Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 46 (2005) 10128–10138
polymer
www.elsevier.com/locate/polymer

A Monte Carlo simulation study of the mechanical and conformational properties of networks of helical polymers. Part II. The effect of temperature

Richard Batman, Gustavo A. Carri*

Department of Polymer Science and The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

Received 30 May 2005; received in revised form 30 July 2005; accepted 3 August 2005
Available online 19 August 2005

Abstract

In a recent article (Carri GA, Batman R, Varshney V, Dirama TE. Polymer 2005;46:3809 [17]) we presented a model for networks of helical polymers. In this article we generalize our results to include the effect of temperature and focus on the mechanical, conformational and thermo-elastic properties of the network. We find that the non-monotonic stress–strain behavior observed at constant temperature also appears in the stress–temperature behavior at constant strain. The origin of this behavior is traced to the induction and melting of helical beads by the application of large strains or reduction in temperature. Other conformational properties of the polymer strands are also discussed. We also study the network entropy and heat capacity, and find a non-monotonic dependence on temperature and strain. Our study shows that the entropy is controlled by the helical content whenever the latter is significant. Otherwise, the entropy corresponds to the one of a network made of random coils. In addition, the study of the heat capacity shows that strain shifts the helix-coil transition temperature significantly. Other results are also discussed.

Keywords: Networks; Elastomers; Helical polymers

1. Introduction

The large deformability and almost complete recoverability of elastomers have made them objects of scientific study for several decades. As in the first experiments of Gough and Joule [1,2] testing has generally involved the measurement of mechanical stress corresponding to some sort of strain, most often uniaxial extension or compression. Additional information relating mechanical properties to molecular structure has been obtained from a variety of experimental techniques including swelling experiments, NMR, SAXS, SANS and others [3].

Experimental studies have shown that elastomers consist of macromolecular chains, cross-linked into a network, that can change their conformations in response to stress. Theories based on this model, described in a recent review by Erman and Mark [4], simplified the calculations by making various assumptions. In the earliest theories [2,5,6] the network strands were treated as perfectly flexible 'phantom chains' that passed freely through each other, interacting only at cross-links. In such networks, the stress arises from the decrease in the entropy of the network chains due to the deformation. Interactions between strands were incorporated into later theories [7].

Computer simulations have generally followed two different methods in studying elastomers. The more direct method of modeling the fully-constructed network is exemplified in the work of Grest and Kremer, and Escobedo and de Pablo [8,9]. The less direct but more common method is the Monte Carlo modeling of a single, isolated chain to obtain the radial distribution function of end-to-end distance, which is then used in the standard three-chain model of rubberlike elasticity to find the stress–strain behavior of the network [2,6]. This method has been extensively used with synthetic systems [4].

Most of the studies have focused on synthetic elastomers. However, biopolymers are richer in terms of their conformational properties; thus, networks made of

---

* Corresponding author. Tel.: +1 330 972 7509; fax: +1 330 972 5290.
E-mail address: gac@uakron.edu (G.A. Carri).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.08.013

biopolymers, called bioelastomers, can be expected to have a more interesting stress–strain behavior. The secondary structures of biopolymers, such as α-helices and β-sheets, as well as their tertiary structures, can be melted at sufficiently high temperatures or pulled apart by sufficiently large strains. These structures would therefore produce significant temperature- and strain-dependence in the mechanical properties of networks. The presence of solvent, which also affects the formation and melting of such structures, would add a further dimension to the behavior of swelled networks.

In order to take full advantage of the potential of novel bioelastomers, much work remains to be done. Indeed, there are very few studies of bioelastomers such as elastin and resilin [4,10]. In general, the investigation of biopolymer mechanics has largely been restricted to single-chain elasticity experiments. These have been greatly encouraged by the recent development of single molecule force spectroscopy (SMFS) which has been applied to RNA and DNA, the polysaccharides dextran and xanthan, the muscle protein Titin, and various other bio- and synthetic polymers [11].

