Preprint
UCRL-JC-136924

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This article was submitted to
31st International Annual Conference of ICT, Karlsruhe, Germany
06/27/00 – 06/30/00

March 15, 2000

U.S. Department of Energy

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Nanostructured Energetic Materials Derived From Sol-gel Chemistry

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Abstract

Initiation and detonation properties are dramatically affected by an energetic material's microstructural properties. Sol-gel chemistry allows intimacy of mixing to be controlled and dramatically improved over existing methodologies. One material goal is to create very high power energetic materials which also have high energy densities. Using sol-gel chemistry we have made a nanostructured composite energetic material. Here a solid skeleton of fuel, based on resorcinol-formaldehyde, has nanocrystalline ammonium perchlorate, the oxidizer, trapped within its pores. At optimum stoichiometry it has approximately the energy density of HMX. Transmission electron microscopy indicated no ammonium perchlorate crystallites larger than 20 nm while near-edge soft x-ray absorption microscopy showed that nitrogen was uniformly distributed, at least on the scale of less than 80 nm. Small-angle neutron scattering studies were conducted on the material. Those results were consistent with historical ones for this class of nanostructured materials. The average skeletal primary particle size was on the order of 2.7 nm, while the nanocomposite showed the growth of small 1 nm size crystals of ammonium perchlorate with some clustering to form particles greater than 10 nm.

Introduction

It is known that the mechanical, acoustic, electronic, and optical properties are significantly and favorably altered in materials called "nanostructures", which are made from nanometer-scale building blocks (usually 1 to 100 nm). This approach enables the formation of new materials, generally having improved, exceptional, or entirely new properties. Modern technology, through sol-gel chemistry, provides an approach to control structures at the nanometer scale. In general, initiation and detonation properties of energetic materials are dramatically affected by their microstructural properties. Here, we exploit sol-gel chemistry as a route to process energetic materials and we describe four specific approaches to fabricating energetic nanostructured materials.

Since the invention of black powder the technology for making solid energetic materials has remained either the physical mixing of solid oxidizers and fuels (e.g., black powder) or the incorporation of oxidizing and fuel moieties into one molecule (e.g., 2,4,6-trinitrotoluene). The basic distinctions between these energetic composites and energetic materials made from monomolecular approaches are as follows. In composite systems, desired energy properties can be attained through readily varied ratios of oxidizer and fuels. A complete balance between the oxidizer and fuel may be reached to maximize energy density. Current composite energetic materials can store energy as densely as 23 kJ/cm^3. However, due to the granular nature of composite energetic materials, reaction kinetics are typically controlled by the mass transport rates between reactants. Hence, although composites may have extreme energy densities, the release rate of that energy is below that which may be attained in a process controlled by chemical kinetics.

In monomolecular energetic materials the rate of energy release is primarily controlled by chemical kinetics and not by mass transport. Hence, monomolecular materials can have much greater power than composite energetic materials. A major limitation with these materials is the total energy density achievable. Currently the highest energy density for monomolecular materials is approximately 12 kJ/cm^3 (about half that achievable in composite systems). The reason for this is that the requirement for a chemically stable material and the current state of the art synthetic procedures limit both the monomolecular oxidizer-fuel balance and the physical density of the material.

We have developed a new synthesis approach to form energetic materials, specifically explosives, pyrotechnics, and propellants, using the chemical sol-gel methodology [1,2]. In energetic nanocomposites we can control oxidizer-fuel balances at the nanometer scale. Sol-gel chemistry involves the reactions of chemicals in solution to produce nanometer-sized primary particles, called "sols". The "sols" can be linked to form a three-dimensional solid network, called a "gel", with the remaining solution residing within open pores. Solution chemistry determines the resulting nanostructure and composition, which in turn determine the material properties. Controlled evaporation of the liquid phase results in a dense porous solid, "<u>xero</u>gel". Supercritical extraction (SCE) eliminates the surface tension and in so doing the capillary forces of the retreating liquid phase that collapse the pores. The results of SCE are highly porous, lightweight solids called "<u>aero</u>gels" [3]. A typical gel structure is characteristically very uniform because the particles and the pores between them are on the nanometer size scale. Such homogeneity ensures uniformity of the material properties, which is one of the key reasons for synthesizing energetic materials using the sol-gel methodology.

