

Nanostructure High Explosives using Sol-gel Chemistry

T. M. Tillotson, R. L. Simpson, L. W. Hrubesh

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Energetic materials such as propellants, explosives, and pyrotechnics are substances that store energy chemically. Since the invention of black powder, 1000 years ago, the technology for making solid energetic materials has remained either the physical mixing of solid oxidizers and fuels (e.g., composites), or the incorporation of oxidizing and fuel moieties into one molecule (e.g., trinitrotoluene, TNT). In this project, we bridge the length scale between these two approaches by preparing nanostructured energetic materials using sol-gel methodologies.

Sol-gel chemistry involves the reactions of chemicals in solution to produce nano-sized primary particles, called "sols," which can be linked to form a 3-D solid network, a "gel," with the remaining solution residing within open pores. Solution chemistry determines the resulting nanostructure and composition, which in turn determines material properties. Controlled evaporation of the liquid phase results in a dense porous solid, "xerogel," while supercritical extraction eliminates the surface tension of the retreating liquid phase, producing highly porous "aerogels." A typical dried gel structure is uniform because the particles and the pores between them are on the nanometer scale. In addition to providing fine microstructural and compositional control needed to produce materials that have both high energy density and extremely fast release rates, sol-gel offers other advantages of safety and stability in energetic material processing, e.g., eliminating the need for hazardous machining.

In FY1999, we focused our research on the synthesis and characterization of energetic nanocomposites. Nanocomposites are multicomponent materials in which at least one of the component phases has one or more dimensions (length, width, or thickness) in the nanometer size range, usually defined as 1 to 100 nm. Energetic nanocomposites are a class of material that (1) has both a fuel and oxidizer component, and (2) has at least one of the component phases that meets the size definition.

We synthesized a prototype nanocomposite by crystallizing ammonium perchlorate (AP) within the pores of an organic gel in FY1998. In this composite, the AP acts as an oxidizer with the hydrocarbon gel skeleton serving as the fuel. In FY1999, small angle neutron scattering (SANS), a non-destructive method for characterizing nanostructures, was conducted at the National Institute of Standards and Technology on both the energetic nanocomposites and the fuel-only samples. Results for the fuel-only specimens were consistent with other SANS data for gels, which typically give average primary particle sizes of a few nanometers. By

comparison, results from the energetic nanocomposite, in addition to displaying the typical structure, also showed extremely small (~1 nm) AP particles and >10 nm particles, which are presumed to be agglomerates of the small AP crystals. A dynamic molecular model suggests that these small nanometer size crystallites of oxidizer can easily fit within the microporosity of the fuel's primary particles, thereby providing mixing of fuel and oxidizer at levels unattainable by state-of-the-art production methods. Differential scanning calorimetry (DSC) of this energetic nanocomposite showed an exotherm at ~260°C, indicating that it is indeed energetic, whereas the trace for neat AP shows no exothermic reaction in the absence of the fuel skeleton.

In addition, we developed a new synthesis route for preparing inorganic oxidizing gel networks from inexpensive hydrated iron salts. By adding a metal fuel (e.g., aluminum) to the sol prior to gelation, we were successful in synthesizing pyrotechnic nanocomposites (thermites, as shown in the figure) with fuel/oxidizer components reversed from the fuel nanocomposites described above. Thermite reactions are extreme exothermic reactions that involve a metal reacting with a metallic oxide to form a more stable oxide and the corresponding metal of the reactant oxide. Production of thermites by this wet chemical process reduces the fire hazards associated with conventional processing and allows more intimate mixing of the fuel/oxidizer components with precise stoichiometric control. Early performance results are quite promising; in future research, we will explore compositional control to tailor the temperature and rate of burn.



Burning iron oxide/aluminum sol-gel derived thermite atop a silica aerogel.