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Sol-gel processing of energetic materials

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Abstract

As part of a new materials effort, we are exploring the use of sol-gel chemistry to manufacture energetic materials. Traditional manufacturing of energetic materials involves processing of granular solids. One application is the production of detonators where powders of energetic material and a binder are typically mixed and compacted at high pressure to make pellets. Performance properties are strongly dependent on particle size distribution, surface area of its constituents, homogeneity of the mix, and void volume. The goal is to produce detonators with fast energy release rate that are insensitive to unintended initiation. In this paper, we report results of our early work in this field of research, including the preparation of detonators from xerogel molding powders and aerogels, comparing the material properties with present state-of-the-art technology.

1. Introduction

The International Symposium on Aerogels (ISA) has traditionally been a forum for the discussion of novel aerogel applications. At the first meeting, Poelz described how aerogel was used in Cerenkov detectors for high energy physics experiments[1]; an application which, along with Teichner's alkoxide synthetic method[2], is largely credited for the resurgence of aerogel research starting in the early 1980's. Aerogel as translucent super-insulation for passive solar energy utilization in trombe walls was introduced by Goetzberger, et al[3] and Fricke[4]. Subsequent symposia have disclosed an increasing number of potential applications. For example, the synthesis of carbon aerogels described by Pekala at ISA3[5], has led many groups to explore the electrochemical application of these aerogels as electrodes in super capacitors[6] and capacitive deionization processes[7]. Later this year, Polystor, Inc. in Dublin, California, plans to start shipping carbon aerogel-based super capacitors for use in small electronics like pagers and cellular phones[8]. At ISA4, Alkemper demonstrated for the first time that silica aerogels could be fabricated into molds for the casting of metals[9], and Tsou reported on NASA's use of ultralow density silica aerogels for intact capture of cosmic dust[10]. NASA continues to explore space applications for aerogels and, on the recent Mars Pathfinder mission, ultra loco-density

(ULD) silica aerogels insulated the electronic components of the rover module from the extreme climatic conditions while achieving a 30% weight reduction. This is just a partial listing of the myriad of potential applications, but all are novel applications arising from the unique nanostructure of sol-gel derived aerogels.

In this paper, we report our pioneering work on the sol-gel processing of energetic materials. Energetic materials are defined here as any material that stores chemical energy in a fixed volume. Explosives, propellants, and pyrotechnics are all examples of energetic materials. Detonation results from either shock or heat. Explosives and propellants may be thought of as a means of storing gas as a "solid". Dynamite was the most widely used explosive for commercial applications until 1955 when it was largely replaced by prills-and-oil and slurry types. Prills-and-oil, or ANFO, is composed of 94% ammonium nitrate prills and 6% fuel oil. Slurry blasting agents are based on gelatinized ammonium nitrate slurries, sensitized with TNT, aluminum, or other solid explosives. Since then, energetic material processing has essentially been a refinement of existing procedures. One example is the pressing of powders of energetic material for detonators. However, low manufacturing rates, difficulty in intimately mixing fine powders, and the inability to produce precise geometric shapes are severe limitations. Using sol-gel chemistry, the intimacy of mixing can be controlled and dramatically improved over the current state-of-the-art technology, while providing a method for casting near net-shape geometric solids. In general, initiation and detonation properties are dramatically affected by the microstructural properties of explosives. Energetic materials produced by sol-gel methods would allow microstructural control on the nanometer scale, possibly producing entirely new and desirable properties.

2. Experimental procedures

The sol-gel method is a procedure where reactants first form nano-size primary particles suspended in a solution, i.e., a "sol". These primary particles continue to cross-link, increasing the solution viscosity until a 3-dimensional solid network is produced with the unreacted liquid residing within the network's open pores, i.e., a "gel". Solution chemistry determines the resulting nano-structure and composition, which in turn, dictates the material properties. Controlled, slow evaporation of the liquid phase of the gel, results in a solid that is ~50% porous, called a "xerogel"[11]. Supercritical extraction (SCE) of the liquid phase eliminates the surface tension of evaporating liquids producing highly porous low density solids, called "aerogels"[12,13]. One can envision numerous synthetic routes utilizing this method in processing energetic materials, but we have focused our early work on four approaches: solution addition, powder/particle addition, nano-composites, and functionalized solid networks. Here, we describe the concept and details of the first two approaches and present some early results. Our more recent work on the latter two approaches will be published in the near future when characterization results are completed.

