



# The new interpretation for the heat build-up phenomena of rubbery materials during deformation



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## ABSTRACT

The first and second laws of thermodynamics can describe the heat build-up phenomena of rubbery materials during deformation. When the force is applied on rubber specimen, the rubber starts to deform and the work is stored as heat inside rubber. The temperature increase due to deformation can be scaled by the heat capacity as a function of the work. This can be well explained by the entropic process. It can be noted that the entropic process is the reversible heat process, but the most of rubber applications are based on the behaviours such as viscoelastic process, which are not reversible heat process. In this paper we measured the phenomenological behaviours of temperature changes on stretching and un-stretching rubber. As a result it was reduced to two processes, which are the reversible process and irreversible process. The non-equilibrium thermodynamics equation was newly derived in order to describe these processes. The reversible process can be associated with the configurational entropic process of rubber elasticity, but in the irreversible process it was suggested that the work is leaked as heat to the external system. Some of work is transferred into the fluctuation of the molecular motion inside rubber. The fluctuation is never recovered as the mechanical force and is mechanically observed as the stress relaxation. This gives us the new interpretation why rubbery materials can produce heat during deformation.

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## 1. Introduction

Since Joule published the paper showing the temperature increase of rubber during deformations in 1859 [1], lots of papers on the rubber elasticity, which were mainly described by the entropic process, were published. The entropic process of rubber elasticity works well on the ideal states of rubber network as in the relaxed states [2–4]. But most of the industrial applications undergo the dynamic deformation process and are no longer dependent only upon entropic process. It can be noted that the entropic process is the reversible heat process, but the most of rubber applications are based on the behaviours such as viscoelastic process which are not reversible heat process. The former is based on the idea derived from the network structure, which the macromolecules are cross-linking with covalent bonds, the latter is from those can be represented by the interaction between molecules [5]. From the recent development in the biomechanics the various functions of the bio-macromolecules are explained by the

weak forces appeared between molecules, which play more important roles than the strong interactions such as covalent bonds forming the gigantic network [6].

For most of industrial applications the rubbers are designed with the viscoelastic properties, which mainly depend upon the interaction between rubber molecules during the deformations. The design of the rubber compounds for tyres is a typical example of the application. To reduce the tyre rolling resistance the heat-build up of rubber during deformations should be lower, but to improve the brake performance it should be higher [7]. From the point of heat build-up it is trading off, but the rubber engineering gives us the solution to control the frequency dependence of rubber heat build-up during deformations. It is said that the frequencies during the deformation of rubber sliding on the micro pitch roughness of the road surface is ten thousand times more than those of tyre rotation. In the other words, the lower rolling resistance prefers the entropic process, but the higher brake performance does the viscoelastic process. In order to control the viscoelastic process, the design of the interaction between rubber molecules plays more important role than those of cross-link between rubber molecules. This is the one of the example of the

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engineering applications of viscoelastic control techniques. These behaviours are mainly described with the spring and dashpot model, such as multiple Maxwell model and Kelvin–Voigt model. But there are few approaches based on the thermodynamics theory. This is due to the fact that the viscoelastic process is considered as the non-equilibrium process, which is different from the thermodynamics process considered as equilibrium process. From the thermodynamics point of view, A. Sakata recently carried out the measurements of the mechanocaloric effect of rubber and found the dissipative effect with rapid deformation of rubber, which indicates the viscoelastic irreversibility [8]. But the authors say that the further study is needed to clarify its physical mechanism. As the computer aided engineering is grown up rapidly, the new approaches using molecular dynamics becomes more popular with the advent of the molecular dynamics calculation software packages such as OCTA [9,10] and the multi-scale computational framework on the viscoelastic properties of polymers [11], which can be achieved by the combination of the coarse-grained molecular dynamics and the finite element analysis. These computational approaches are also expected to reveal the viscoelastic process from the molecular dynamic point of view.

This paper shows phenomenological behaviors of heat-build up process on rubbers and proposes the new interpretation, which can bridge the reversible heat process and irreversible heat process of rubbers with non-equilibrium thermodynamics [12–16]. This will also help us to derive the constitutive equation which can consider the heat-build up process of rubbers during the deformation, and especially it can be expected to use the nano-mechanical analysis of the filled rubbery materials using the nano-scale finite element analysis [17]. It should be also noted that this can be applied to the similar processes, which appears in the other macromolecular materials and be also seen in biomaterials. We hope that this may help the design and mechanical analysis for the heat process of both the industrial applications for the rubber engineering and the biomaterials developed for the tissue engineering.

