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.

Keywords: Network, defect, molecular dynamics

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 cm² in area and 50 μm thick has a volume of 5 x 10⁺²¹ Å³. If a typical atom has a volume of approximately 1 Å³, 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 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, ξ , which is the number of complete loops in the network,

$$G_{ph} = \xi k_B T/V,$$

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, ξ , is the difference between the number of elastically active chains, ν_e , and the number of elastically active junctions, μ_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 ϕ is the functionality of the crosslink junctions (3 or 6 here). An oft quoted example is that ξ 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, 11, 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 :

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

where

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

σ is the length scale in the LJ potential, r is the distance between bead centers and ε 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.

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

where $k = 30\varepsilon/\sigma^2$ 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 0.005τ , where $\tau = \sigma(m/\varepsilon)^{1/2}$ is the Lennard-Jones unit of time. After equilibration, the network is dynamically crosslinked at constant temperature and zero load. After each period of 100 time steps (0.5τ) potential bonding partners that have open functionalities and are separated by a distance less than 1.3σ are identified, and the nearest potential bonding partners are cross linked with a probability of 10%. This low probability allows the network to form fairly slowly and reduce bonding heterogeneity.

Two different cross linking scenarios were studied. In the first, crosslinking was performed at several temperatures between $T = 1$ and $T = 0.1$, since in practice coating and composite polymers are cured at various temperatures, including many crosslinked systems that must be cured and used at ambient temperatures, e.g. epoxy adhesives and coatings, polyurethanes, alkyd paints, etc. Conversion was continued until it was increasing slower than logarithmically with the number of crosslinking time steps. Below the eventual glass transition, mobility was restricted and conversion slowed rapidly; at temperatures above the glass transition there was enough mobility that conversion proceeds more readily. Only when the temperature was close to the glass transition was there a need to continue to crosslink for longer time. At high temperatures, high conversions are achieved in the 3-functional system in fewer time steps than for the 6-functional system because fewer crosslinks need to be formed.

For comparison, following a very common, simpler simulation approach, crosslinked networks were prepared with the same range of conversions but crosslinked at the highest temperature, $T = 1.0$ (the temperature at which the precursors were equilibrated), at which all the components have a high degree of mobility. Having two approaches to curing provides insight into the effect of cure temperature, since it is well known that mechanical properties of crosslinked polymers exhibit a strong dependence on the curing temperature.

To analyze the resulting networks we developed a network search algorithm following Refs. [5, 9, 21] to determine the number of elastically active junctions, μ_e , where an active junction is a crosslink site that is connected by at least three paths to the gel; the number of elastically active chains, ν_e , where an active chain is a path that is composed of chain extender beads and inactive junctions but that is terminated by active junctions on both its ends, and the number of elastically active beads, which includes all beads that are located in either the active junctions or the active chains, as well as a number of local quantities such as the number of dangling chains and primary loops. To identify the elastically active chains and junctions, we first identify the largest cluster (the backbone or gel) which forms the network, using a depth-first search. The backbone is then searched using a ‘burning’ algorithm [21] to characterize the connectivity of the network junctions, i.e. whether they connect to the gel, form a loop back to the cross linker or end without connecting to the gel (tree pendants). When determining the elastically active network, nodes which would divide the network into pieces if removed need to be excluded (along with the rest of the pendant) because the omitted nodes are not elastically active. The connectivity of the remaining junctions is the number of crosslinks that connect to the gel. Only those links which have at least a functionality of three are active links. The curvilinear distance between them is the length of the active strands.

4. Results and Discussion

4.1 Crosslinking

As explained above, two crosslinking scenarios were considered. In the first, crosslinking is performed at temperatures ranging from $T = 1.0$ to $T = 0.1$, starting from equilibrated precursor configurations. Five independent realizations are simulated at each temperature using the

procedure outlined in the previous section; unless otherwise noted, the data presented in the following is the average of results for the five independent realizations.

Figure 1: Conversion as a function of time while cross-linking at fixed temperature and zero load. Data for $T = 1.0$ to 0.1 in increments of 0.1 are shown. The data on the diagram for the 3-functional system (a) show the conversion over 12 million timesteps and that for the 6-functional system (b) over 6 million timesteps.

