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# Molecular simulation guided constitutive modeling on finite strain viscoelasticity of elastomers

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## ABSTRACT

Viscoelasticity characterizes the most important mechanical behavior of elastomers. Understanding the viscoelasticity, especially finite strain viscoelasticity, of elastomers is the key for continuation of their dedicated use in industrial applications. In this work, we present a mechanistic and physics-based constitutive model to describe and design the finite strain viscoelastic behavior of elastomers. Mathematically, the viscoelasticity of elastomers has been decomposed into hyperelastic and viscous parts, which are attributed to the nonlinear deformation of the cross-linked polymer network and the diffusion of free chains, respectively. The hyperelastic deformation of a cross-linked polymer network is governed by the cross-linking density, the molecular weight of the polymer strands between cross-linkages, and the amount of entanglements between different chains, which we observe through large scale molecular dynamics (MD) simulations. Moreover, a recently developed non-affine network model (Davidson and Goulbourne, 2013) is confirmed in the current work to be able to capture these key physical mechanisms using MD simulation. The energy dissipation during a loading and unloading process of elastomers is governed by the diffusion of free chains, which can be understood through their reptation dynamics. The viscous stress can be formulated using the classical tube model (Doi and Edwards, 1986); however, it cannot be used to capture the energy dissipation during finite deformation. By considering the tube deformation during this process, as observed from the MD simulations, we propose a modified tube model to account for the finite deformation behavior of free chains. Combining the non-affine network model for hyperelasticity and modified tube model for viscosity, both understood by molecular simulations, we develop a mechanism-based constitutive model for finite strain viscoelasticity of elastomers. All the parameters in the proposed constitutive model have physical meanings, which are signatures of polymer chemistry, physics or dynamics. Therefore, parametric materials design concepts can be easily gleaned from the model, which is also demonstrated in this study. The finite strain viscoelasticity obtained from our simulations agrees qualitatively with experimental data on both un-vulcanized and vulcanized rubbers, which captures the effects of cross-linking density, the molecular weight of the polymer chain and the strain rate.

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## Nomenclature

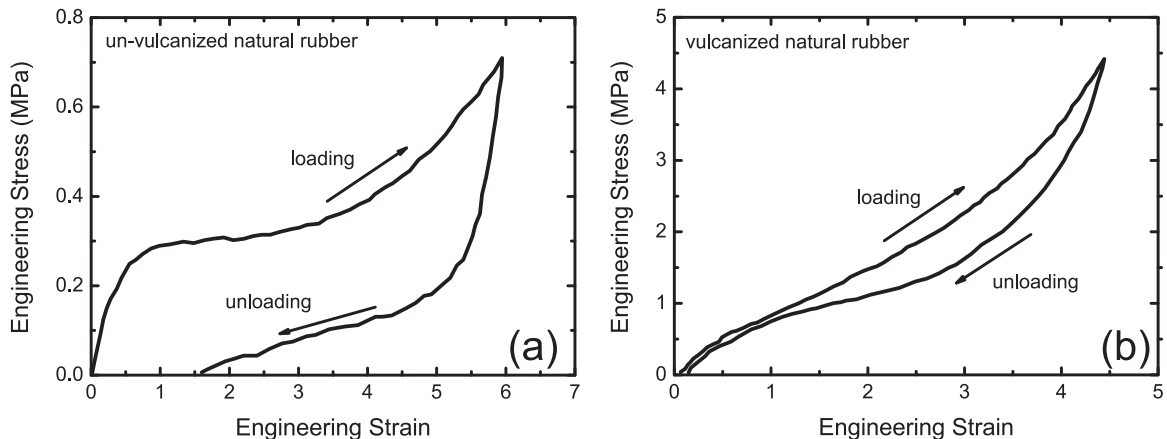
Definitions are given here in the following sequence: Roman alphabetical order followed by Greek alphabetical order. Bold quantities denote vectors or tensors.

$a_{pp0}, a_{pp}$	tube diameter in reference/undeformed, current/deformed frame
$b$	Kuhn length of polymer chain
$\mathbf{B}$	left Cauchy–Green tensor $\mathbf{F}\cdot\mathbf{F}^T$
$D_c$	diffusion coefficient of polymer chain
$\mathcal{E}$	relaxation contribution to the kernel $\Upsilon$
$G$	modulus entering $\sigma^V$
$G_c$	cross-linking modulus of polymer chains entering $\sigma^E$
$G_e$	plateau modulus induced by polymer chain entanglement entering $\sigma^E$
$\mathbf{F}$	deformation gradient tensor
$F_t$	tensile force in primitive chain of tube model
$I_k$	$k$ th tensor invariant of $\mathbf{B}$
$k_B$	Boltzmann constant
$L_{pp0}, L_{pp}$	contour length of primitive path in reference/undeformed, current/deformed frame
$N, N_\nu$	polymerization degrees of chains
$N_e$	entanglement length, which is number of monomers between two entanglements
$n_\nu$	number of polymer chains per unit volume
$\mathbf{P}^E$	elastic part of first Piola–Kirchhoff stress tensor
$\mathbf{P}^V$	viscous part of first Piola–Kirchhoff stress tensor
$p$	mode number variable (odd integer) in tube model, $p = 1, 3, \dots, \infty$

$R_{ee0}, R_{ee}$	end-to-end distance of polymer chain in reference/undeformed, current/deformed frame
$s$	segment index/contour length variable along primitive chain
$T$	temperature
$\mathbf{v}_k$	$k$ th eigenvector of $\mathbf{B}$
$W$	strain energy density function $W = W(\mathbf{F})$
$\langle Z_{\text{kink}} \rangle, \langle Z_{\text{coil}} \rangle$	number of entanglements per chain given by kink assumption and random coil assumption
$\alpha$	argument in the generalized Mittag–Leffler function $E_{\alpha,1}(x)$
$\sigma^E$	elastic part of Cauchy stress tensor
$\sigma^V$	viscous part of Cauchy stress tensor
$\gamma$	shear strain
$\lambda$	stretch ratio
$\lambda_{\text{max}}$	limiting network stretch
$\lambda_j$	principle stretch, square root of $j$ th eigenvalue of $\mathbf{B}$
$\Lambda$	quantification of the rotation of the primitive chain contributing to viscous stress
$\nu_0, \nu$	unit tangent vector of primitive chain in current/undeformed, reference/deformed frame
$\Psi$	probability that chain segment $s$ remains in the tube of reptation at time $t$
$\phi$	crosslink functionality
$\rho_m$	monomer mass density
$\Upsilon$	integration kernel for the calculation of $\sigma^V$
$\tau_{d0}, \tau_d$	disentanglement time of polymer chain in current/undeformed, reference/deformed frame
$\xi$	friction coefficient of a polymer bead

## 1. Introduction

Elastomers consist of long polymer chains joined together by chemical bonds through cross-linkers. They are usually capable of recovering their original shapes after finite deformation due to covalent cross-linkages. Under equilibrium conditions, long polymer chains making up an elastomer are irregularly coiled together. However, when the elastomer is under tension, polymer chains tend to stretch out and straighten along the pulling direction. Upon unloading, the chains



**Fig. 1.** Experimental results on uniaxial stress–strain curves during loading and subsequent un-loading of (a) un-vulcanized and (b) vulcanized natural rubber (NR) with strain rate  $0.003 \text{ s}^{-1}$  at room temperature. Results taken from [Annuyapornsi et al. \(2012\)](#).

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