A Mesoscale Approach to Characterize Material Properties of Polymeric Media

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Over time, changes in the network microstructure of filled or reinforced elastomers due to chemical bond scission and crosslinking can alter the physical properties of these materials. In particular, chemical aging can strongly affect the elastic properties of the network through modifications to the network as well as changes in the interactions between the polymer and filler particles. Furthermore, changes in the mechanical properties can depend on the strain history. For example, an elastomer that undergoes additional crosslinking in a state of strain can acquire a permanent set or deformation when the stress is removed. The ability to accurately predict the mechanical behavior of these materials through robust models to assess lifetime performance in different environments is essential. We have adopted a mesoscale network model that retains information about the microstructure and is not limited by some of the assumptions found in constitutive descriptions.

Project Goals

In our second year, our goals were to improve the understanding of the robustness of the network model by 1) evaluating the model's applicability to materials of programmatic interest (filled elastomers and foams); 2) adding the capability to manipulate the microstructure in a predetermined manner; and 3) examining the relationship between microstructure, material response, and aging parameters.

Relevance to LLNL Mission

This effort has enabled LLNL to play a key role in the multiscale modeling of mission-critical materials through the linkage of scales. Specifically, we examined the relationship between a coarse-grained representation of the microstructure and the mechanical properties and lifetime performance of these materials. A variety of ongoing programs will benefit from these capabilities. A specific early adopter of this technology will be the Enhanced Surveillance Campaign (ESC).

FY2009 Accomplishments and Results

The mesoscopic network model consists of a set of nodes with selected node pairs linked by a single "bond" that represents a crosslink in the network. Initially the connectivity is arranged on a simple cubic lattice with periodic boundary conditions (Fig. 1). The bond interactions are described by a FENE spring potential and the standard Lennard-Jones potential. Bonds within the initial cubic lattice are randomly selected and deleted from the lattice to obtain the desired crosslink density. The ensemble of bonded nodes is then relaxed via energy minimization to obtain the initial structure.

The material we focused on in the first year had a fairly linear stress response over moderate strains so it was relatively straightforward to parameterize the model to capture this behavior. Another filled silicone elastomer, TR-55, exhibited a similar linear response over small and large strains while having a non-linear transition for intermediate

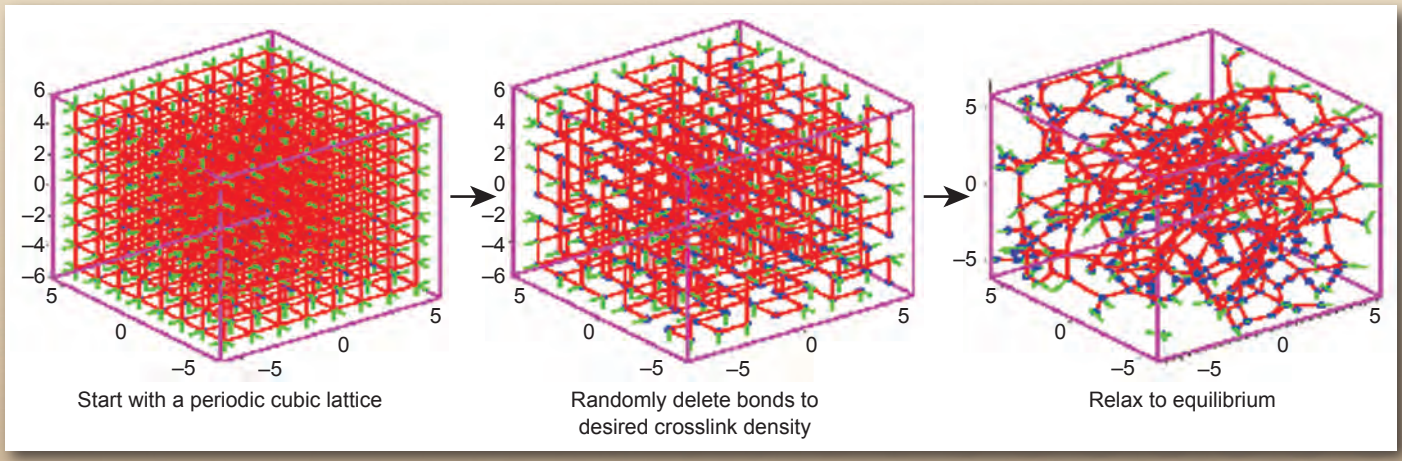

Figure 1. Initializing the microstructure in the mesoscopic model.