The sol-gel approach to energetic materials offers the ability to precisely control the composition and morphology of the solid at the nanometer scale, a result that is difficult or not possible to achieve by conventional techniques. With sol-gel chemistry the process may, in some cases, be carried out with equipment no more complicated than a beaker. We believe that such control of the nanostructure could enable the creation of entirely new energetic materials with desirable properties. One promising result from this work, that supports the our previous contention, is a *decrease* in the impact sensitivity of sol-gel derived energetic nanocomposite materials. For example, we have shown that energetic ingredients processed by conventional methods exhibited drop-hammer impact sensitivities less than 10 cm, whereas the same constituents processed with sol-gel chemistry showed more than 130 cm sensitivity. This finding, with its implications to the safety of energetic materials, may be important in and of itself.

In addition to providing fine nanostructural and compositional control, sol-gel methodology offers other safety advantages in energetic material processing. For example, ambient temperature gelation and low temperature drying schemes prevent degradation of the energetic molecules, and the water-like viscosity of the sol before gelation allows easy casting to near-net shapes, which may be preferred to the alternatives.

Although sol-gel chemistry is a well-known means of producing nanostructured materials, it was not proposed as a route to create energetic materials until our effort [4]. We have developed four new classes of energetic materials that can be derived through the sol-gel method. Figure 1 graphically depicts the four material classes and their general structures.

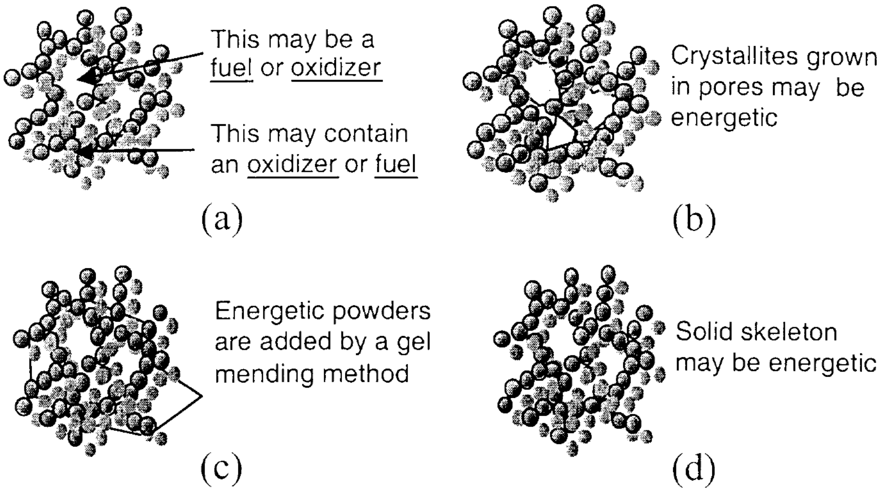

Figure 1. Classes of sol-gel derived energetic materials. (a) Energetic nanocomposite structures. (b) Energetic nanocrystalline materials. (c) Powder addition energetic materials. (d) Energetic skeletal structures.

Energetic Nanocomposites

Using a sol-gel procedure first described by Pekala [5] to make aerogels, a porous hydrocarbon solid matrix, was prepared by the polycondensation of resorcinol with formaldehyde (RF) in water. Subsequent crystallization of an oxidizer, ammonium perchlorate (AP), within the pores of the gel matrix, completes the synthesis. The oxidizer was first dissolved in water, then added to the reacting RF sol prior to gelation. Gelation of the RF sol occurred first. Crystallization of the AP was then induced by exchanging the liquid residing in the pores for a solvent in which the oxidizer was insoluble. The final step of removing the pore fluid was done by either a slow evaporation, resulting in a dense solid, or by supercritical extraction with carbon dioxide leading to a low density, highly porous material.

