>-1</sup> indicating entry into the isothermal domain.



157  
 158 Fig. 1: Temperature variation measured after retraction ( $\Delta T_2$ ) at different strain rates between  
 159 0.005 s<sup>-1</sup> and 16 s<sup>-1</sup> for NR<sub>1.53</sub>

160  
 161 The NR<sub>1.53</sub> sample was stretched under adiabatic conditions at a strain rate of 16 s<sup>-1</sup>,  
 162 from  $\lambda = 1$  to  $\lambda_{\max} = \{4.5; 5; 5.5; 6; 6.5\}$  and then maintained at constant elongation for 200 s  
 163 before returning to  $\lambda = 1$  as shown in Fig. 2-a. The step of the mechanical program which occurs  
 164 at constant elongation will be called holding step. The corresponding temperature change  
 165 profiles are given in Fig. 2-b and the stress-elongation curves are plotted in Supporting  
 166 Information, Fig.S4.



168  
 169 Fig. 2: a) Mechanical loading conditions: the NR<sub>1.53</sub> sample with a thickness of 0.63 mm was  
 170 stretched to different maximal elongations  $\lambda_{\max}$  between 4.5 and 6.5 at  $\dot{\lambda} = 16 \text{ s}^{-1}$ ; b)  
 171 Corresponding temperature changes profiles ( $\Delta T = T_{\text{measured}} - T_{\text{room}}$ ); c) Adiabatic temperature  
 172 variations after loading ( $\Delta T_1$ ) and unloading ( $|\Delta T_2|$ ) (blue and orange dots, respectively) as well  
 173 as the entropic contribution  $\Delta T_{\text{entropic}}$  (grey dashed line)

174 Firstly, while stretching the sample, a positive temperature variation  $\Delta T_1$  was measured.  
 175 It resulted from the entropic elasticity and the strain-induced crystallization (SIC) [6,16]. A  
 176 negative temperature variation  $\Delta T_2$  was observed when the sample was unloaded after heat  
 177 exchange and its absolute value increased with the elongation. This cooling effect was due to  
 178 the melting of crystallites and to entropic elasticity recovery [6].

179 The second observation was related to the kinetics of heat exchange. For each  
 180 elongation, the area under the peak  $\Delta T_2$  presented in Fig. 2.b was much wider than the one under  
 181 the peak  $\Delta T_1$ . Indeed, when the sample was stretched, its thickness decreased and its exchange  
 182 surface became larger [26] wherefore the convective heat flow  $\phi$  increased as well. The small  
 183 thickness of the sample also helped reduce the thermal gradient within the thickness of the  
 184 rubber films. The Biot number remained below 0.1 in all the experiments ( $Bi = hL/k$ , where  $h$  is  
 185 surface heat exchange coefficient  $\sim 12 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ ,  $L$  is the thickness of the samples which is



186 inferior to 1.15 mm for each experiments, and k is the thermal conductivity of natural rubber  
 187  $\sim 0.15 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ ). Therefore, the temperature of the NR film may be considered as uniform, and  
 188 the heat flow  $\phi$  across the external rubber surfaces may be linked directly to convection via the  
 189 difference in temperature with the ambient temperature  $\Delta T$ :

$$190 \quad \phi(t) = h \times S(\lambda) \times \Delta T(t) = \frac{\rho \times C_m \times V}{\tau(\lambda)} \times \Delta T(t) \quad (1)$$

191 Here,  $S(\lambda)$  is the external surface of the sample,  $\rho$  the density,  $C_m$  the heat capacity,  $V$   
 192 the volume and  $\tau(\lambda) = \frac{\tau(\lambda=1)}{\sqrt{\lambda}}$  the heat exchange time constant at a certain elongation  $\lambda$  [29].  
 193 In turn,  $\tau(\lambda=1)$  is the time needed for the sample to absorb 63% of the heat from the  
 194 surroundings to reach the ambient temperature at  $\lambda=1$ . This value was directly determined from  
 195 the second part of the temperature profile by analogy with the time constant of a first-order  
 196 system, and was found to be  $(52 \pm 5)$  s for NR<sub>1.53</sub> and  $(92 \pm 6)$  s for NR<sub>1.46</sub>.