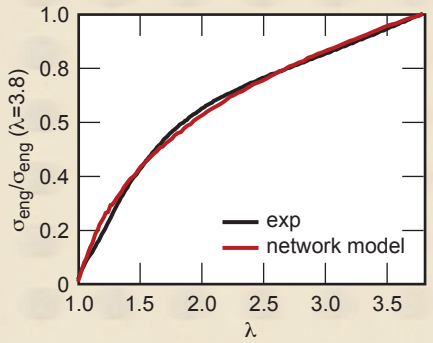

Figure 2. Normalized stress response of a sample of TR-55, a filled elastomer (black curve), compared with the mesoscopic model representation of this material (red curve).

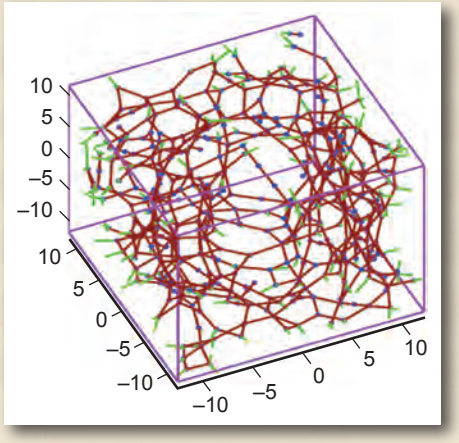

Figure 3. Mesoscopic model microstructure of a foam material. Blue circles represent nodes; red lines are bonds; and green lines denote periodic bonds that intersect the domain boundary. Note the center of the domain is devoid of bonds.

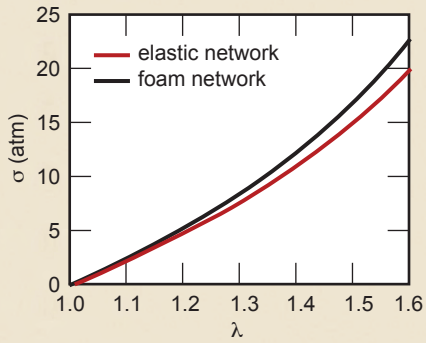

Figure 4. Comparison of the stress response of a representative elastomer network (no voids) and the model foam network depicted in Fig. 3.

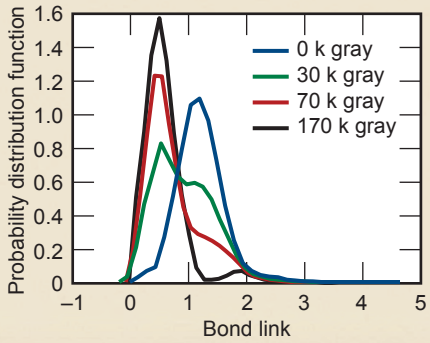

Figure 5. Distribution functions of the polymer length between crosslinks as a function of exposure to ionizing radiation or artificial aging.

strains. By varying the appropriate bond parameters, the network model produced a stress curve very similar to the experimental data from a sample of this material. Figure 2 shows the normalized stress results from this comparison. In terms of accuracy, the predicted stress curve from the model was comparable to some of the more sophisticated constitutive equations, which contain more free parameters.

Elastomeric foams are also of interest, so we enhanced the capability of the model to include void regions to approximate microstructures for these materials. Figure 3 shows the model foam structure after creating a void in the central region and equilibrating. Using this result we were able to address the relationship between the network topology and the elastic properties of these materials. We compared the stress response of an elastomeric structure without any voids and the new foam structure with a single void. The crosslink densities of both models were set equal to avoid inconsistencies in the shear modulus. The results in Fig. 4 indicate that the stress of the foam model is consistently larger than the elastomer stress.

Finally, we examined the changes in elastomer microstructure resulting from exposure to ionizing irradiation. In this aging process chain scission occurs but crosslinking dominates and increases with dosage. The network modifications can be simulated with the mesoscopic model by adding and removing bonds. One method of monitoring the microstructural changes is the distribution of bond or chain lengths between crosslinks. These distributions are plotted in Fig. 5 for several dosages. The shift toward lower chain lengths and the gradual narrowing and increase of the peak is consistent with an increase in net crosslinking. These predictions qualitatively agree with quantum NMR measurements of these aged materials.

Related References

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