555e The Effect of Amines Catalyst on Benzothiazole Accelerated Sulfur Vulcanization

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Vulcanization reaction kinetics has been a long standing area of research; however, a fundamental understanding is far from complete. A formulated rubber is a complex mixture of elastomer, sulfur, accelerator, activator and various other components like anti-oxidants, where all the components interact in a complex manner throughout the service lifetime of the part. The pre-vulcanization chemistry plays a crucial role in the vulcanization kinetics; specifically, scorch delay is required for the rubber to be processed in the mold before it solidifies through cross-linking and the delay is dependent on accelerator type and its concentration. Ghosh, et al.1 recently developed a population based model describing reaction kinetics that explicitly accounted for the polysulfidic nature of the various species and demonstrated the feasibility of a quantitative description of the complex vulcanization chemistry; however, there are alternate mechanisms that must also be critically examined and the chemistry affects due to the other components in the system such as amine ligands, anti-degradants, etc. must be incorporated into the kinetic framework.

The affect of amines, in particular Morpholine and 6-PPD on the kinetics were studied. Amines are present either as anti oxidants or as reaction intermediates that are produced from the dissociation of sulfonamide accelerators. It is conventionally postulated that sulfur is pickup by 2-bisbenzothiazole-2-2'-disulfide (MBTS) to form 2-bisbenzothiazole-2-2'-polysulfides (MBTPs) as the first step in the pathway for cross-link formation. It was observed that morpholine, which is formed from reaction of MBT and MBS, substantially decreases scorch delay, and increases the rate of cure, i.e. it catalyzes the vulcanization process. Thus, amines in vulcanization chemistry must be included in a quantitative description of the vulcanization chemistry. In this communication, we present (i) vulcanization cure curves for MBS, MBT and MBTS accelerated systems in order to discriminate reaction mechanisms and (ii) extensive DFT quantum chemistry simulations on bond dissociation in order to obtain a much higher fidelity description of the reactivity of the various polysulfidic species as a function of different sulfur length and end group type. We are currently extending the mechanistically sound chemistry principles contained in the Ghosh, et al. model1 to encompass the affects of additional classes of accelerators and the presence of amine catalyst.

1. Ghosh, P.; Katare, S.; Patkar, P.; Caruthers, J. M.; Venkatasubramanian, V. Rubber Chemistry and Technology 2003, 76, 592.