197 Fig. 2.c includes the total temperature changes measured after stretching  $\Delta T_1$  and  
 198 retraction  $|\Delta T_2|$  as well as the contribution of entropic elasticity  $\Delta T_{elast}$  which is assumed to be  
 199 proportional to the volumetric work given to the sample during adiabatic loading ( $W_{loading}$ ), as  
 200 mentioned by Mitchell et al [16]:

$$201 \quad \Delta T_{elast} = \frac{W_{loading}}{\rho \times C_m} \quad (2)$$

202 These three temperature variations increase from  $\Delta T_1 = 1.3^\circ\text{C}$ ,  $|\Delta T_2| = 2.2^\circ\text{C}$  and  $\Delta T_{elast} = 1.3^\circ\text{C}$   
 203 at  $\lambda=4$  to  $\Delta T_1 = 11.7^\circ\text{C}$ ,  $|\Delta T_2| = 13.3^\circ\text{C}$  and  $\Delta T_{elast} = 3.8^\circ\text{C}$  at  $\lambda=6.5$ . This difference between  
 204 the temperature variation values after loading and unloading reflects the fact that during  
 205 retraction, the number of crystallites that melt is greater than that created just after stretching.  
 206 This result comes from the existence of kinetics of crystallization which is responsible for the  
 207 increase of the crystallinity index  $\chi(t)$  during the holding step. The previous thermal  
 208 measurements made it possible to describe the crystallinity index as a function of time using an  
 209 equation similar to the one proposed by Plagge. [39] The main difference is that we fix the term  
 210 which multiplies  $(T(t) - T_{room}(t)) * \sqrt{\lambda(t)}$  (equ3) and do not consider it as an adjustable  
 211 parameter. In the work of Plagge et al. the adjustment is done in order to assure that crystallinity  
 212 is null at  $\lambda=1$ .

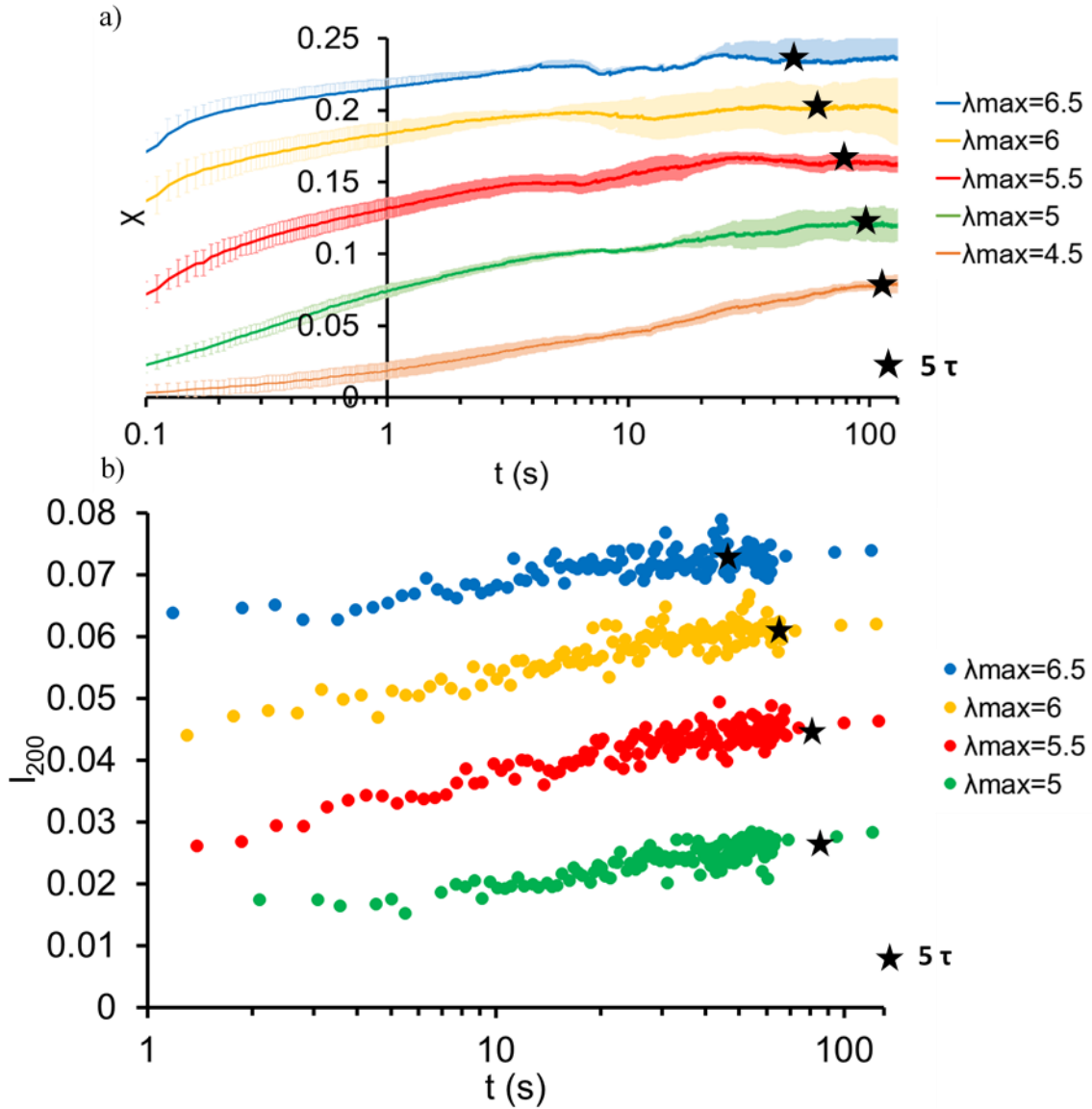
$$213 \quad \chi(t) = \int_{t_0}^t \frac{C_m}{\tau(\lambda) * \Delta h_f} (T(t) - T_{room}(t)) dt + \frac{C_m}{\Delta h_f} (T(t) - T_{\lambda_f}) + \frac{C_m}{\Delta h_f} \left( \Delta T_{\lambda_f} - \frac{W_{loading}}{\rho \times C_m} \right) \quad (3)$$