Transmission electron microscopy (TEM) was performed on a nanocomposite synthesized using the procedure described above and is shown in Fig. 2. Inspection of Fig. 2 shows a solid structure composed of interconnected clusters of nanometer-size primary particles, and AP crystallites smaller than 20 nm. Near-edge x-ray absorption was also performed on this nanocomposite. This technique creates an image by scanning a monochromatic x-ray beam, from a synchrotron source, across the sample and recording the near-edge x-ray absorption intensity of nitrogen. Since the only source of nitrogen in the material is AP the distribution of the oxidizer in the nanostructured material can be examined. The results are shown in Fig. 3. It can be seen that that nitrogen is uniformly distributed in the material on a scale less than 43 nm, which was the limit of resolution for the instrument. These results for the nanostructure were consistent with other published reports on the structure of sol-gel derived materials [6].

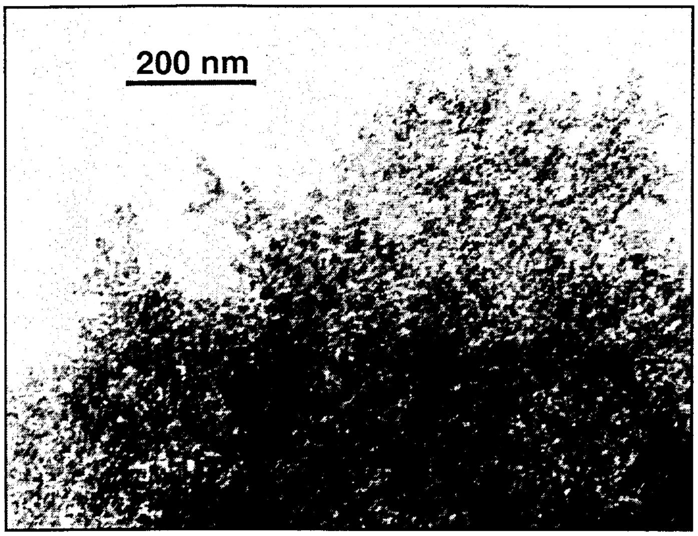

Figure 2. Transmission electron micrograph of a dried resorcinol-formaldehyde sol-gel containing crystallites of ammonium perchlorate showing only nanometer-size particles.

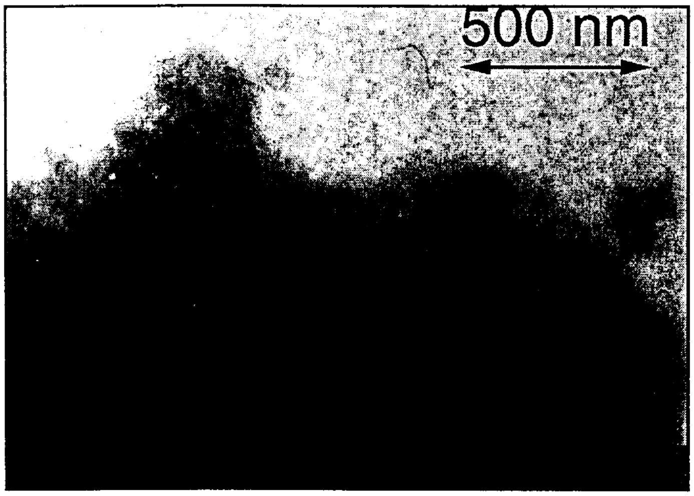

Figure 3. High-resolution image of the nanostructure of a dried resorcinol-formaldehyde sol-gel containing crystallites of ammonium perchlorate produced by near-edge x-ray absorption microscopy. This indicates the uniform distribution of nitrogen within the material. Resolution is 43 nm.

Small-angle neutron scattering (SANS), a non-destructive method for characterizing nanostructures, was also performed on this material. This technique, which measures the neutron scattering intensity as a function of incidence angle, derives information about the average size of scattering particles from the change in slope of a log-log plot of intensity versus momentum transfer. The results, shown in Fig. 4, for the fuel-only (RF) specimens is consistent with other SANS data for gels, which typically give average primary particle sizes of a few nanometers [8,9]. By comparison, the results for the RF-AP nanocomposite bulk material and thin films, indicate extremely small, ≈ 1 nm particles (probably oxidizer crystals that have grown within the gel pores), as well as a significant portion of particles larger than 10 nm in diameter. These larger particles are presumed to be larger oxidizer crystals that have grown to occupy several pores. The sol-gel chemistry ultimately offers a means to control the distribution and size of crystals within the gel matrix.