Fig. 1 shows the conversion as a function of the number of time steps when crosslinking at temperatures ranging from $T=1$ down to $T=0.1$ in increments of 0.1. Earlier simulations of these models using the same crosslinking protocol at $T = 1.0$ determined the gelation points given in the figure. Both systems gel quite early in these simulations. At the highest temperatures, $T > 0.6$, the conversion increases rapidly and saturates on the time scale of our simulations for both models. In the 3-functional system the conversion at the intermediate temperatures, $T = 0.4$ and 0.5 , continues to increase logarithmically (or slower) with time, even after 12 million crosslinking time steps. At the lowest temperatures, $T=0.1, 0.2$, and 0.3 , the conversion effectively saturates a short time after the gel point is reached. The glass transition temperatures of the 3-functional system were found to be approximately 0.45 regardless of crosslinking temperature or resultant conversion. Systems crosslinked at the lowest temperatures are therefore deep in the glassy phase and further conversion can be expected to proceed only slowly, if at all. The behavior we observe at intermediate temperatures is consistent with what one would expect near T_g .

For the 6-functional system there would still be a slight increase in the conversion after 6 million time steps when crosslinking at temperatures less than or equal to $T=0.5$, but conversion increases more slowly with time compared to the 3-functional model, especially at intermediate crosslinking temperatures. The glass transition temperature is somewhat higher for this model, increasing from a T_g of approximately 0.46 for the lowest conversion to approximately 0.49 at the highest conversion. The higher functionality of the crosslinker beads in this case results in a lower gel point and makes the system less sensitive to mobility changes around the glass transition temperature. As would be anticipated, in both cases the final conversion decreases as the curing temperature is decreased.

The influence of curing temperature on final conversion is summarized in Fig. 2. This and the results in Fig. 1 show that the simulations reflect experience with actual crosslinking polymers [22, 23]. Reactive coatings are often cured at temperatures above their eventual glass transition temperature, to ensure a useful degree of conversion in the manufacturing process, since curing

below T_g would be too slow and incomplete. Even then, it is a common experience that curing continues for periods of weeks or longer after the initial curing. In practice, it may be possible to alleviate such problems by using a more highly functionalized system that provides network integrity and less sensitivity to the temperature and time of cure, as the 6-functional system appears to do here. Always, there is a compromise between time and temperature, with the realization that systems seldom cure completely. In these simulations, as in practice, curing was continued until the conversion had reached a value that would not change enough to significantly affect other parameters.

Figure 2: Conversion after cross-linking for twelve million time steps (3-functional) and six million time steps (6-functional) at fixed temperature and zero load.

4.2 Structural Properties

Fig. 3 shows the concentration of elastically active chains, ν_e/N (red), where N is the number of nodes in the simulation, and the concentration of elastically active junctions, μ_e/N (blue), as a function of conversion. The values are normalized by the number of beads to remove the system size dependence. In fact, the density of the crosslinked systems is very close to 1 in the system of units used here, so that if volume concentrations are desired, they are practically indistinguishable from the number fractions used in the graphs. The square symbols are data for systems crosslinked at different temperatures and the triangles are results for crosslinking at $T = 1.0$. The insert shows the same results as a function of the crosslinking temperature.

Figure 3: Number of elastically active chains, ν_e , and number of elastically active junctions, μ_e , as a function of the conversion or temperature. (a) 3-functional system, (b) 6-functional system. Square symbols are for systems crosslinked at different temperatures; triangles are results for crosslinking only at $T = 1$. The insert shows the same data plotted as a function of crosslinking temperature. Values are expressed as concentrations with respect to the number of beads (11424) in the simulation.

The curves for the 3-functional system are monotonic, but one striking feature in the 6-functional system is that both ν_e and μ_e decrease as the crosslinking temperature is increased from $T = 0.7$ to $T = 1.0$. As will be seen later, this is due to the number of primary loops, i.e. minimal three bond loops that come back to the same crosslinker node, which increases rapidly with temperature in this regime, even though the overall conversion remains essentially constant. At high temperature, the high mobility allows the free end of the short chain extender to have a good chance of looping back and reacting with another available functionality on the same node where its other end is already attached. One consequence of the increased number of primary loops formed at high temperature is that both ν_e and μ_e are significantly larger in 6-functional networks crosslinked at lower temperature than those crosslinked to the same conversion at $T = 1$. In this case, for a given level of conversion, the networks are better linked, and more homogenous if they are formed at a lower temperature (although, in practice, this would require much more time). Apart from this, both ν_e and μ_e decrease approximately linearly with decreasing conversion. There is a much less striking difference in the 3-functional system between the two crosslinking scenarios. Data for the reduced cycle rank, ξ/N , calculated using $\xi = \nu_e - \mu_e$, will be presented later, when these results are discussed in more detail.