## 2. Experimental section

All the rubbers used for this study are commercially available, particularly in tyre applications. The matrix polymers were a polystyrene-butadiene rubbers (SBR), which are the random copolymers containing styrene, vinyl and butadiene units. The ratio of these units was determined to optimize the viscoelastic properties for this work. The SBRs used here were characterized by the three different glass transition temperatures ( $T_g$ ), which depend on the conformation of the micro-structures. The SBR was unfilled and cross-linked using a sulfur curing system providing conventional sulfur cross-links. The cross-linking formulations are given in Table 1. These are non-strain induced crystallizing rubbers. The respective repeat units of the micro structures are also shown in Table 1. The number included in sample code represents the

**Table 1**  
Unfilled rubber compounds used for this work and formulations.

Materials <sub>p,h,r</sub>	SBR41/19	SBR20/60	SBR48/19
SBR with low $T_g$	100	–	–
SBR with medium $T_g$	–	100	–
SBR with high $T_g$	–	–	100
Stearic acid	2.0	2.0	2.0
ZnO	3.0	3.0	3.0
Acc. <sup>a</sup>	1.5	1.5	1.5
Sulfur	1.50	1.50	1.50
Styrene content/%	41	20	48
Vinyl content/%	19	60	19

<sup>a</sup> N-Cyclohexyl-2-Benzothiazyl-sulfenamide, Diphenylguanidine.

percentage of the styrene and vinyl contents. Following mixing, the rubbers were pressed into sheets of nominal thickness of 2 mm with a pressure of 20 MPa at the temperatures of 145 °C. The curing time was 33 min.

The temperature measurements under strain were carried out at 25 °C using a conventional tensile testing machine equipped with a high resolution thermography (FSV-7000E, Apiste Corporation). The temperature was captured with flame speed of 1/60 s. Rubber strip samples of dimensions 50 × 6 × 2 mm were used. The detail of the experimental set-up is shown in Fig. 1. Since thermography can measure the surface temperature, which is cooled by the heat flow to the atmosphere, the temperature change inside rubber was estimated from the measured surface temperature using following equation [18].

$$T_{Bulk} = T_{Surf} + \frac{d}{h_c}(\alpha + \beta)$$

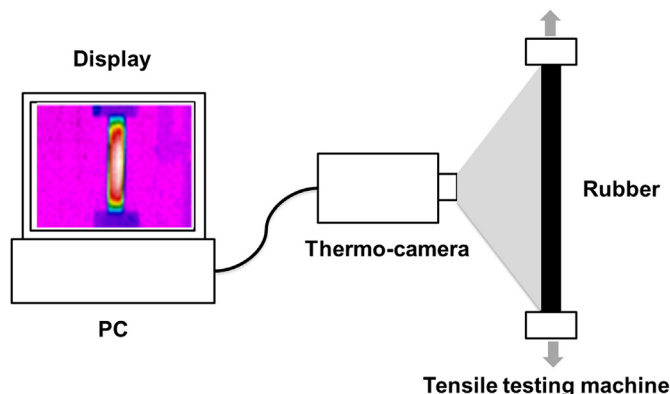
$$\text{with } \alpha = h_j \cdot (T_{Surf} - T_{Room}), \beta = h_F \cdot \zeta \cdot (T_{Surf}^4 - T_{Room}^4),$$

where  $T_{Bulk}$  is the estimated temperature inside rubber,  $T_{Surf}$  is the surface temperature measured by thermo-vision,  $T_{Room}$  is the atmosphere temperature,  $d$  is the thickness of the specimen,  $h_c$  is the heat conductivity of the specimen,  $h_j$  is the heat conductivity of the air in static mode,  $h_f$  is the ratio of surface heat radiation and  $\zeta$  is  $5.670400 \times 10^{-8} \text{ j/s/m}^2/\text{K}^4$ , the Stefan–Boltzmann constant.

The force was measured using a 50 N load cell and the extension ratio was calculated from the cross-head displacement. Most of the tests were carried out at a cross-head speed of 26.4 mm/s corresponding to a finite strain rate of  $3.3 \times 10^{-1} \text{ s}^{-1}$  with triangle deformation mode. The specimen was stretched from both sides of the rubber strip to fix the center position for monitoring the temperature. In addition all data were plotted in the form of the Mooney–Rivlin equation to derive the values of  $C_1$  and  $C_2$ , which were used to calculate the work done on the system as a function of strain up to 200%.

The viscoelastic measurements were carried out using a commercial viscoelastic analyzer (Rheometric Scientific, Inc. ARES) with which  $G'$ ,  $G''$  and  $\tan\delta$  can be measured in shear mode as a function of temperature. The measurements were carried out over a range of temperature from –70 °C to 100 °C at the frequency of 10 Hz and the strain of 0.01.

The heat flux type differential scanning calorimeter (T.A. Instrument, Q100 DSC) was used to measure the heat capacity. The measurements were carried out varying over the temperature range –70 °C to 100 °C with scanning rates of 1 °C/min. The system can output the heat flow of the specimen and the heat capacities at



**Fig. 1.** The set-up of the apparatus for the temperature measurement.

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