2.1 Solution addition

The idea is to crystallize the energetic material within the pores of a sol-gel derived solid. In practice, the energetic material is dissolved in a solvent which is compatible with the reactants and used for density control of the resulting gel. Optimum composition for use as detonators would be 90 wt % energetic material/10 wt % inert matrix. Due to the solubility limits of most energetic materials the preparation of low density porous solids are necessitated to meet this requirement. For this work, energetic molecules, hexahydro-1,3,5 -trinotro-1,3,5-triazine (RDX) and 2,2-bis[(nitroxy)methyl]-1,3-propanediol dinitrate (PETN), were crystallized within the pores of silica matrices.

Either single- or two-step silicon alkoxide synthesis methodology described elsewhere[2,14,15] may be used to prepare the silica matrix. We found it necessary to prepare and mix three solutions in this synthesis, to avoid unwanted precipitation of the energetic material. A 100% excess of water was added to promote the hydrolysis reactions. Either an acid or base catalyst may be used, but for reasons discussed later, fluroboric acid is our catalyst of choice. A typical recipe would consist of : solution A- 1.25g tetramethoxysilane (TMOS) + 1.00g acetone; solution B- 1.00g acetone + 0.60g water + 150µl fluoroboric acid; solution C- 6.00g acetone + .400g RDX. Subsequential additions of solutions B and C are poured into a stirring solution A. This combined solution is stirred for a few minutes and poured into molds, where gellation occurs in <24 hours. The mass weight of the silica matrix is controlled by the amount of alkoxide added to solution A, while the mass weight of RDX is limited to its solubility in acetone. Xero-gelling was done at 25°C by poking pinholes in the polyethylene foil covering the mold held in place by rubber bands. Supercritical extraction of the gels into aerogels was done by the low temperature CO_2 process. To prevent loss of the solubilized energetic molecules during SCE, the RDX or PETN was first crystallized within the pores of the matrix by replacing the pore liquor with a solvent in which the energetic material is insoluble, but one which is still miscible in CO_2. Ethanol was used for these experiments. The pore liquor was exchanged, while the crystallization of the energetic molecules proceeded by immersing the gel into large excesses of ethanol, three times over a 24 hour period. Low temperature extraction was preferred to the high temperature autoclave process because most energetic molecules, like RDX and PETN, are extremely heat sensitive and they will either degrade or detonate at temperatures >100°C.

2.2 *Powder /particle addition*

Loading particles/powders uniformly inside gels is problematic because even ultrafine particles will tend to settle before the gel sets up, producing a non-uniform distribution. Also, particles can aggregate in solution, exacerbating this problem further. We describe here, for the first time, a methodology which we call the gel mending approach that dramatically improves this homogeneity. Conceptually, it makes use of the observation that a monolithic gel can be re-generated from gel fragments. First, a gel is prepared. Then the gel is fractionated by any process that breaks the gel into small fragments, i.e.. a blender. With continued mixing, the powder/particles are added until a uniform dispersion is reached. Gels made from metal alkoxides tend to self-mend and reform a monolith including the dispersed powder/particles, with the addition of a small amount of solvent. At this point, the gel can be dried by the above mentioned processes to produce xerogels and having with a uniform distribution of the powder or particles.

For this work, we made silica gels from TMOS, dispersing either RDX or PETN, and reforming the gel with a small addition of methanol. The reformed gels were translucent to opaque depending on the wt% concentration of the energetic material. Xerogel molding powders were produced by the above described xerogeling process and then pressed into pellets for drop hammer sensitivity and shock initiation experiments. One advantage of this approach over the solution addition approach, is the ease of preparing highly concentrated energetic materials with precise wt% ratio's.

2.3 *Characterization methods*

Characterization of these materials is more difficult than for typical sol-gel derived materials due to the energetic component of the matrices. Differential scanning calorimetry (DSC) was used to determine if the energetic material was present in the final dried products. Optical, scanning and transmission electron microscopy were used to study the microstructure.

The drop hammer test, a standard energetic material characterization technique, was used to measure the impact sensitivity of our produced materials. In this test, a 2.5kg weight is dropped from a pre-set height onto a 35mg pressed pellet of material, and explosion or non-explosion is recorded. Depending on this outcome, the hammer is raised or lowered resulting in a series of drops with either explosion or non-explosion being recorded. The criterion for "explosion" is an arbitrary level of sound produced by the explosive on impact. The test results are recorded as H_{50}, the height in centimeters for which the probability of explosion is 50%[17].