It should be noted that loops here are an undesirable, elastically ineffective, outcome of the random processes that produce the final topology. Elsewhere, work on networks has dealt with other types of loops, or “cyclisation”, due to deliberate chemistry designed to form the elastically effective cycles that form a strong network [24].

The molecular weight of chains between crosslinks is a quantity often used to characterize the crosslinking density of a network because it can be related to the chemical composition of the reactants used to make the network. In an ideal network it is directly proportional to the inverse of the number of elastically active network chains. For non-ideal networks, such as those studied here, the molecular weight, or length, of elastically active chains is not so easy to determine. Results for the average length (defined as the number of bonds or links) of elastically active chains as a function of the conversion and crosslinking temperature (insert) are shown in Fig. 4.

Figure 4: The average length (number of bonds or links) of elastically active chains as a function of the conversion, (a) 3-functional system (b) 6-functional system. The insert is a plot of the same data but as a function of the crosslinking temperature. Filled circles are for systems crosslinked at different temperatures; open circles are results for crosslinking only at $T = 1$.

In both curing regimes, for both systems, the chain length diminishes as curing temperature increases. The length of elastically active network chains increases monotonically with decreasing conversion, due in part, to the reduced coordination number of elastically active nodes at lower conversions. The two curing regimes produce much the same results for the 3-functional system. In contrast, the 6-functional networks crosslinked to a fixed conversion at $T = 1.0$ have somewhat longer chains than those crosslinked at lower temperatures. In this case, the difference in the average chain lengths for the two crosslinking scenarios is due to the significantly larger number of primary loops formed when the crosslinking is performed at the high temperatures, even at lower conversions.

Figure 5: Frequency histogram of the number of crosslinker junction connections to the gel as a function of the crosslinking temperatures (a) 3-functional system (b) 6-functional system. The arrows show how the direction of the temperature variation from $T=0.1$ to $T = 1.0$. Note the shift to lower coordination numbers as T diminishes. For the 3-functional system a gap occurs between $T = 0.4$ and 0.5 .

Fig. 5 shows how the coordination number of junctions (number of connections to the gel) in the backbone changes as a function of the crosslinking temperature. The upper bound on the sum of the frequency values at a particular temperature will be the number of crosslinkers originally present in the precursor mixture, i.e. 1632 [19].

Behavior in the 3-functional system is comparatively simple. At crosslinking temperatures below $T = 0.4$, mobility restrictions seem to limit the possibility for additional connections to the gel. There is a substantial change in behavior when the crosslinking temperature is above 0.5 , where, as the curing temperature increases, it becomes more likely that all the functionalities on each crosslinker have an opportunity to react. This was discussed previously in relation to the conversion progress at the various temperatures since, as noted, the eventual T_g of this system is 0.45 [19].

The behavior in the 6-functional system is more complex. For high conversions there is a strong oscillation in frequency of connections, with 4-fold and 6-fold coordinated vertices comprising most of the junctions. Correspondingly, the numbers of 3- and 5- fold coordinated junctions are small. In addition, the number of 6-fold coordinated vertices increases as the crosslinking temperature is reduced from $T = 1$ to $T = 0.7$. The reason for this is the large number of primary loops in networks crosslinked at high temperatures, see Fig. 6. Above $T = 0.5$ there is a comparatively large increase in the numbers of crosslinked nodes which are either 4 or 6-fold connected, because either there are six paths to the gel or there is a primary loop formed on a

crosslinker along with four paths to the gel. In particular, this means that the density of 5-fold connections must decrease. At lower crosslinking temperatures, the coordination number is more broadly distributed with few achieving complete 6-coordination.

As the cross linking temperature is further reduced, the total coordination number of the junctions decreases, along with the number of primary loops, so the frequency of 4- and 6-fold coordinated vertices continues to decrease while the number of vertices with lower coordination number increases. Finally, when crosslinking at the lowest temperatures, 3-fold coordinated junctions are the most prevalent.

