



On rheology of cross-linked polymers: 1. Slippage of polymer chains and its macroscopic modeling



Victor L. Berdichevsky, John N. Herman*

Mechanical Engineering, Wayne State University, Detroit, MI 48202, USA

ARTICLE INFO

Article history:

Received 14 September 2014

Revised 20 January 2015

Accepted 30 January 2015

Available online 11 March 2015

Keywords:

Micromechanics

Rheology

Creep

Stress relaxation

Cross-linked polymers

Polymethacrylimide

ABSTRACT

A model is proposed to describe the rheologic behavior of cross-linked polymers. It is based on hypotheses of the micromechanical origin of the time-dependent behavior. Starting from the dynamics of one polymer chain, a complete thermodynamic description and a closed system of equations governing the deformation of polymers and polymer foams is constructed. The first paper of the two-paper series is concerned with the theory, while the second describes the experimental results on creep and stress relaxation in polymethacrylimide foams and compares the results with theoretical predictions.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The time-dependent behavior of solid polymers is so diverse that, at the moment, no better recipe exists to describing the material behavior other than fitting experimental results by either Volterra non-local stress–strain relations or their finite-dimensional truncations. The latter can be interpreted as a combination of springs and dashpots. Needless to say, the physics of the deformation process is completely lost in such an approach. In the case of non-linear material responses, the situation becomes much worse. The variety of nonlinear versions of Volterra relations is boundless. Therefore, it seems important to restrict the class of feasible models suggesting possible micromechanisms of the time dependence, and deriving the macroscopic relations from statistical reasoning. This is the aim of our work.

We employ a highly simplified picture of the deformation of a cross-linked polymer chain schematically shown in Fig. 1. Two ends of the chain, A and B , are pinned at cross-links. The chain is moving inside the polymer, which is composed of an ensemble of polymer chains. Some parts of the chain come close to other chains and form weak links that, in contrast to cross-links, are easily broken by deformation. The horizontal line cc' represents another chain; point C is a weak link. During elongation in the x -direction, the cross-links A and B follow macroscopic deformation. If the distance between A and B changes, point C is no longer in equilibrium; there is a non-zero force acting on C . To compensate, point C starts moving along cc' changing the overall distribution of internal forces. This is the assumed microscopic origin of the time-dependent behavior to be discussed further.

To model the behavior of point C , we assume that it is similar to the motion of a point in a periodic potential $H(x)$ under the action of a random force, see Fig. 2. The origin of the random force is the conformation motion of the polymer chain.

* Corresponding author.

E-mail address: jherman@bosalusa.com (J.N. Herman).

The assumption of periodicity is made only to make this problem treatable analytically. One obtains qualitatively similar results for the random potential as well.

We end up with a model which is schematically presented by Fig. 3. The most essential feature of the model is the highly nonlinear dashpot behavior. Statistical reasonings employed determine the dependence of the model parameters on temperature.

As will be shown, our model captures correctly the most salient feature of macroscopic response: in a stress relaxation test, the fast decay of stresses at the beginning of the process followed by a long slow evolution, and in a creep test, the fast occurring strain at the beginning of the process followed by a long slow evolution.

In Section 2, we start with a reminder of some basic facts from thermodynamics of polymer chains, which are the building blocks of our model. In Section 3, we derive the dynamic equation for polymer chains with one fixed end and one end loaded by an external force. Section 4 and Appendix B discuss in detail the problem of particle motion in a periodic potential. Section 5 derives the dynamic equation for a polymer chain, a piece of which is weakly connected to another chain. In Section 6, thermodynamic functions of a cross-linked polymer are constructed. The closed system of macroscopic equations is formulated in Section 7. Its linearized version is considered in Appendix A. In Section 8, we construct a modification of nonlinear theory that yields Treloar theory for equilibrium states. Finally, we extend the results to polymer foams in Section 9.

It can be shown that our model, up to physical interpretation of the terms involved, is mathematically equivalent in the linearized case to the model proposed by Bergstrom (1999). In the nonlinear regime, which is of major interest at least due to nonlinearity the dashpot, the models are different.

2. Some facts from thermodynamics of polymer chains

2.1. Thermodynamics of a polymer chain

The internal energy U of a polymer chain is usually assumed to be a function of temperature T only:

$$U = nu(T). \tag{1}$$

Where n is the number of monomers in the chain, and $u(T)$ is the energy per monomer, which depends on the composition of the monomer. It is essential that the internal energy does not depend on the distance R between the chain ends. Such a dependence arises in the free energy \mathcal{F} ,

$$\mathcal{F} = U - T\mathbb{S}, \tag{2}$$

through the dependence of entropy \mathbb{S} of the chain, on R ,

$$\mathbb{S} = nS(R), \tag{3}$$

where $S(R)$ is the entropy per one monomer.

Based off a detailed analysis of the stochastic model with freely rotating Kuhn segments, in what follows, we use for $S(R)$ the quadratic approximation

$$S(R) = -\frac{3}{2} \frac{R^2}{\ell^2 n^2}. \tag{4}$$

It holds, if one means by n the number of Kuhn segments, i.e. the number of segments that can be viewed as rotating independently. Accordingly, $S(R)$ is the entropy per one Kuhn segment. Total entropy of the chain is also a quadratic function

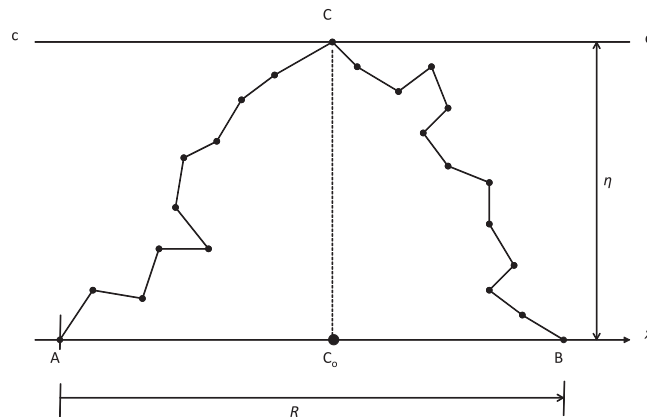


Fig. 1. A sketch of the interaction of a polymer chain with neighboring chains.

Download English Version:

<https://daneshyari.com/en/article/824701>

Download Persian Version:

<https://daneshyari.com/article/824701>

[Daneshyari.com](https://daneshyari.com)