The shock initiation experiments used to determine if our materials were detonable were done by the flyer-plate technique, another energetic material standard. In this technique, an explosive charge is ignited. The expanding gas pressure bursts a metal foil, sending a shock wave through a pressed pellet which is observed through a lithium fluoride crystal, by a laser velocimeter[17].

3. Results

Our first concern was whether the energetic materials, RDX and PETN, survived the sol-gel processing. Differential scanning calorimetry analysis shown in Figure 1, confirms their presence. PETN based materials had a small endotherm at 143°C followed by a exotherm at 200°C, characteristic of neat PETN. Corresponding agreement with RDX was found in the RDX based aerogels and xerogels. Some slight degradation of the energetic materials was observed in materials prepared using base catalysis. This degradation was more pronounced in materials made by the solution addition method than those prepared by the powder addition approach.

Monolithic aerogels prepared by the solution addition of RDX are depicted in Figure 2. Monolithicity was maintained in compositions up to 45 wt% RDX in a 55 wt% SiO_2 matrix. In the lowest composition, 17 wt% RDX, the crystals are naked to the visible eye while increasing compositions of RDX visibly show the growth of orthorhombic crystals. An optical micrograph of these crystals in a 30 wt% RDX aerogel is shown in figure 3. Crystal growth by this solution addition method appears to be non-uniform with crystal concentration radiating outward from the center of the cylinder, leaving a void region near the cylinder surface. Increasing wt% RDX compositions, also show a higher RDX crystal gradient at the bottom of the cylinder when cast upright.

The impact sensitivity of an energetic material to unintended initiation is an important safety factor in their use. Drop-hammer sensitivity tests summarized in Table 1 gave some surprising results. Results show that pellets pressed from xerogel molding powders prepared by the powder addition method, have significantly lower sensitivities than current state-of-the-art powder mixing technology. This result was counter to expectations. Earlier work at our laboratory had shown *increased* sensitivities when fumed silica was used as a inert matrix at similar wt% compositions.

Desensitized materials are only an improvement in technology if they are still able to be ignited with reasonable power outputs. The shock initiation experiment shown in figure 4 demonstrated this possibility when an 80 wt% RDX xerogel molding powder, pressed into a detonator pellet, was able to be ignited. Previous experiments with 33 wt% RDX concentrations were not able to be ignited. The lower limit of ignitabilty is currently being investigated.

4. Discussion

The DSC analysis points to some optimum processing conditions. Since there is a slight degradation with base catalysis, maximum retainment of either RDX or PETN is best realized in low pH solutions, prompting the need for acid catalysts. However, use of acidic catalysts greatly increases gel times, except in the case of fluorine containing acids. Iler postulated that the fluoride ion may allow the temporary expansion of the coordination number of silicon from four to five or six, just as in the case of the hydroxy ion[18], or base catalyst, to dramatically reduce gel time in low pH sol-gel solutions. As such, we recommend the use of fluoroboric acid (HBF_4) for gel times less than 24 hours. Also, from a safety standpoint fluocoboric acid is *considerably* less dangerous to handle than hydrofluoric acid (HF), as a source of fluorine ions.

The radial non-uniform distribution of crystals, RDX or PETN, in the monolithic aerogel cylinders prepared by the solution addition approach, is perhaps not surprising when considering the dynamics of the process used here to induce crystallization. The replacement of pore liquor in a gel with a miscible solvent, is a diffusion limited process. As the ethanol diffused into the gel cylinder it is quite possible that the insoluble energetic molecules redistributed in the acetone rich interior. The non-uniformity, evidenced by the higher concentration of crystal growth at the base of the cylinder, could be due to convective flow in the solution prior to gelation. Future work will investigate the use of crystal growth inhibitors to control the size of crystals, as a means for increasing the wt% energetic material.

The impact sensitivity results for the xerogel molding powders made by the powder addition approach, are not well understood. This unexpected finding that the presence of the gel structure significantly decreases the impact sensitivity might be due to a more intimate mixing of energetic material and inert matrix than is possible with current-state-of-the-art powder mixing technology. Another possibility is that the porous gel structure is influencing the sensitivity by providing a protective insulating barrier around the energetic molecules, RDX or PETN. This structure may absorb and transport the heat generated on, impact away from the energetic molecules, thereby alleviating the possibility of run-a-way reactions and detonation. Further investigations to understand this phenomena are also in progress.