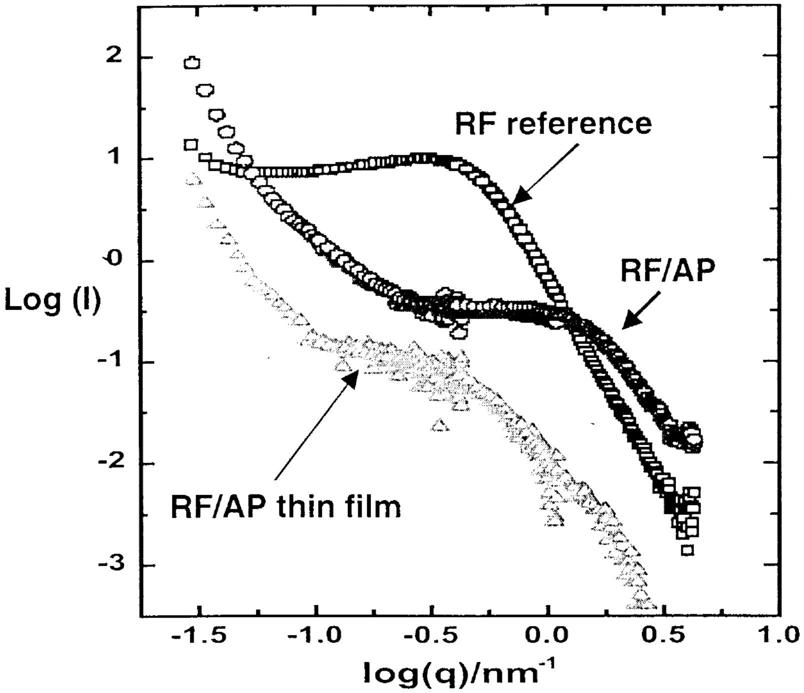

Figure 4. A log-log plot of the intensity of scattered neutrons versus the scattering wave-vector by SANS, is used to characterize the average sizes of scattering particles.

The surface area of the RF-AP nanocomposite was measured using standard BET (Brunauer-Emmett-Teller) adsorption isotherm techniques. The highest surface areas ever recorded on ultralow density, pure RF aerogels are 700-1000 m^2/g [5]. The RF/AP energetic nanocomposite had a measured surface area of 292 m^2/g. This surface area is six or more times greater than the highest surface areas of conventional explosive powders.

The characterization described above shows that the RF-AP material is nanostructured. To determine whether the material was energetic differential scanning calorimetry (DSC) was performed. DSC plots for neat ammonium perchlorate and the RF-AP nanocomposite are compared in Figs. 5a and 5b. The trace for the RF-AP nanocomposite shows a large exotherm beginning at about 250°C, indicating that it is indeed energetic. In contrast, the DSC of pure AP has significantly less integrated decomposition enthalpy in the absence of the gel skeletal fuel (RF). Hence, the RF-AP nanocomposite is indeed energetic.