4.3 Local Defects

The two principle network defects that are local in nature are dangling chain ends and primary loops. Both are associated with a single crosslink site or network junction. A simple dangling chain occurs when one chain extender is bound to a crosslinker molecule at only one end. It is the shortest pendant which can occur. A primary loop occurs when one chain extender molecule makes both bonds to a single network junction. A useful quantity to consider is the effective functionality, f_{eff} , of a network junction [18, 19]. It is defined by

$$f_{eff} = [\text{bonds made}] - 2 \times [\text{primary loops}] - [\text{dangling chains}]. \quad (7)$$

f_{eff} is the number of bonds of a crosslink junction that lead to neighboring crosslink sites. This can be expressed as a fraction of the nominal functionality for each system (see later). Simulation results for the number of dangling chains and primary loops on the network backbone (the gel) as a function of conversion are shown in Fig. 6.

Figure 6: The number of dangling ends and minimal loops per network junction on the gel backbone as a function of the conversion, (a) 3-functional system (b) 6-functional system. Filled circles are for systems crosslinked at different temperatures; open circles are results for crosslinking at $T = 1$

For the 3-functional system, the two crosslinking scenarios yield approximately the same results, with the number of dangling chains diminishing to low values as the conversion increases. As conversion increases, of course, there are increasing chances for primary loops to be completed. However, even near 100% conversion, fewer than 10% of the junctions have a primary loop (and there are only approximately 2% of junctions with a dangling chain). One should remember that

a 3-functional junction, if two of its functionalities are taken up with a minimal loop, forms a pendant chain.

Circumstances in the 6-functional system are more interesting. Again, for large conversions, primary loops are much more prevalent than dangling chains. Here, at the highest conversion studied, over three quarters of the 6-functional network junctions have a statistical chance of bearing a minimal loop. There is a more or less linear decrease in the number of loops with conversion when crosslinking at $T = 1$. In the other scenario, when the crosslinking temperature is decreased from $T = 1.0$ to $T = 0.8$ the number of loops decreases extremely rapidly (at approximately the same value of conversion); for lower crosslinking temperatures the number of primary loops decreases much more slowly as conversion decreases. In fact, the rate of change in the number of primary loops with conversion in this regime is parallel for both crosslinking scenarios, albeit with an appreciable offset. These results indicate that crosslinking at high temperatures results in a large number of primary loops very early in the crosslinking process, possibly well before the gel point. The number of primary loops in short chain thermosets, when crosslinking at high temperatures (i.e. rapidly), has significant implications for network quality and resultant durability. These results, and those for larger, non-local defects [19], show that network defects increase with conversion and could explain the experimental observations that water absorption in some coatings increases with degree of crosslinking [25] because water would find easier ingress in the presence of a greater number of defects. In the current simulations, at the highest conversion for 6-functional system, each junction has a $\sim 75\%$ chance of having a primary loop, which would then reduce it to 4-functionality, and there is a $\sim 10\%$ chance that a dangling end is attached to it.

Regardless of the nature of these imperfections, they are all places where the network connectivity is reduced. One could expect that an external penetrant with molecules that are equivalent to a few beads in size or less would be able to diffuse or percolate more rapidly near these features than if the network were ideally formed. These, and larger scale defects thought to permit cavitation under stresses in service [19], would provide the postulated nano-scale features [26] where absorbed water would be located and also contribute to the formation of hydrophilic pathways through the polymer.

Figure 7: The number of (a) elastically active crosslink junctions in the gel (as a fraction of the original number of crosslinker precursors) and (b) the fractional effective functionality of crosslinks in the gel, both as a function of the conversion at the different crosslinking temperatures.

Fractional effective functionality (Eq. 7) is shown in Fig. 7 as a function of the final conversion together with data for the number of elastically active nodes, expressed as a fraction of the initial number of crosslinkers. Both quantities are reduced by loops and pendant chains and display what one might expect from the previous discussion. The 3-functional system retains a greater fraction of its functionality and elastically active junctions at high conversion. However, the 6-functional system has a greater fraction of its junctions elastically active at lower conversions because each junction has 6 possible pathways out instead of 3. After increasing somewhat as the crosslinking temperature is decreased from $T = 1$ to 0.7, the effective functionality for the 6-functional system decreases smoothly with decreasing conversion. Most of this decrease is because network junctions form fewer bonds as the crosslinking temperature decreases. It is interesting to note that that value for the fraction of the overall concentration of nodes that are elastically active is numerically similar to the fractional effective functionality for the 6-functional system.