Researchers are already beginning to build new materials from biopolymers [12], in the hope of harnessing the endless variety and complexity of their behavior, which has motivated the modeling work in this article. Our method follows the common scheme in which the simulation of a single chain generates the radial distribution function, which we use as input in the Three-chain model. We describe the helical polymer using a model recently developed by us [13]. The study of helical polymers, which exist in a helical conformation at low temperature and melt into a random-coil conformation in response to an increase in temperature or a change in solvent quality [13,14], will allow us to focus on the simplest of secondary structures, the α-helix. The transition described above produces a complex mechanical behavior that changes at around the transition temperature of a single chain. We will also compare our simulation results to the theoretical ones of Kutter and Terentjev for networks of helix-forming polymers [15].

The Monte Carlo algorithm of Wang and Landau [16] is used to simulate the homopolypeptide chain. The simulation results, in conjunction with the three-chain model, will be used to calculate the stress–strain behavior of the network, as well as the conformational properties of the constituent chains for different temperatures and degrees of strain.

This article is organized as follows. In the second section, we briefly describe our simulation protocol and the three-chain model. In the third section, we present our results for the stress–strain and thermo-elastic behavior of the network and single chain, and rationalize the effect of temperature and strain on various equilibrium properties, including the entropy of the network. Finally, we conclude the present article by summarizing the most important findings of our work and with the appropriate acknowledgements.

2. Simulation protocol and theoretical model

2.1. Model and simulation methodology

The helical polymer was modeled using the freely rotating chain model, in which each bead represents an amino acid residue. The interactions between pairs of beads were modeled with a hardcore potential energy, and the tendency toward the helical conformation was modeled using a criterion based on the concept of torsion of a curve [13,17]. Each bead that satisfied this criterion was considered to have a helical conformation and was assigned a negative enthalpy called C, which stabilizes the helical conformation. Otherwise, the bead was considered to have a random coil conformation, which was used as the reference state. We chose $C=-1300$ K, so that the helix-coil transition temperature is close to 300 K. These concepts were implemented in a Monte Carlo simulation based on the Wang–Landau algorithm [16]. The outcome of this procedure is the density of states, which we used to compute the free energy and radial distribution function of the polymer [17]. The latter is the input required by the three-chain model of rubberlike elasticity. More details about the simulation protocol and model employed can be found in Ref. [17].

2.2. The three-chain model

The three-chain model assumes that inter-chain interactions are independent of deformation and averages the free energies of three chains oriented in three orthogonal orientations, which are deformed in the affine limit at constant volume. The macroscopic deformations of the network are $\lambda_i = L_i/L_{i0}$, where L_i and L_{i0} indicate the deformed and undeformed dimensions of the network in the ith direction, respectively. For uniaxial extension the conservation of volume implies that $\lambda_x=\lambda, \lambda_y=\lambda_z=\lambda^{-1/2}$. Thus, the total free energy of a network made of ϕ chains per unit volume relative to the unstrained state is given by the equation

$$\Delta f_{\text{net}} = \phi\left(\frac{f(R_0\lambda)}{3} + \frac{2f(R_0\lambda^{-1/2})}{3} - f(R_0)\right) \tag{1}$$

R_0 is the average end-to-end distance of a chain in the undeformed state and $f(x)$ is the free energy (in units of Boltzmann's constant, k_B) of a single chain with end-to-end distance x. $f(x)$ is obtained from $f(x)=\Delta f(x)+F(T)$ where $F(T)$ is the free energy of a chain, independent of x [13] and $\Delta f(x)$ is the free energy (relative to the free chain) of a chain with end-to-end distance equal to x. The latter is given by $\Delta f(x)=-T\ln(W(x))$, where $W(x)$ is the probability distribution of the end-to-end distance obtained from the Monte Carlo simulation. Differentiating Eq. (1) with respect to λ at constant temperature gives the nominal stress of the network