283g A Gaussian Slip-Link Model for Cross-Linked Polymers

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Simulating the molecular structure of cross-linked polymers has difficulties mainly caused by the heterogeneous distribution of the cross-links; the presence of entanglements; and the displacement of both entanglements and cross-links under deformation. We have developed a slip-link model with cross-links, which are deformed affinely at the equilibrium, and assuming Gaussian chains neglecting the presence of chain segments not in the network. Simulation consists of two steps: preparation and deformation. In the preparation step, cross-links and slip-links are assumed to be distributed uniformly along the chain, but with independent parameters describing their statistics: the average number of Kuhn steps between entanglements,N_e, and the average number of Kuhn steps between cross-links,N_c . The dynamic variables include the number of Kuhn steps for the slip-link strands and the slip-link strand vector. In the second step, the variables of the preparation step become the parameters of the deformation step and the stress tensor can be found as a function of the deformation. The Mooney plot of the simulation result has a good agreement with experimental data for uni-axial and equibiaxial elongation deformations for cross-linked natural rubber, poly(dimethyl-siloxane), and poly(butadiene). The model is used to predict values for the Mooney plot parameters (C_1 and C_2) as a function of N_e and the average number of the slip-link strands $< z >$. The average number of the slip-link strands $< z >$ is proportional to N_c / N_e ratio. The C_2 / C_1 ratio is found to be strongly dependent on $< z >$, but weakly dependent on N_e. From the experimental data for a given cross-linked polymer, this observation provides a new way of predicting the cross-link density and separating it from the entanglement density. However, for systems of known N_e (from the plateau modulus for the melt or the Cornet criterion) and known cross-link density (such as calorimetry experiments), the model requires no adjustable parameters. The model has been tested also for planar elongation deformation of poly(dimethyl-siloxane) and it captures the first and second normal difference stresses in comparing with the experimental data.