Stress-Strain Behavior of Polymeric Elastomers

A polymeric elastomer is defined by the American Society for Testing and Materials (ASTM) as "a material that, at room temperature, can be stretched repeatedly to at least twice its original length, and, upon immediate release of the stretch, will return with force to its approximate original length". First developed in Germany in 1937, production of (polyurethane) elastomeric fibers has increased in demand over the last forty years, primarily due to the development of fibers that can move with and physically support the human body[1].

Polymeric elastomers chemically consist of long, randomly coiled domains of aliphatic polyethers or polyesters, joined by stiff regions of urethane linkages. Together, these two groups form blocks or segments on the polymer, which are soft or spring-like in the former case and hard in the latter. The soft blocks usually make up 65-90% of the molecular weight of the polymer, and are essentially unoriented in a relaxed fiber. The hard blocks provide long range molecular attractions by sharing π electrons[2]; this results in the formation of what are known as virtual crosslinks. There is some experimental evidence from both x-ray diffraction techniques and differential scanning calorimetry for the formation of these clusters. A schematic of these virtual crosslinks is illustrated in Figure 1.
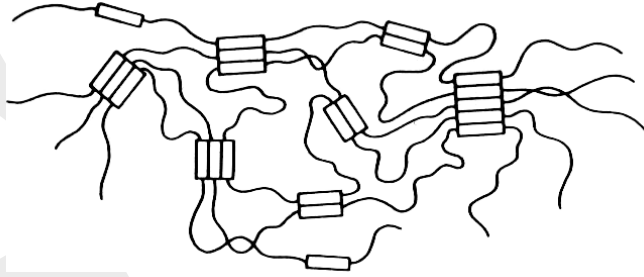

Figure 1: Virtual crosslinks formed by attractions between hard blocks in a polymeric elastomer.

What makes polymeric elastomers so useful is their unusual stress-strain behavior, which is shown in Figure 2. Upon stretching, it is immediately noted that there is a large flat region in the stress-strain curve. This essentially means that after an initial elongation, there is a region of stretching which occurs without increasing strain. The purpose of this project is to produce a model of the elastomers that can duplicate this behavior. There are two different aspects to this project. First, it is desired to produce a model that can represent an elastomer fiber immediately after production, before ever being stretched for the first time. Secondly, after formation, the polymer network will "ripen" or continue to develop while still in the production tanks. It is expected that the stress-strain behavior of a fiber after this ripening period will be different than that of a fiber immediately after formation. The model should be capable of duplicating these conditions.
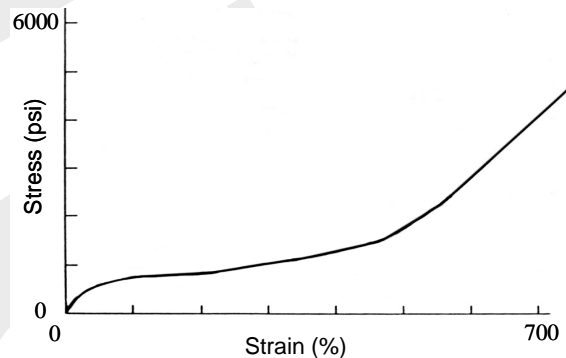

Figure 2: The unusual stress-strain behavior of polymeric elastomers.

The model used in this study consists of a lattice upon which molecules are laid down one at

Professor Marc Donohue
Department of Chemical Engineering
Johns Hopkins University

a time. The model polymers consist of two hard blocks, connected by a soft block of a specified length. Lattice sites are allowed to have multiple hard blocks on them. After randomly laying down all of the segments, the lattice is checked for percolation, which is a condition in which there is an unbroken path that connects the top and the bottom of the lattice. By an unbroken path, we mean a continuous path that is made up of polymer segments that have overlapping hard blocks. Percolation insures that if the fiber is stretched, there will be a resistance. If the system is percolated, the stress-strain behavior is calculated by replacing each polymer with a combination of circuit elements. Specifically, the voltage across the system is ramped to a specified value and the current through the network is measured.

To capture the time dependant behavior of the fiber, the system is allowed to ripen in the following manner. Hard blocks are given an attractive potential. A hard block on the lattice is selected at random. The algorithm then attempts to move that hard block to a second, randomly selected site that is within a radius from the other end of the chain specified by the length of the soft block. System energies for each location are calculated, and the proposed move is accepted or rejected according to the Metropolis algorithm. After a specified number of attempted moves, the system is again checked for percolation, and if it is, the stress-strain properties are obtained as described above. In this manner, the change in the stress-strain behavior can be obtained as a function of time.

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[1]Hepburn, C. *Polyurethane Elastomers*, 2nd ed.; Elsevier Science Publishers: New York, 1992.

[2]Couper, M. In *Handbook of Fiber Science and Technology*; Lewin, M., Sello, S. B. Eds.; Marcel Dekker: New York, 1983.

Professor Marc Donohue
Department of Chemical Engineering
Johns Hopkins University