4.4 Comparison with Miller-Macosko Theory

Building on earlier work by Flory [2, 27], Stockmayer [28, 29] and Gordon [3], Miller and Macosko (MM) [10, 12, 30, 31] developed their method for deriving average properties of branching polymers based on the theory of stochastic branching processes. Their approach employs the same ideal network assumptions as Flory: all functional groups of the same type are equally reactive; all groups react independently of one another, and no intramolecular reactions occur in finite species. The presence of intramolecular loops is not accounted for. MM calculations were used to model the systems investigated here, and Fig. 8 shows the predicted distribution in coordination number of the crosslinker nodes as a function of the conversion.

Figure 8: Miller-Macosko theory results for the number of connections to the gel from junctions as a function of the crosslinking temperatures, (a) 3-functional system (b) 6-functional system. The results are for conversions of 0.82, 0.86, 0.90, 0.94, 0.99 for the 3-functional system and 0.98, 0.95, 0.9, 0.8, 0.75 and 0.7 for the 6-functional system.

The predictions from MM are reasonably representative of the simulation results for the 3-function system. Comparing with the simulation results in Fig. 5, we see that whereas the MM approach predicts a monotonic increase in frequency with coordination number at large conversions, simulation data shows strong oscillations for the 6-functional case. The primary reason for this difference is the preponderance of primary loops. As can be seen in Fig. 6, over 75% of the junctions have a primary loop at the highest conversions, which greatly reduces the

number of 5- and 3-fold coordinated junctions. However, the number of primary loops decreases rapidly at lower conversions, and there is good qualitative agreement between the two results at low conversions.

MM theory and molecular dynamics simulation results for μ_e/N , ν_e/N and the reduced cycle rank as a function of conversion are compared in Fig. 9.

Figure 9: Comparison of the predictions of the Miller-Macosko theory (dashed line) for the number of elastically active chains, ν_e , (red), the normalized cycle rank, ξ , (green), and the number of elastically active junctions, μ_e , (blue) with simulation data; (a) 3-functional system (b) 6-functional system. All quantities are expressed as a fraction with respect to the total number of beads used in the simulation. Open squares are data obtained when crosslinking at different temperatures, and the open triangles are data after crosslinking at $T = 1$.

The results from the simulations for elastically active chains, ν_e , and number of elastically active junctions, μ_e , are the same data as presented in Fig. 3, with the addition of cycle rank calculated from their difference.

Simulation results for these quantities are significantly lower than predicted by MM theory, again due to the large number of primary loops not accounted for in theory. Because the number of primary loops decreases rapidly at lower conversions, the discrepancy with the molecular dynamics simulations is less at lower conversion. It is interesting to note how the discrepancy between theory and simulation is quite large for models with short chain extenders (meant to model rigid crosslinked polymers), as here, because short chain extenders are much more likely to form minimal loops. Simulations of long chain randomly crosslinked polymer networks [5] yield results which are much closer to the theoretical predictions.

The simulation results for ν_e , μ_e , and ξ for the 3-functional system are all approximately 80% of the value predicted by the MM theory at high conversion. Thus, the rubbery modulus of the systems produced by molecular dynamics would have 80% of the value predicted by MM, regardless of whether one used ν_e to calculate it from the affine network theory or ξ in the phantom network theory; in the same vein, the swelling in solvent of the simulated network would be more than that predicted by the MM calculations. Equation 3 predicts that for a 3-functional system the cycle rank, ξ , should be given by $\nu_e/3$ in a perfect network. The molecular dynamics results for the 3-functional system are close to this ratio.

For the 6-functional system the discrepancy between simulation results and MM calculations is greater. Simulation results for the cycle rank increase as the crosslinking temperature decreases from $T=1$, reaching its highest value at $T = 0.7$; its subsequent decrease with conversion mirrors that of the number of elastically active nodes and chains, as discussed earlier. At high conversion the cycle rank is 56% of that predicted by the MM calculations because ν_e is substantially lower, but μ_e is not smaller by the same proportion. As discussed before, this difference is due to the greater number of minimal loops when the network is crosslinked at high temperatures. The value of elastically active chains, ν_e , from MD simulations is approximately 70% of the MM value and the value of the elastically active junctions from simulations is 84% of the value from MM, at the highest conversion. Depending on whether one is exploring the use of the affine network theory or the phantom theory, rubbery modulus would be either only 70% or 56% of the expected result. The ratio between simulations and MM results changes as conversion changes, in contrast to results the 3-functional system where the ratio remains essentially constant. The cycle rank in the 6-functional networks is comparatively higher than the concentration of elastically active junctions, as expected, and in contrast to the 3-functional system. For a 6-functional system, Eq. 3 predicts that the cycle rank, ξ , should be 67% ($2/3$) of the value of ν_e in a perfect network whereas at the highest conversion, the cycle rank from simulations is 57% of the value for the concentration of the elastically active network chains. These simulations indicate that mechanical modulus will be reduced more, and swelling will increase over predictions of the MM calculations for the 6-functional system, even more than for the 3-functional system. If swelling is more likely due to the increase in the number of defects at higher levels of conversion, it means that polymer density measured in dilatometers or density gradient columns that use water or solvent could give slightly low results at high levels of conversion [32 - 34].

