Ab initio study of aging fuels – Thermodynamics

Hydroxyl-terminated polybutadiene (HTPBD) is a common binder for composite solid rocket propellants. HTPBD is typically cured with a cross-linking preventing agent, such as isophorone diisocyanate (IPDI) to prevent degradation of the physical properties of the polymer. HTPBD-IPDI based binders have a long shelf life and can be safely stored for long periods of time. However, they do degrade over the course of decades. Experimentally simulating degradation over long times usually relies on accelerating aging methods. These accelerated aging methodologies rely on abnormal conditions than those present in a typical storeroom. For example, higher temperatures, higher oxygen concentration, higher humidity, and the presence of other species that might accelerate aging through free-radical mechanisms. These accelerated conditions could potentially fail to replicate the actual aging process, and/or suggest the existence of certain degradation pathways that would be unfeasible at normal conditions.

An approach that has been left untouched for aging simulations is the use of *ab initio* quantum chemistry to predict the probable degradation and cross-linking patterns that may occur in an HTPBD system.

In this study, a quantum chemical analysis of the degradation and cross-linking of an HTPBD system is proposed. The weakest, most-prone-to-break bonds are located by using the quasi-atomic orbital (QUAO) bonding analysis. These bonds provide an insight into the possible cleavages that might occur in the system after an extended period of time. The bonding insight is then used to propose degradation and crosslinking pathways. Finally, composite methods are used on the resulting degradation and cross-linked products to predict thermodynamical quantities such as heats of formation.