142ag Computer Aided Design for Engineering Elastomers

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Sulfur vulcanized rubber is a major engineering material with a variety of applications, where the mechanical properties of rubber depends on the distribution of crosslinks. Formulated rubber is a mixture of elastomer, sulfur, accelerator, activator and anti-oxidants. The vulcanization chemistry is quite complex due to the synergistic affects of reactants and the large number of poly-sulfidic species that are present in the reaction mixture, where the number of species exceeds 100 for a system with a single accelerator and can exceed 1000 species for mixed accelerated systems.

Sulfenamide accelerators are widely used to expedite cross-link formation. The presence of amine moiety in the accelerator is important, since it is responsible for controlling the scorch and cure rate. The accelerator can undergo dissociation to form radicals, which can then pick up sulfur. Higher poly-sulfidic species can form via subsequent dissociation and combination reactions. The strength of the individual sulfur-sulfur bond in the various poly-sulfidic species depends upon the type of end group and size of the species. Extensive DFT calculations on bond dissociation energies were performed to obtain relative rate constant values for dissociation and combination reactions. Other important classes of reaction present in vulcanization chemistry are radical transfer, exchange reactions and concerted cyclic rearrangement. There are several potential reaction pathways for cross-link formation. Experiments were carefully designed to discriminate these different reaction mechanisms, which may be operative in MBS, MBT and MBTS accelerated systems.

Population based approach has been adopted to explicitly account for cross-link distribution. However, because of reaction complexity, system based tools are to needed to manage and analyze. We have developed a “Reaction Modeling Suite” (RMS) to integrate experimental data, fundamental quantum chemistry simulation results and expert knowledge. Major components in RMS include a reaction parser, ODE equation generator, parameter estimator and statistical analyzer. With these system tools, thousands of ordinary differential kinetic equations can be generated automatically from a simple English language chemistry rules. Non-linear optimization is employed to get model parameters which are usually activation energies and pre-exponential factors. The ODE solver is the computational bottleneck; consequently we have optimized the ODE's for computational efficiency and have developed the optimization code for massive parallel computations. These system tools facilitate in rapid model generation, solution and evaluation.