214 Here,  $t_0$  is the moment when the maximal elongation  $\lambda_{max}$  is reached,  $\rho=910 \text{ kg/m}^3$  the density

215 [40],  $C_m = 1900 \text{ J/(kg.K)}$  the heat capacity [16],  $\tau(\lambda)$  the heat exchange time constant,  $T$  the  
216 measured temperature,  $T_{\text{room}}$  the room temperature,  $T_{\lambda_f}$  the temperature reached just after  
217 elongation and  $\Delta h_f = 64 \text{ J/g}$  the melting enthalpy [4].

218 All the results obtained via equation (3) during the holding steps at different elongations  
219 are presented in Fig. 3.a. Firstly, for each test, the index of crystallinity increases with  
220 elongation and tends to stabilize to a maximum ( $\chi_{max}$ ) when the temperature no longer changes  
221 after a specific time that depends on the maximal elongation  $\lambda_{max}$ . The lowest  $\chi_{max}$  (8% for  $\lambda_{max}$   
222 =4.5) is reached after 100 s and the highest one (24% at  $\lambda_{max} = 6.5$ ) after 70 s. These durations  
223 coincide with the time needed to evacuate all the heat generated after loading ( $5\tau$ : indicated in  
224 Fig. 3.a by black stars).

225 To verify that this slowdown of kinetics is not dependent on the employed method used,  
226 the evolution of the crystallization was characterized by WAXS using a synchrotron source.  
227 The intensity  $I_{200}$  diffracted by the (200) plane was followed during the holding step at different  
228 maximal elongations between 5 and 6.5. It was not possible to do the same for  $\lambda_{max}=4.5$  because  
229 the low level of crystallinity reached, made detection too difficult with this technique. The time  
230 at which the acquisition started was however increased at 1 s after the deformation (instead of  
231 0.1 s for the thermal acquisition), because of the minimum acquisition time of the X-ray patterns  
232 (around 500 ms).



