



# Nanomechanics on non-equilibrium thermodynamics for mechanical response of rubbery materials



Keizo Akutagawa\*, Satoshi Hamatani, Hiroshi Kadowaki

Bridgestone Corporation, 3-1-1 Ogawahigashi-cho, Kodaira-shi, Tokyo, 187-8531, Japan

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## ABSTRACT

The proposed mathematical model of nanomechanics for rubbery materials provides seven parameters to characterize the stress-strain response of rubbery materials as a function of time and temperature. Especially, two parameters of an attractive energy,  $\kappa$ , and an internal variable,  $\xi$ , are newly introduced to describe the departures from the classical thermodynamics of rubber elasticity. The mathematical model can reproduce the entropy and energy components on stress with various conditions such as the degree of cross-links, the extent of swelling, the temperature dependence and the strain rate dependence. It also offers physical insights represented by the quantitative molecular structural parameters such as the number of non-bonding interactions and its potential energy. As a conclusion the energy component can be associated with the non-bonding potential energy of the dipole-dipole interaction (0.3–0.9 kJ/mol) and the steric interaction to rotation about the chain backbone (16–20 kJ/mol).

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## 1. Introduction

Commercial applications of rubbery materials play an important part in the modern world, which include tires, automobile, footwear, cables, belts, hoses, seals, sports goods, health care and medical applications. The most important requirement for these applications is a specific response of rubber to the application of force and deformation in use. It can be characterized by its unique elastic response to the application of force and deformation in which most of the work done is stored and some is recoverable and the other is lost on removal of the force. In addition a lot of systematic fundamental works on the thermal or thermo-elastic properties have been carried out since the pioneer work of Joule [1] in the mid-nineteenth century. Nevertheless, in most of industrial applications these mechanical properties are phenomenologically linked to microstructures such as chemical composition

so that the physical principal behind the link is still not clear. Against this background the digital revolution is under way and integrates technologies across the information technologies coupled with advances in characterization and experiment.

Several attempts have been made to bridge the molecular structural characteristics to the requirements of commercial applications [2–8]. Some of them can be simulated using continuum methods with the meso-scopic 3D-structural model of filled rubbers, while those in the nano-scopic scale can be described using the constitutive equations, which include the molecular characteristics such as quantum and statistical physics. Similar approaches are carried out in the field of medical application. This is due to the fact that mechanical response of bio-elastomers can be expressed with regard to their rubberlike elasticity as hyper-elastic materials [9–13]. In food systems, some of the common points between hyper-elastic materials and food gels are discussed [14]. But the majority of mathematical models used for these approaches are phenomenological models, which are not necessarily derived from physical principles. An example is the Mooney-Rivlin equation, which was developed to describe the stress-strain behavior of

\* Corresponding author.

E-mail address: [keizo.akutagawa@bridgestone.com](mailto:keizo.akutagawa@bridgestone.com) (K. Akutagawa).

cross-linked rubber networks. The departure from the simple statistical theory is represented in this equation by the magnitude of the additional term  $C_2$ . Even if the Mooney-Rivlin equation is used, the discrepancies between the simple statistical theory and the real world application still exist. Alternatively, a simple coarse-grained molecular dynamics, CGMD, simulation model could be chosen to bridge the molecular structure and the mechanical response [15,16]. These approaches provide us a meaningful physical interpretation, but it is based on the calculated results limited in the size of structure model and computational capacity. Because the computation time for the molecular model of real application size is still longer than that for the continuum mechanical approaches. In addition there still exists the difficulty to determine the initial chain network structure in 3D arrangements. In this situation a constitutive model based on basic physical principles [17–19] is more desirable than that on the phenomenological approaches. It will offer physical insight that helps to bridge the continuum mechanical approaches and full atom simulation model. It will also become a useful tool to analyze both of experimental and computational results. But no one has yet successfully derived such a constitutive model for rubber from the physical principles governing the molecular response of rubbery materials [17].

The present work shows a mathematical mechanical model of rubbery materials for computational simulation, which can represent the behaviors observed in real world application. This work can be expected to contribute the digital revolution in rubber science and technology and give us a hint to design the advanced rubbery materials as fast as possible, at a minimum fraction of the cost.

