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# The Viscoelastic Relaxation of Cross-Linked Polymer Networks

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## Summary

Theoretical interpretations of the viscoelastic relaxation behavior of cross-linked elastomers are discussed. The dangling chain retracing mechanisms of deGennes and Pearson-Helfand, which assume that the stress contribution of a dangling chain decreases as it assumes successively lower entropy configurations, are replaced by an alternative relaxation mechanism, based on the hopping model of hindered diffusion.

## Introduction

The long-time stress relaxation behavior of cross-linked elastomers has been extensively studied by Chasset and Thirion (1,2) who find that:

1. the tensile force can be factorized as a function of time and extension.
2. the tensile force decreases with time according to a power law of time.

It was originally proposed by Ferry (3) that this stress relaxation behavior originates in the diffusion of dangling chains in the presence of entanglements.

## Unentangled Loop Models

Two theoretical models of the dangling chain relaxation process have recently been put forth. Both assume that after the application of a step strain, diffusion of the free end of a dangling chain towards the fixed end of the chain occurs by a retracing or retracting process which results in the formation of an unentangled loop; that is, a chain with coincident ends having a tree structure with zero topological path.

In the deGennes model (4,5) the probability of forming an unentangled loop is estimated to be

$$P_N(\ell) = \beta e^{-\alpha N}$$

where N is the number of segments in the dangling chain and $\beta$ has a power law dependence on N (this expression can also be obtained using the model of a loop in a tube (6)). The time needed for the retracing process to be completed is assumed to be

$$T_r \sim [P_N(\ell)]^{-1} \sim \tau_1 e^{\alpha N}$$

It is argued that at time t, n of the segments of the dangling chain will have relaxed by the retracing process and that the relationship between n and t is given by the analog of the above equation

$$t \sim \tau_1 e^{\alpha n}$$

Finally, it is asserted that at time t, the stress contribution of the dangling chain is proportional to the fraction of the chain segments which has not yet relaxed, ie.,

$$\sigma(t) \sim [1 - \frac{n(t)}{N}] \sim [1 - \frac{\ln (t/\tau_1)}{\alpha N}]$$

It has been shown by Curro and Pincus (7) that the combination of the deGennes mechanism with an assumed distribution of dangling chain lengths resulting from a random cross-linking process is capable of yielding a transient stress term having the required power law time dependence.

A different analysis of the retracing mechanism has been given by Pearson and Helfand (8). They state that the continuous decrease in entropy that occurs as the free end of the dangling chain moves towards the fixed end of the chain in the retracing process creates an increasing potential field through which the free end must diffuse. It is assumed that at time t, the stress contribution of the dangling chain is proportional to the distance between the chain ends that has not hitherto been reached by the free end. This quantity is calculated using the first-passage time problem analysis for the one-dimensional diffusion of a particle in a potential field.

It has been shown by Curro, Pearson and Helfand (9) that the application of the Pearson-Helfand mechanism to a randomly cross-linked network structure can produce the desired power law time dependent transient stress term.

Both the deGennes and the Pearson-Helfand mechanisms of dangling chain retracing assume that the stress contribution of a dangling chain decreases as it adapts successively lower entropy configurations. The behavior of a dangling chain is therefore directly opposite to the behavior of a network chain whose stress contribution increases as it adapts successively lower entropy configurations. This leads us to suggest an alternative model of the relaxation of the dangling chain.

## The Hopping Model

The following dangling chain relaxation mechanism is proposed:

After the initial deformation of the dangling chain, which occurs due to the presence of entanglements along the chain, the chain relaxes by diffusing amongst and through the entanglements. The process can be viewed as a hindered diffusion, consisting of an alternation of movements, or releases, and pauses, or captures. Each movement represents a relatively rapid diffusion of the chain following its release from the constraints of a given entanglement and involves the chain assuming higher configurational entropy states. Each pause represents a relatively slow diffusion of the chain while it is still subject to the constraints of a given entanglement and involves the chain assuming lower configurational entropy states as it disentangles itself. The overall relaxation process therefore involves passage over a series of free energy barriers (saddle points).

This relaxation mechanism is mathematically expressible by the continuous-time random walk or multiple trapping model of itinerant diffusion (10-12). The important quantity in the model is the waiting or hopping or pausing time distribution, $\Psi(t)$. In the classical random walk or diffusion model, $\Psi(t)$ has the form $\exp(-\lambda t)$ and, as a result, there is a finite average time $\langle t \rangle$ between movements. In the hopping model, the pausing time distribution has the form

$$\Psi(t) \sim t^{-1-\alpha}$$

and, because of the long inverse power tail, the mean pausing time $\langle t \rangle$ is infinite. This means that movements do not take place at any finite constant rate; but instead, are bursts separated by pauses of various durations. As the magnitude of $\alpha$ decreases, the pausing times become longer and, as a result, diffusion becomes more hindered.

This model of hindered diffusion leads to a relaxation function of the form

$$\Phi(t) = e^{-\beta_1 t^{\alpha_1/2}}$$

This is the one-dimensional form of the well known Kohlrausch-Williams-Watts function which has been used to describe various relaxation processes in many materials, including polymers.

We are presently examining the ability of the KWW function to fit experimental stress relaxation data. For the purpose of comparison, we are also fitting the empirical power law form $\Phi(t) = \beta_2 t^{-\alpha_2}$. Our preliminary results (13) indicate that both two-parameter functions fit the data of Chasset-Thirion equally well, yielding $\alpha$ values in the same range ($.1 < \alpha < .3$).

Finally, while the proposed general mechanism of dangling chain relaxation by a hindered diffusion process consisting of a series of sporadic starts and stops as the chain wends its way around and through obstacles that are created by the entanglement of the chain with other chains and itself seems quite reasonable, it remains to develop a more specific model of the process and to account for the experimentally observed values of the quantity, $\alpha$. We are presently pursuing this goal.

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