



# Influence of crosslinking functionality, temperature and conversion on heterogeneities in polymer networks



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## ABSTRACT

Crosslinked polymer formation commonly occurs when two or more multi-functional precursors react to form a three-dimensional network. The resulting networks may contain a significant number of topological imperfections such as loops or dangling ends when formed using crosslinkers with high functionality or when crosslinking at high temperatures. We employ molecular dynamics simulations to analyze these topological imperfections in coarse-grained networks generated from precursors consisting of ‘chain extenders’ composed of two beads (dimers) and a crosslinker of functionality  $f = 3$  or 6 for a wide range of crosslinking temperatures and final conversions. It is shown that these imperfections result in networks in which the number of elastically active chains, the cycle rank and the number of elastically active junctions is smaller than predicted by the Miller–Macosko theory. Such defects must adversely affect the mechanical properties, resistance to solvent swelling and, possibly, the long-term protective properties of polymer networks.

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## 1. Introduction

Crosslinked network polymers, which include epoxies, polyurethanes, rubbers, etc., are an extremely valuable class of materials. Any attempt to characterize or predict the overall properties or nature of a crosslinked network usually relies on the statistical theories of Flory, Manfred Gordon and others. In these approaches a network is idealized as a collection of chains that can be described using a Gaussian distribution of their lengths [1–3]. They lead to more or less simple algebraic equations that are very useful in describing the overall mechanical properties or swelling in solvent and we are accustomed to using crosslink chain density or molecular weight between crosslinks as averaged, single values to gauge the likely properties of a crosslinked polymer or to compare with estimated values from the known chemistry used to make the network.

Crosslinked networks are used in high performance composites, protective coatings, sealants, caulks, gaskets etc., but unfortunately, adhesive joints may fail unexpectedly and rust spots appear at unplanned places on a painted metal part and joints may leak.

Exposure in service leads to molecular bonds being broken and material loss, which results in the deterioration in properties. A better understanding of the network at the start of its service would provide more insight into later durability. A coating 1 cm<sup>2</sup> in area and 50 μm thick has a volume of 5 × 10<sup>+21</sup> Å<sup>3</sup>. If a typical atom has a volume of approximately 1 Å<sup>3</sup>, then there must be a considerable number of local atypical network configurations. These imperfections, created during the crosslinking process, can provide points of access for corrosive penetrants such as water or salt even before environmental degradation.

Such molecular scale heterogeneities are difficult or impossible to characterize experimentally, but simulations can provide a detailed understanding of local network structure and how it depends on precursor architecture and crosslinking protocol. For example, Duering et al. [4,5] studied tetra-functional rubber networks with strand lengths ranging from 12 to 100 monomers formed in a dynamic crosslinking process; they used a cluster search algorithm to determine the number of active strands and crosslink junctions, and used a ‘burning’ method from percolation analysis to determine the gel fraction of chains with no free ends and the fraction of elastically active beads. This microscopic characterization of the networks allowed them to compare their results to the predictions of rubber elasticity theories. In the present work we employ a similar approach to determine not only network

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parameters, including the number of elastically active chains and crosslinks, and cycle rank, but also to quantify the occurrence of ineffective looped molecular chains and dangling ends and pendants in the more highly crosslinked networks that are typical of high performance coating and composite binders. Although such loops and dangling ends are a natural consequence of the random crosslinking process involving a huge number of reacting molecules, they will be referred to here as imperfections or defects since they are locations where the anticipated crosslinking did not take place and thus necessarily cause some level of diminished performance.

## 2. Background

There is a considerable literature on calculating the properties of crosslinked networks from the statistical distribution of chain lengths between junctions. This will not be reviewed here because many useful books and reviews can easily be found. However, even in the development of these theories it was realized that unreacted chain ends, ineffective loops and other imperfections must be accounted for [1,6], and that spatial neighbors might not be directly connected via the network [7]. Flory used the concept of cycle rank, from graph theory, to express the concentration of independent, elastically active loops in a network as distinct from the concentration of network chains, thus accounting for the elastically ineffective chains leading from such crosslinks.

In “phantom” networks, the shear modulus,  $G_{ph}$ , in the rubbery regime is proportional to the cycle rank,  $\xi$ , which is the number of complete loops in the network,

$$G_{ph} = \xi k_B T / V, \quad (1)$$

where  $T$  = temperature,  $V$  is the volume of the system and  $k_B$  is Boltzmann's constant.