233

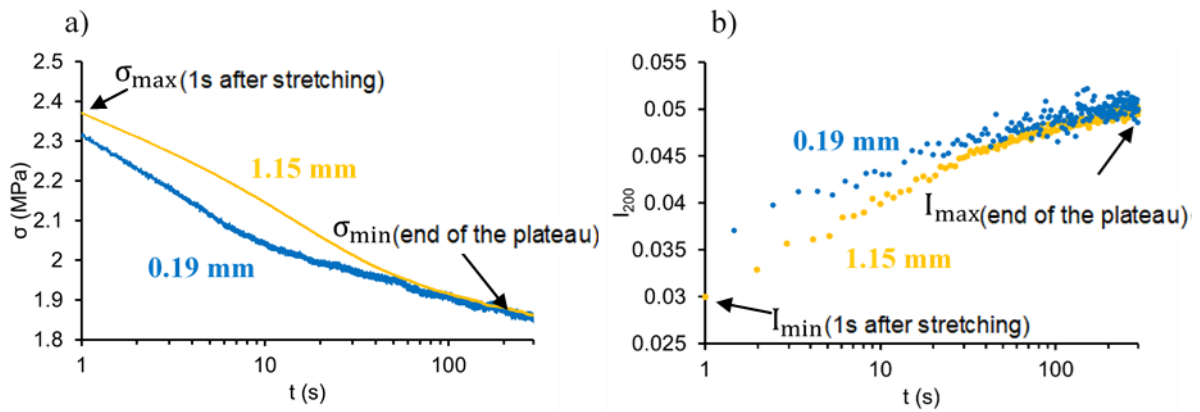
234 *Fig. 3: Evolution of (a) the crystallinity index determined using eq (3) and (b) the intensity of*  
 235 *(200) planes diffraction measured via WAXS in NR<sub>1.53</sub> during the holding steps at different*

236 *elongations as a function of time after fast stretching at  $\dot{\lambda} = 13 \text{ s}^{-1}$  ( $5\tau$  corresponds to  $\frac{5 * \tau (\lambda=1)}{\sqrt{\lambda}}$ )*

237

238 As can be seen in Fig. 3.b, the intensity  $I_{200}$  evolves significantly during tens of seconds  
 239 (black stars added on each curve of the same figure) and then slower after. This duration also  
 240 corresponds to the time needed to evacuate the heat generated after adiabatic stretching (as  
 241 presented on Fig 2.b). These results therefore suggest the existence of a link between the  
 242 crystallization kinetics and the heat exchange which will be studied in more detail in the next  
 243 experiment.

244 NR<sub>1.46</sub> samples with two thicknesses (0.19 mm and 1.15 mm) were prepared in order to vary  
 245 the characteristic heat exchange time constant  $\tau(\lambda)$ . It decreases from  $(92\pm 6)$  s to  $(20\pm 3)$  s  
 246 when the thickness is reduced from 1.15 mm to 0.19 mm (Figure S.5). Subsequently, two main  
 247 physical quantities were used to study the evolution of crystallinity during the holding step:  
 248 stress and  $I_{200}$  intensity. Fig.4 shows these quantities for NR<sub>1.46</sub>, at constant elongation  $\lambda=6$ . It  
 249 clearly evidences that stress relaxation occurs faster for the thin sample for times lower than  
 250 70s and with the same kinetics for times longer. Regarding the  $I_{200}$  intensity, it increases faster  
 251 for the thin sample during the first 70s.



252  
 253 Fig. 4: a) Stress ( $\sigma$ ) and b) Intensity  $I_{200}$  of X-ray Diffraction during the holding step at  $\lambda=6$  as  
 254 a function of the time for two sample thicknesses: 0.19 mm and 1.15 mm of NR<sub>1.46</sub> after fast  
 255 stretching at  $\dot{\lambda} = 13 \text{ s}^{-1}$

256 It is difficult to compare stress and  $I_{200}$  intensity directly since the stress decreased whereas the  
 257 intensity increased. Consequently, their variations were compared using two indices.