The lower functionality system with the longer chains between junctions (Fig. 5) is not an “ideal” network, but by comparison, it conforms more closely to expectations.

5 Conclusions

Polymer networks are unlikely to form in an ideal fashion throughout but, depending on circumstances, may have an appreciable number of topological heterogeneities that may substantially affect their performance and durability. Statistical network theories that are usually used to understand and characterize crosslinked networks provide information only about the average properties of a polymer network. A natural limitation of these approaches is that they do not include steric effects, such as reactive groups becoming isolated and thus unable to react, nor do they include the possibility of a reactant molecule forming a loop back onto the same crosslink junction. For example, Miller-Macosko calculations predict a monotonic increase in the probability that junctions are fully connected to the gel at large conversions, but these simulation data show strong oscillations in the number of chains leading to the gel from a crosslinker node. The primary reason for this difference is the formation of primary loops. In particular, for the 6-functional system studied here, molecular dynamics simulations show that 75% of the junctions have a primary loop at the highest conversions, which greatly reduces the number of 5- and 3-fold coordinated junctions. The number of primary loops decreases rapidly at lower conversions, and there is good qualitative agreement with MM calculations at low

conversions. This behavior is not observed in the 3-functional system so that, as might be expected, the simulations results are in much better agreement with MM calculations.

The simulations show that the number of elastically active chains, the number of elastically active junctions and thus cycle rank are reduced by the occurrence of loops and pendants. The effect is particularly striking in the 6-functional model. As the crosslinking temperature is reduced from $T = 1$ there is a rapid decrease in the number of primary loops with essentially no change of conversion until starting at a crosslinking temperature of $T = 0.7$, there is a more gradual decrease in the number of loops with conversion. At the lowest crosslinking temperatures studied, however, there is still a 40% chance that each crosslinker has a primary loop. When crosslinking at $T = 1$ there is a parallel decrease in the number of loops with conversion, albeit with a significant offset. In contrast, the number of dangling chains decreases essentially linearly with conversion in both crosslinking scenarios so that at the highest conversions, there is only about a 10% chance that a crosslinker node has a dangling chain. As a result, both ν_e and μ_e are significantly larger in networks crosslinked at lower temperature than those crosslinked to the same conversion at $T = 1$, indicating that crosslinking at high temperatures results in a larger number of primary loops very early in the crosslinking process, possibly well before the gel point. MD shows that a lower curing temperature might achieve a better-connected network, although this may not be practical in reality due to the significant increase in curing time that would be necessary to achieve high conversion, and thus good properties, at lower temperatures.

The situation is somewhat simpler in the 3-functional system. In this case, both ν_e and μ_e decrease as the crosslinking temperature is increased from 0.7 to 1.0, with a corresponding decrease in the cycle rank, again due to the number of short loops. There is a much less striking difference in the 3-functional system between the two crosslinking regimes, and results for ν_e and μ_e are much closer to the predictions of MM theory; the cycle rank is the same fraction of ν_e as it would be in an ideal network. In this case, fewer loops can form after a functionality on a crosslinker bead has been consumed by a reaction because there are only two of its sites remaining to compete with unreacted sites on neighboring beads. In contrast to the 6-functional model, network properties such as the number of elastically active chains, the cycle rank, and even the number of dangling ends and primary loops were found to depend primarily on the final conversion, and not the crosslinking temperature.

Primary loops and unreacted chain ends substantially reduce the number of elastically active chains and the cycle rank, and could have a significant effect on the long-term durability and protective qualities of a crosslinked polymer. Thus, the rubbery modulus will be reduced, and solvent swelling will be increased (and measured density may be diminished) over ideal network expectations. Loops and pendants are locations where the network is not connected, so penetrant molecules that are a few beads in size or less, e.g. water and corrosive ions, would be able to pass more easily, absorb more and swell the network more than if the network were ideally crosslinked.

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