5. Conclusion

We have shown that sol-gel processing of energetic materials produces desensitized detonators which are still capable of initiation. This result could have dramatic international impact on handling and processing energetic materials.

Acknowledgment

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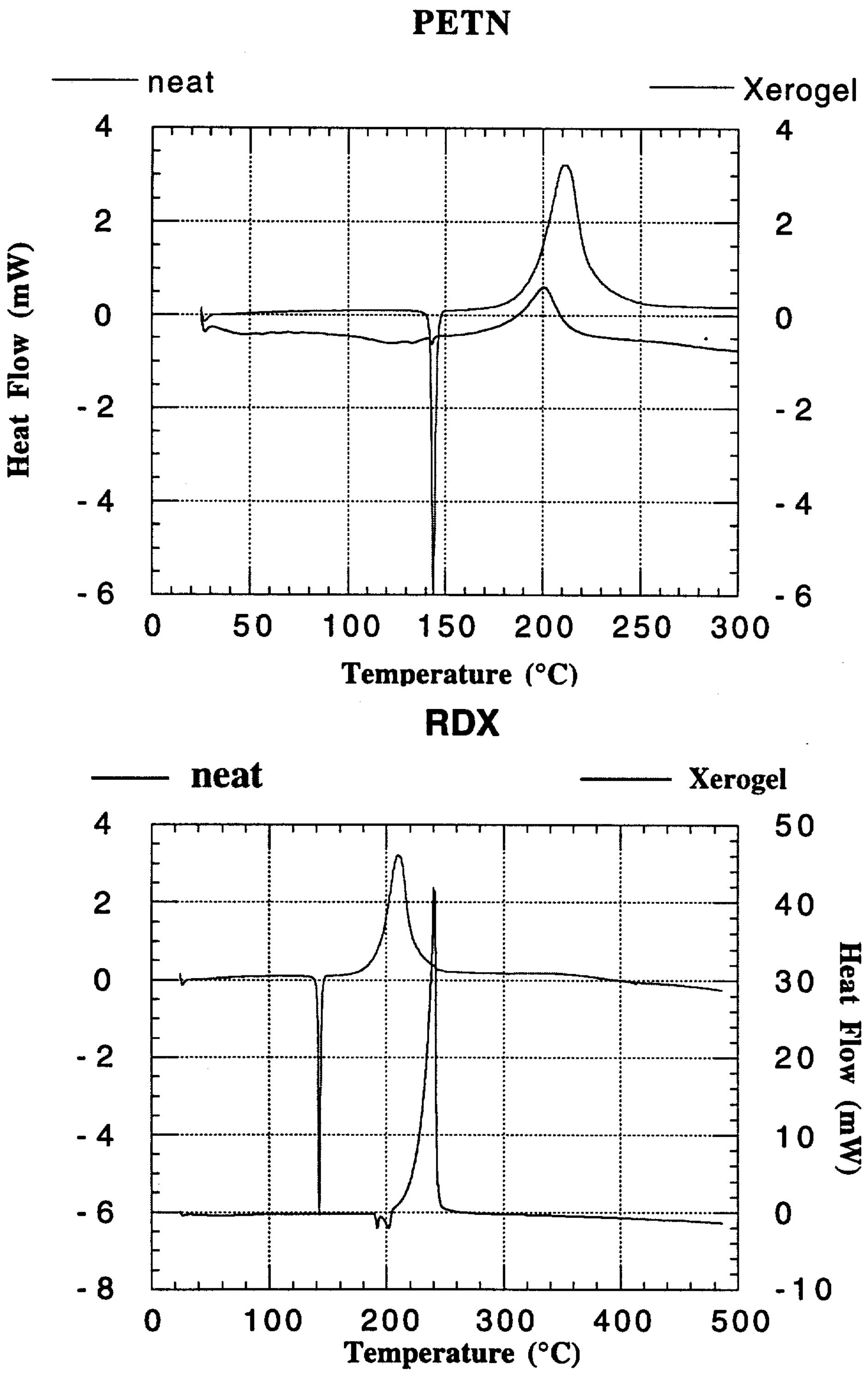
PETN
neat
Xerogel
Heat Flow (mW)
4
2
0
- 2
- 4
- 6
0
50
100
150
200
250
300
Temperature (°C)
RDX
neat
Xerogel
4
2
0
- 2
- 4
- 6
- 8
50
40
30
20
10
0
-10
Heat Flow (mW)
0
100
200
300
400
500
Temperature (°C)