258 The first index was calculated via equation (4) and is presented in Fig. 5. It is based on the stress  
 259 relaxation, and related to the SIC as shown by Flory [41]:

260

$$261 \quad \frac{\Delta\sigma(t)}{\Delta\sigma_{max}} = \frac{\sigma(t) - \sigma_{min}}{\sigma_{max(1s \text{ after stretching})} - \sigma_{min}} \quad (4)$$

262 where  $\sigma_{max}$  is the maximum stress 1s after loading and  $\sigma_{min}$  is the stress reached at the end of the  
 263 holding step.

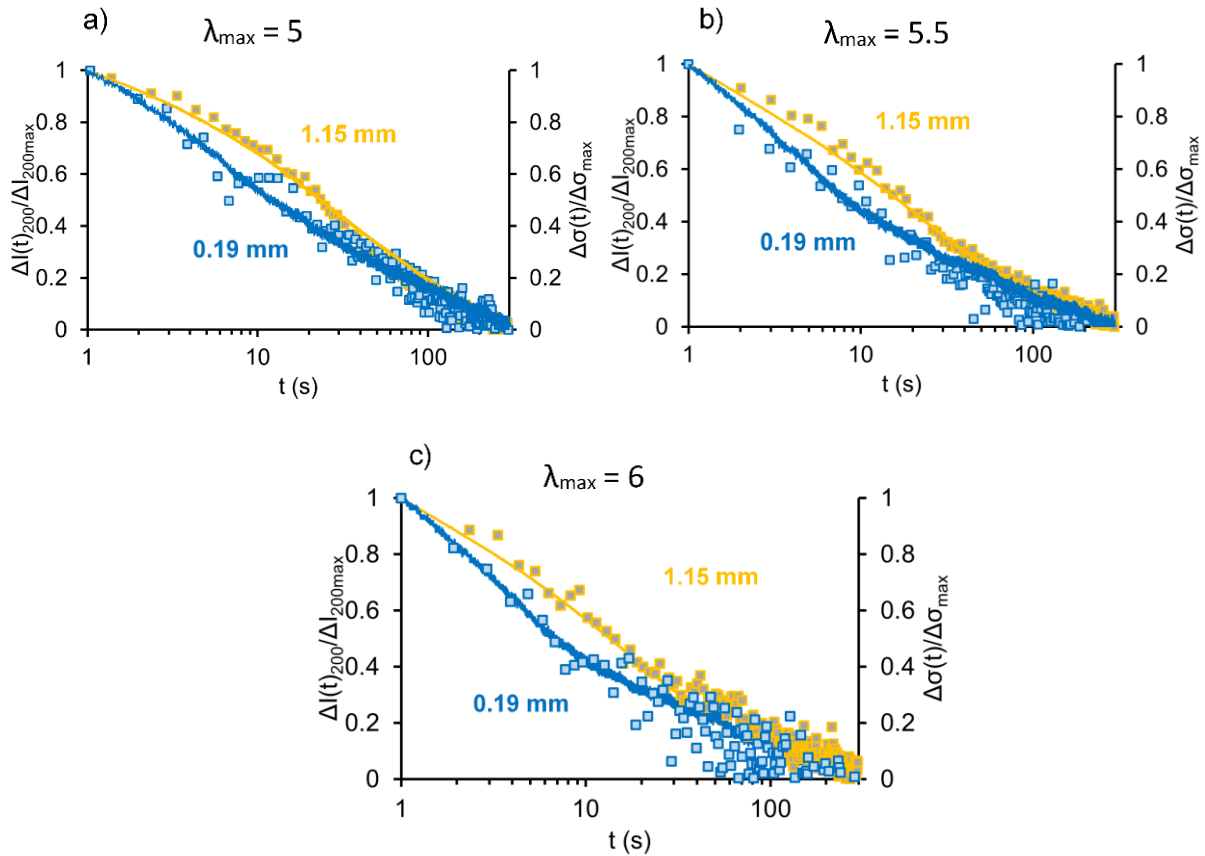
264 From 1s to 70 s after deformation, a large difference is found between the stress curves  
 265 (continuous lines) of thick (1.15 mm) and thin (0.19 mm) samples. This trend was also observed  
 266 on the same specimen with other thicknesses (0.13 mm and 0.34 mm) and on another material