## 2. General purpose

Rubbers are so named because they exhibit large elastic deformations, particularly when they are cross-linked, up to large deformations. However, the stress-strain curves are rate dependent and if a constant strain rate test is stopped the stress decays to an equilibrium value, a phenomena known as stress relaxation. Both of those phenomena are due to the fact that even a very simple rubber shows a mechanical response characterized by non-equilibrium thermodynamics rather than simply by equilibrium thermodynamics. The essential feature of present work is the derivation of constitutive equations from the physical principles of non-equilibrium thermodynamics. It can describe the mechanical response of rubbery materials up to higher strain region. It was also helped by lots of early attempts to account for the thermodynamic features in terms of fundamental concept of rubber elasticity [18].

The proposed mathematical model provides seven parameters to characterize the stress-strain response of rubbery materials as a function of time and temperature. Especially, two parameters of an attractive energy,  $\kappa$ , and an internal variable,  $\xi$ , are newly introduced to describe the departures from the classical thermodynamics of rubber elasticity. The attractive energy,  $\kappa$ , is defined as the interaction energy between molecules. The internal variable,  $\xi$ , is defined as the scaling parameter for number of non-bonding interactions with  $\kappa$ . It is assumed that the stress decay during the deformation up to equilibrium state can be represented by the reduction in these interactions as a function of time and the magnitude of deformation. The rest of five parameters describe the mechanical behaviors at equilibrium state.

The proposed model was also applied to interpretation of the some experimental results of stress-strain relations picked up from a lot of experiments carried out in past. The model shows a better fit of the functional forms to the stress-strain curves over a wide range of strain. The physical meanings of seven parameters derived from those fitted on experimental data are also discussed. As a

conclusion this mathematical model can reproduce the mechanical response of rubbery materials with various conditions such as the degree of cross-links, the extent of swelling and the temperature dependence. It also offers physical insights represented by the quantitative molecular structural parameters such as the number of interactions and its interaction energy. These can be associated with the non-bonding potential energy of the dipole-dipole interaction or the steric interaction to rotation about the chain backbone. The former is affected by the intermolecular interactions (long range interactions), and the latter is by the intra-molecular interactions (short range interactions).

## 3. Theory

The most important part of derivation of constitutive equation with physical meanings is the determination of the form of the thermodynamic equation. The fundamental concept of present work is based upon the constitutive equation proposed by Thomas, A.G. [19]. He considered an additional term of the internal attractive force on to the entropy term of rubber elasticity. It is assumed that the attractive force between two molecules with distance,  $r$ , decreases in effect as  $r$  increases. The modified stored energy function,  $e$ , of a single chain was expressed by

$$e = B \cdot r^2 + A \cdot r^{-1} \quad (1)$$

where  $A$  and  $B$  are constants and  $n = 2$  determined from swelling experiment. The first term represents entropy term from the simple statistical thermodynamics. The second term represents the attractive energy to explain the departure from the statistical theory. This model is only referred to the total amount of the attractive energy,  $A$ , of equation (1). An attempt to use the idea of renormalization technique [20,21] under the mean field assumption is carried out. This procedure can extend Thomas equation (1) into  $N$  chains system, where  $N$  is defined as the number of the segment of molecules between successive points of cross-links. The attractive energy,  $A$ , was replaced by the affinity force,  $A_f$ , and  $\xi$ . The distance,  $r$ , is also replaced by the strain invariants to describe the renormalized displacement during deformation. The second term of equation (1) represents the decreasing function with increasing  $r$  so that equation (1) was renormalized into the exponential form of decreasing function about the distance between molecules [20].

$$A \cdot r^{-n} \rightarrow A' \cdot e^{-r/\alpha} \quad (2)$$

where  $\alpha$  is temperature dependent factor and  $A'$  is a function of  $\kappa$ . The non-equilibrium thermodynamics equation used for the renormalization was derived from the heat build-up experiments. Under these treatments the renormalization technique as shown in equation (2) was applied to equation (1). It transfers a single chain model into the  $N$  molecular system combined with the non-equilibrium thermodynamic theory.

A brief summary will be given here of the non-equilibrium thermodynamics equation obtained from the analysis of phenomenological data on heat build-up experiments [22]. Temperature change on stretching and un-stretching process can be reduced into two processes, reversible process and irreversible process. The reversible process can be described as the configurational entropic process of rubber elasticity. The irreversible process is partly associated with the energy process parameters such as heat capacity,  $C$ , and glass transition temperature,  $T_g$ . On the bases of this analysis the non-equilibrium thermodynamic equations are summarized in Table 1. Both mechanical and thermodynamic equations are derived from the differentiation of a heat build-up equation derived from the experimental results [22].

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