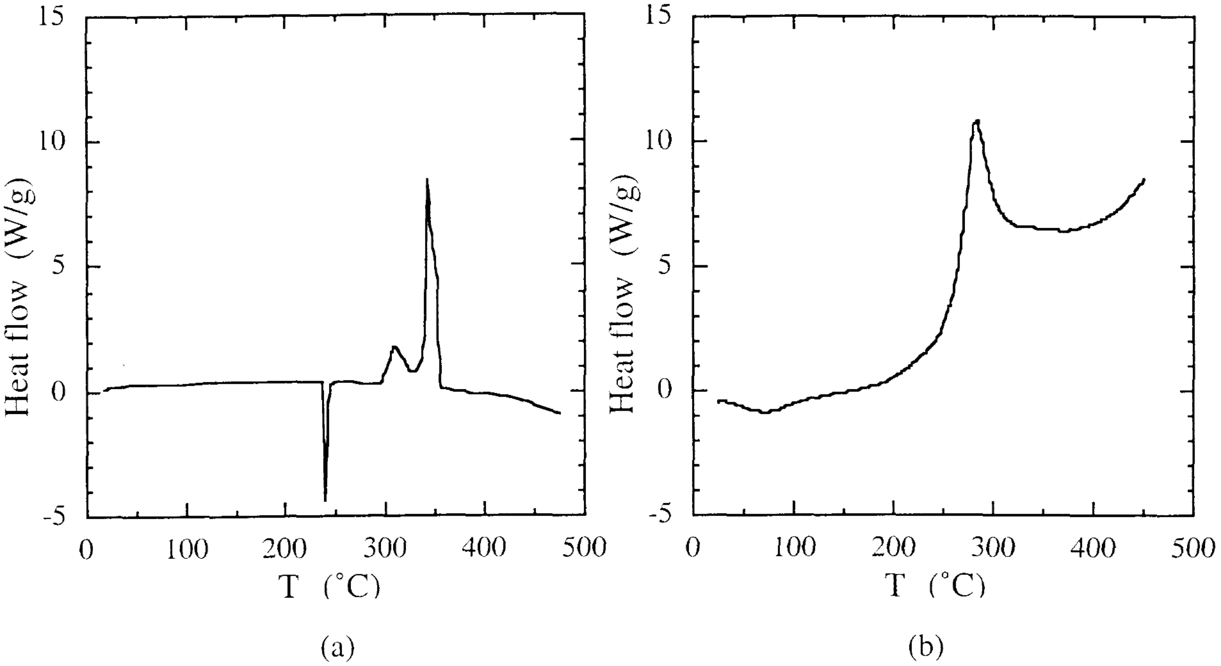

Figure 5. (a) Pure AP showing no significant energy release. (b) RF-AP nanocomposite releasing significant energy above 250°C. The sweep rates were 10°C/min.

Safety of Nanostructured Materials

All of the four classes of sol-gel derived energetic materials have been tested for sensitivity to impact. In the nanostructured energetic materials tested to date the impact sensitivities were found to be significantly less than those observed for analogous conventional materials. For example, a 90wt% PETN/10% SiO_2 xerogel made by the powder addition method (Fig. 1c) resulted in a drop hammer H_{50} value of 133 cm, much greater than with the result for neat PETN, which has an H_{50} value of 17 cm. These results are intriguing because conventionally mixed powders generally exhibit increased sensitivity with the addition of silica powders. PETN-based compositions made by blending with fumed SiO_2 were found to have impact H_{50} values less than 17 cm. The reason for the decrease in impact sensitivity in the sol-gel-derived materials is not fully understood. There are several hypotheses. First, the impact test is essentially a frictional ignition and burn propagation test. Pure aerogels and xerogels have very low convection and conduction thermal transport properties. These characteristics may impede deflagration. Second, whereas most energetic materials have mechanical stress-risers on the order of microns the sol-gel materials have structures on the nanometer scale, hence, impact stresses will be more uniformly distributed. What hot spots are made are likely to be smaller than those that would be generated in conventional materials. At the initial stage of impact induced stress localization the ratio of thermal dissipation to chemically driven thermal generation of the hot spots will be larger with the nanocomposites than with conventional materials. Thus it is more likely that the nanocomposites will have ignition sites below the critical size required for ignition. Decreased sensitivity is one exciting example of the new and different properties attributed to the nanostructured nature of these energetic materials.

Conclusions

The development of sol-gel nanostructured energetic materials appears very promising. We are just beginning to explore the possibilities. A new class of energetic materials may be obtained with improved properties using chemistry that doesn't require complex equipment and processing techniques. Some of the property enhancements of sol-gel derived materials include desensitization and safe processing and handling. The homogeneity may lead to more precise performance. Accurately controlling the crystal size might allow one to tailor the power output in high-energy composite energetic materials.

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Acknowledgements

We would like to acknowledge Drs. L. Terminello and W. Meyer-Ilse, of the Lawrence Livermore National Laboratory, for performing the near-edge x-ray absorption microscopy at the Lawrence Berkeley National Laboratory. Mr. M. Wall, also of the Lawrence Livermore National Laboratory, provided outstanding transmission electron microscopy. The neutron scattering work was carried out by Dr. C.J. Merzbacher of the Naval Research Laboratory. Our thanks are given to Dr. Merzbacher for not only the scattering data but for many important discussions about its interpretation.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.