267 (NR<sub>1.53</sub>) (see supporting information, Fig.S6). The results show that the thicker samples relax  
268 more slowly, likely due to slower crystallization kinetics. The largest relative difference (40%)  
269 is observed at about 8 s after deformation. Beyond 70 s, all curves merge indicating that both  
270 samples have the same crystallization behaviors when the heat exchange ends. However, the  
271 stress does not appear to be stabilized at the end of the time interval studied, probably because  
272 the crystallization continues to evolve very slowly over a longer duration than the one of our  
273 study or because of viscoelastic effects [9,17]. This points at the fact that stress relaxation is not  
274 completely driven by the heat exchange, and that it may also be related to the relaxation of the  
275 amorphous phase which decreases the local elongation and delays the SIC [15].

276 The relative evolution of the stress relaxation was then compared to that of the intensity of the  
277 peak 200 (square symbols) calculated via equation (5):

$$278 \quad \frac{\Delta I_{200}(t)}{\Delta I_{200_{\max}}} = \frac{I_{\max} - I(t)}{I_{\max} - I_{\min(1s \text{ after stretching})}} \quad (5)$$

279 The results of this comparison displayed in Fig. 5 show a good correlation between the  
280 evolution of the stress relaxation and the intensity for both thicknesses. The modelling of stress  
281 relaxation using a modified model of Flory supports also these results (Fig.S.7). Furthermore,  
282 they confirm that the crystallization kinetics is faster in the thinner sample. This suggests that  
283 the heat generated by SIC and entropic elasticity, could significantly delay the crystallization  
284 kinetics of the thicker sample.

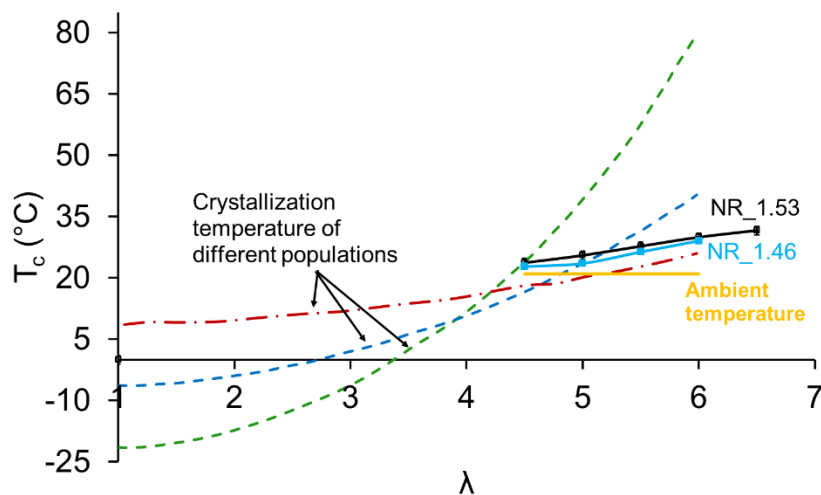


285

286 Fig. 5: Stress relaxation (solid lines) and intensity variation (squares) during the holding step  
 287 (after rapid stretching  $\dot{\lambda} = 13 \text{ s}^{-1}$ ) for the thicknesses 0.19 mm (blue) and 1.15 mm (yellow) at  
 288 three final elongations: (a)  $\lambda=5$ , (b)  $\lambda=5.5$  and (c)  $\lambda=6$ .

289 It is generally admitted that SIC is governed by the successive nucleation of crystallites  
 290 (characterized by their dimensions). Their appearance depends on the spatial heterogeneous  
 291 distribution of the topological constraints resulting from the successive appearance of the  
 292 crystals, and from the crosslinks initially existing in the material. [15,42]With the assumption  
 293 of an initially homogeneous elastomer network, the first crystals to appear induced a decrease  
 294 of the elongation of the remaining amorphous phase and a release of latent heat; both  
 295 phenomena delaying the crystallization kinetics. The second assumption is supported by the  
 296 fact that, depending on the type of crosslinking, it has been shown that the network created in  
 297 natural rubber can be more or less heterogeneous[22,43,44]. With this in mind, Candau et  
 298 al.[22] proposed a model that assumes the presence of several populations of crystallites, each  
 299 with a different crystallization temperature/elongation couple depending on the local elastically  
 300 active chain density. The discretization of the crystallites into different populations was based  
 301 on the evolution of size of the crystals with elongation. The crystals were supposed to reach  
 302 their final size instantaneously, and the size of the crystal was supposed to be linked to the local