The earlier, simpler “affine” model for rubber elasticity considers all the network chains to be effective and calculates the modulus as

$$G_{aff} = \nu_e k_B T / V. \quad (2)$$

The cycle rank,  $\xi$ , is the difference between the number of elastically active chains,  $\nu_e$ , and the number of elastically active junctions,  $\mu_e$ . In an ideal network, the cycle rank can be expressed in terms of the number of effective chains and the functionality of the network junctions [8]:

$$\xi = \nu_e \left( 1 - \frac{2}{\phi} \right), \quad (3)$$

where  $\phi$  is the functionality of the crosslink junctions (3 or 6 here). An oft quoted example is that  $\xi$  is simply  $\nu_e/2$  for a tetra-functional network [9].

The Macosko–Miller (MM) theory uses the concentration and functionality of the precursor reactants as input and predicts values for the chain length between crosslinks, cycle rank, etc. that can then be used to calculate modulus in either the “affine” or “phantom” model of networks. It employs a recursive calculation that is readily codified so that short, versatile computer programs have been written [10–12] that allow investigation and comparison of several types of crosslinking systems. The recursive calculations used in this approach have no explicit recognition of heterogeneities in a network. These calculations give very useful estimates of average properties that correlate well with experimental values of related properties. Other work with similar goals has targeted a number of specific combinations of reactants [13].

Molecular dynamics simulations [14] of rubbery materials have shown that the technique is very useful in discovering the variations possible in crosslink density, molecular chain length between crosslinks, and the effect on elasticity of long dangling chains and varying sizes of loops. The work here examines such heterogeneities in much more highly crosslinked networks and uses the coarse-grained approach to examine topology, independent of specific chemical choices. MM calculations are used to provide the characteristic values of elastically active chain density, cycle rank etc. for an ideal network, corresponding to the systems used here in order to compare with the MD simulation results and quantify the effect of topological defects.

## 3. Model and simulation method

Simple coarse-grained networks studied here are generated from precursors consisting of ‘chain extenders’ composed of two beads (dimers) and a crosslinker of functionality,  $f = 3$  or 6. These, and similar models, have been used by Stevens et al. [15–17] to study interfacial fracture in highly cross-linked polymer networks and by us to determine the influence of crosslink density on the structural and thermo-mechanical properties [18] and void formation [19] in crosslinked networks. As in these earlier investigations, the 6-functional network is formed with one chain extender molecule already bonded to the 6-functional crosslink node (bead) prior to starting the dynamics. It has been shown that this pre-bonding has no noticeable effect on the resulting network connectivity [19]. In the 3-functional model the crosslinker consists of a central 3-functional bead connected to three beads, each having a single reactive functionality.

All non-bonded beads interact with a Lennard–Jones (LJ) potential,  $U(r)$ , which has a cut-off at a radius,  $r_c = 2.5\sigma$  and is shifted upward so that the potential is equal to zero at  $r_c$ :

$$U(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c) & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c \end{cases}, \quad (4)$$

Where

$$U_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (5)$$

$\sigma$  is the length scale in the LJ potential,  $r$  is the distance between bead centers and  $\epsilon$  is the energy parameter. This potential models the van der Waals attractive forces between all the beads and has a strong repulsive core that defines the extent of the bead. Covalent bonds between beads that were pre-existing or formed during reaction are described using a potential that prevents chain crossing. This bond potential is the sum of the purely repulsive LJ interaction with a cutoff at  $2^{1/6}\sigma$  (the minimum of the LJ potential) and a finite-extensible nonlinear elastic (FENE) attractive potential.

$$U_{FENE}(r) = \begin{cases} -0.5R_0^2 k \log_e \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] & \text{for } r < R_0 \\ \infty & \text{for } r \geq R_0 \end{cases} \quad (6)$$

where  $k = 30\epsilon/\sigma^2$  and  $R_0 = 1.5\sigma$  as used previously [18,19]. The MD simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [20].

As before, stoichiometric mixtures of crosslinkers and dimers were used with an overall system size of 11,424 beads. Before crosslinking, the mixture of precursors is equilibrated at a high temperature,  $T = 1.0$ , and at zero load using a Nosé–Hoover thermostat and barostat with a time step of  $0.005 \tau$ , where  $\tau = \sigma(m/\epsilon)^{1/2}$  is the Lennard–Jones unit of time. After equilibration, the network

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