European Polymer Journal 87 (2017) 136–146

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Effect of chain length distribution on mechanical behavior of polymeric networks

Mohammad Tehrani, Alireza Sarvestani *

Department of Mechanical Engineering, Ohio University, Athens, OH 45701, USA

ARTICLE INFO

Article history:
Received 27 October 2016
Received in revised form 9 December 2016
Accepted 12 December 2016
Available online 19 December 2016

Keywords:
Rubber elasticity
Chain length distribution
Softening
Polydispersity

ABSTRACT

The effect of network chain distribution on mechanical behavior of elastomers is one of the long standing problems in rubber mechanics. The classical theory of rubber elasticity is built upon the assumption of entropic elasticity of networks whose constitutive strands are of uniform length. The kinetic theories for vulcanization, computer simulations, and indirect experimental measurements all indicate that the microstructure of vulcanizates is made of polymer strands with a random distribution of length. The polydispersity in strand length is expected to control the mechanical strength of rubber as the overloaded short strands break at small deformations and transfer the load to the longer strands. The purpose of this contribution is to present a simple theory of rubber mechanics which takes into account the length distribution of strands and its effect on the onset of bulk failure.

1. Introduction

A major assumption of classical rubber elasticity is the monodispersity of the constitutive strands, the sub-chains between the two consecutive crosslink points. The conventional crosslinking techniques, however, are essentially uncontrolled processes and hence, the formation of ideal monodisperse networks is not probable. Direct measurement of randomness in internal structure of rubber compounds is unfeasible due to insolubility of the polymer networks. First efforts to indirectly quantify the structural polydispersity of vulcanizates go back to the pioneering works of Toboslky [1], Beuche [2], Gehman [3], and Watson [4], using relaxometry of stressed networks or measurement of swelling pressure.

The effect of strand polydispersity on the overall mechanical behavior of polymer networks is of great research and technological importance. The simplest polydisperse networks can be formed by end-linking of functionally terminated crosslinkers with a multimodal length distribution. Mark and his co-workers conducted a comprehensive study on bimodal polymer networks ([5] and the references therein). Their results point to a great enhancement in ultimate mechanical properties of the network, namely an increase in the toughness and larger elongation at break. These findings were attributed to the distribution of stress between the short and long chains. The enhancement in strength is primarily due to the limited deformability of non-Gaussian short chains. Following the rupture of short chains, the stress is transferred to the long strands which exhibit larger deformation at break.

In vulcanizates, the strand length distribution is expected to be non-uniform and range from very short to very long strands [6]. This assumption is validated by a number of computer simulation studies. Grest and Kremer [7], for example,

* Corresponding author.
E-mail address: sarvesta@ohio.edu (A. Sarvestani).

http://dx.doi.org/10.1016/j.eurpolymj.2016.12.017
0014-3057/

simulated the equilibrium structure of randomly crosslinked networks with the number of crosslinks well above the percolation threshold. The network was formed by instantaneous crosslinking of long primary chains in a melt state. In the ideal case of completely random crosslinking, the association of chains can be regarded as statistically independent events. Theoretically, this means that the distribution of crosslink points along the primary chains must be Gaussian and hence, the distribution of strand length between crosslink points must follow a simple exponential form with a decay length. The simulation results of Grest and Kremer support these predictions.

Modeling fracture and mechanical failure of polymer networks continues to be a subject of ongoing research [8–11]. The ultimate mechanical properties of polymer networks are affected by a host of influences, ranging in a wide spectrum of length scales. This includes the microstructure of a single polymer chain (e.g., helicity, interatomic potentials, crosslinking, isomerization, etc.) as well as the chain's local environment (entanglements, cracks, etc.). The focus of current study is to develope a theoretical model to evaluate the role of strand polydispersity in the bulk failure of polymer networks.[1] The importance of strand length distribution for the mechanical strength of vulcanizates was first highlighted by Gehman [6]. He proposed that upon deformation of a random network, shorter strands break at considerably smaller deformations compared to the longer ones. This deformation-induced network alteration continues concurrent with increasing deformation and controls the onset of mechanical failure. This proposition is adopted here and forms the basis of the proposed micromechanical model for the elasticity and damage initiation in elastomers with a random distribution of strand length. This study is inspired by the recent work of Itskov and Knyazeva [12] who proposed a model for rubber elasticity based on the chain length statistics. Here, their approach is advanced by introducing a failure criterion based on the interatomic pair potential and considering damage accumulation using a simple first-order kinetic theory.

2. Model

Bueche [2] and Watson [13,14] originally proposed an expression for the strand length distribution function in a random network. Consider a network formed by vulcanization of infinitely long polymer chains. Let n_j be the number of strands with j statistical segments. If the placement of crosslink points is taken to be completely random with probability p, then the probability distribution of having a strand with j statistical segments, $P(j)$, can be expressed as

$$P(j) = \frac{n_j}{\sum_j n_j} = (1-p)^{j-1}p \tag{1}$$

where $\sum_j n_j$ is the total number of existing strands. The assumption of completely random placement of crosslinks warrants the probability p to be a constant and equal to the reciprocal of average strand length $\bar{j} = \frac{1}{p}$. At the limit of large $\bar{j}$ values, Eq. (1) leads to a distribution function

$$P(j) = \frac{1}{m}\left(1+\frac{1}{m}\right)^{-j} \tag{2}$$

where $m = \frac{1}{p} - 1$. For large m values, the approximation $\left(1+\frac{1}{m}\right)^m \approx e$ holds and thus the distribution (2) accept a simple exponential form

$$P(j) = \frac{1}{\bar{j}} e^{-j/\bar{j}} \tag{3}$$

Note that Eq. (3) represents the probability distribution of strand length in an ideally random crosslinked network, where the positions of crosslinks are taken to be statistically independent.

Now consider a network of crosslinked flexible strands subjected to a quasi-static finite deformation. To keep the formulation simple, throughout this paper it is assumed that the network is incompressible, although extension of the presented theory to the compressible networks is possible. The end-to-end vector of each strand in the reference and current configurations is represented by $\mathbf{R}_0$ and $\mathbf{R}$, respectively (Fig. 1). The network is formed by random crosslinking of the strands whose length follow distribution (3). The effects of other structural properties such as crystallinity or entanglement are not taken into account. The conformational entropy of a strand with j statistical segments, stretched by λ, is

$$S(\lambda, j) = -jk_B\left(\frac{\lambda}{\sqrt{j}}\beta + \ln\frac{\beta}{\sinh\beta}\right) - S_0 \tag{4}$$

where

[1] Following Volokh [8], here, the concept of bulk failure refers to the "continuum damage mechanics" in which the material failure is controlled by damage accumulation and evolution of internal structure of the bulk material. This approach is different from the so called "cohesive zone" models in which the properties of bulk material remain unchanged and fracture is presented by introducing interface cohesive elements whose behavior is controlled by some traction-seperation laws.