303 EAC. Figure 6 recalls the  $T_c(\lambda)$  curves of varying crystallite populations calculated by Candau  
 304 for a material very similar to the one of the present study (crosslinked with sulfur and with a  
 305 similar elastically active chain density). On the same curve, we reported the maximum  
 306 temperature reached during adiabatic strain, for different values of  $\lambda_{\max}$ , up to 6.5 (black dots).  
 307 One can deduce from this figure that the appearance of the two first populations (green and blue  
 308 curves) is not inhibited by the generated heat, because their  $T_c$  is, for an elongation above 5,  
 309 higher than the temperature of the sample (black curve). Conversely, for crystallite populations  
 310 formed by longer chains (low local cross-link density, red curve), the temperature variation  
 311 reached just after elongation is greater than  $T_c$ , which means that the generated heat must first  
 312 be partially removed for these populations to appear. The duration of the crystallization kinetics  
 313 is thus extended since the nucleation rate is slowed down due to the time required to decrease  
 314 the local temperature (i.e., to lower the energetic barrier of nucleation).



315

316 Fig. 6: Crystallization temperature as a function of elongation for different crystallite  
 317 populations: 1<sup>st</sup> in green dashed lines, 2<sup>nd</sup> in blue dashed lines and the 3<sup>rd</sup> in red dashed lines.  
 318 The curves were reproduced using equation 10 of the reference [22]. The points represent the  
 319 maximum temperatures reached by our materials just after stretching at different  $\lambda$ .

#### 320 4. Conclusion

321 The majority of the models that describe the crystallization kinetics of NR relate it  
 322 entirely to the germination, stress relaxation and mobility of the macromolecular chains at a  
 323 stabilized temperature and do not consider the temperature changes during the cycle. This study  
 324 highlights the impact of the heat generated by entropic elasticity and crystallization on SIC  
 325 kinetics and stress relaxation. A difference of at least 10% in the relaxed stress of samples of  
 326 different thicknesses (200  $\mu\text{m}$  and 1 mm) was observed. It is expected to increase as the

327 difference in thickness of the samples increases. Consequently, the heat exchange time constant  
328 is a parameter that should be considered while modeling SIC and the mechanical behavior of  
329 NR. Furthermore, heat transfer could also be partly at the origin of the kinetics of melting of  
330 NR crystallites mentioned in the work of Samaca Martinez et al.[27]. Further studies would be  
331 needed to confirm it.

332 In view of being applied to elastocaloric devices[45], these results confirm that a non-  
333 negligible crystallization occurs during a few tens of seconds during the heat transfer. In  
334 addition, the interplay between stress, temperature and the kinetics of the strain-induced  
335 crystallization is believed to have a great impact on the mechanical losses of natural rubber and  
336 thus on its coefficient of performance (COP), especially in the case of non-uniform temperature  
337 as for regenerative elastocaloric devices (typically when using a liquid as a heat transfer fluid  
338 leading to a Biot number above 1). Further work is however necessary to evaluate the impact  
339 of non-homogenous crystallization and temperature on the mechanical behavior. It also leads  
340 to questions about the impact of the conductive heat diffusion on the crystallization at  
341 microscopic and low time scales [46], since the local temperature variation induced by  
342 crystallization can reach  $\Delta T = \frac{\Delta H_f}{C_m} = 38^\circ\text{C}$ [47].

343 Finally, from a more general point of view, the high toughness of natural rubber and its  
344 dynamic mechanical response are strongly dependent on its ability to crystallize. Consequently,  
345 the increase in heat transfer could accelerate the kinetics of SIC and have a significant influence  
346 on its fatigue resistance in a marine environment (with a high convective heat transfer  
347 coefficient)[48–50]. The dependence of the SIC kinetics on temperature and heat transfer could  
348 also be taken into account when investigating crystallization at the crack tip where heat  
349 exchange is very specific.

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