Figure 1

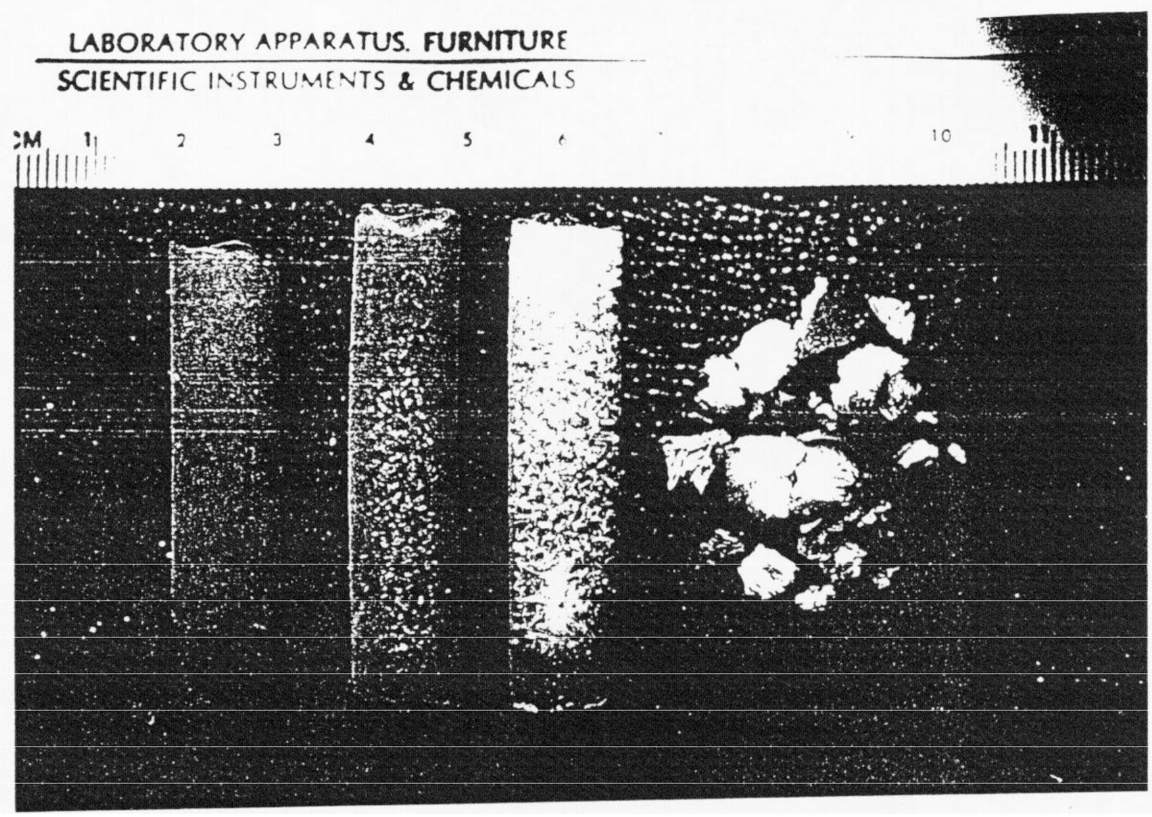

Figure 2

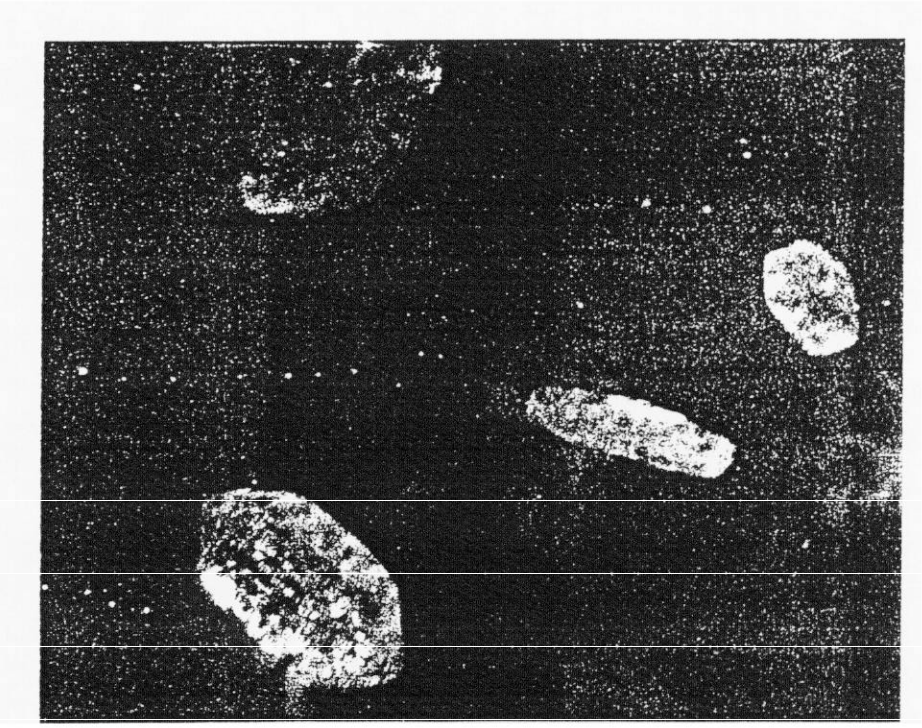

Figure 3

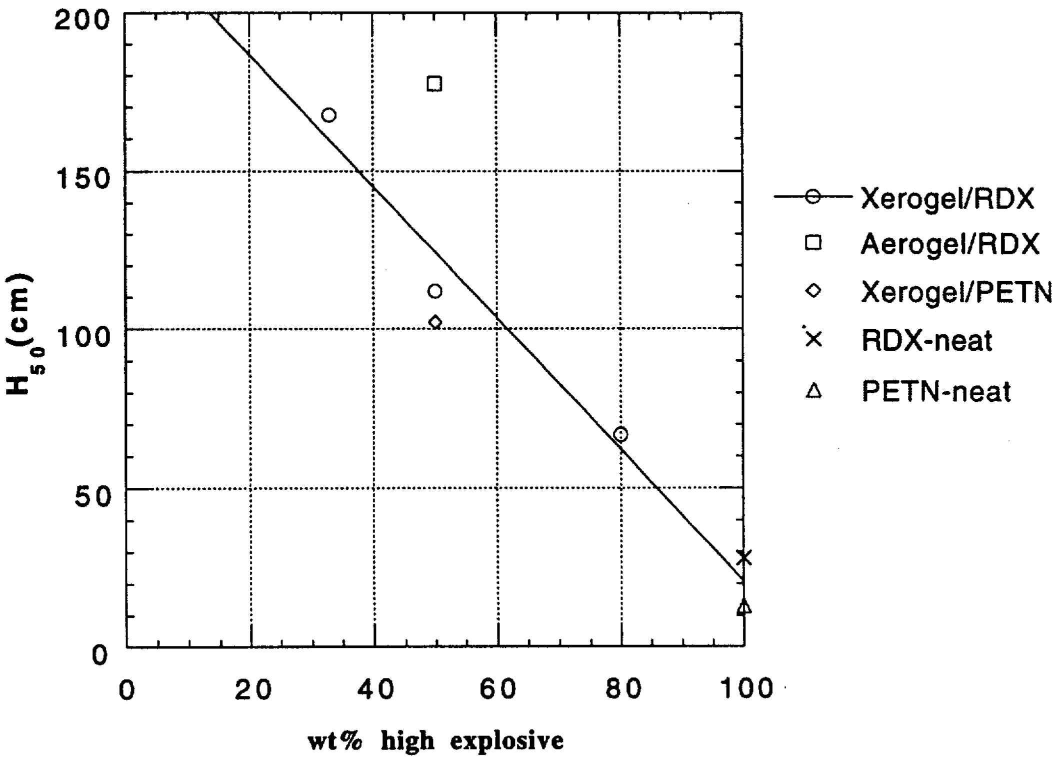
200
150
100
50
0
H_{50}(cm)
0
20
40
60
80
100
wt% high explosive
Xerogel/RDX
Aerogel/RDX
Xerogel/PETN
RDX-neat
PETN-neat

Figure 4

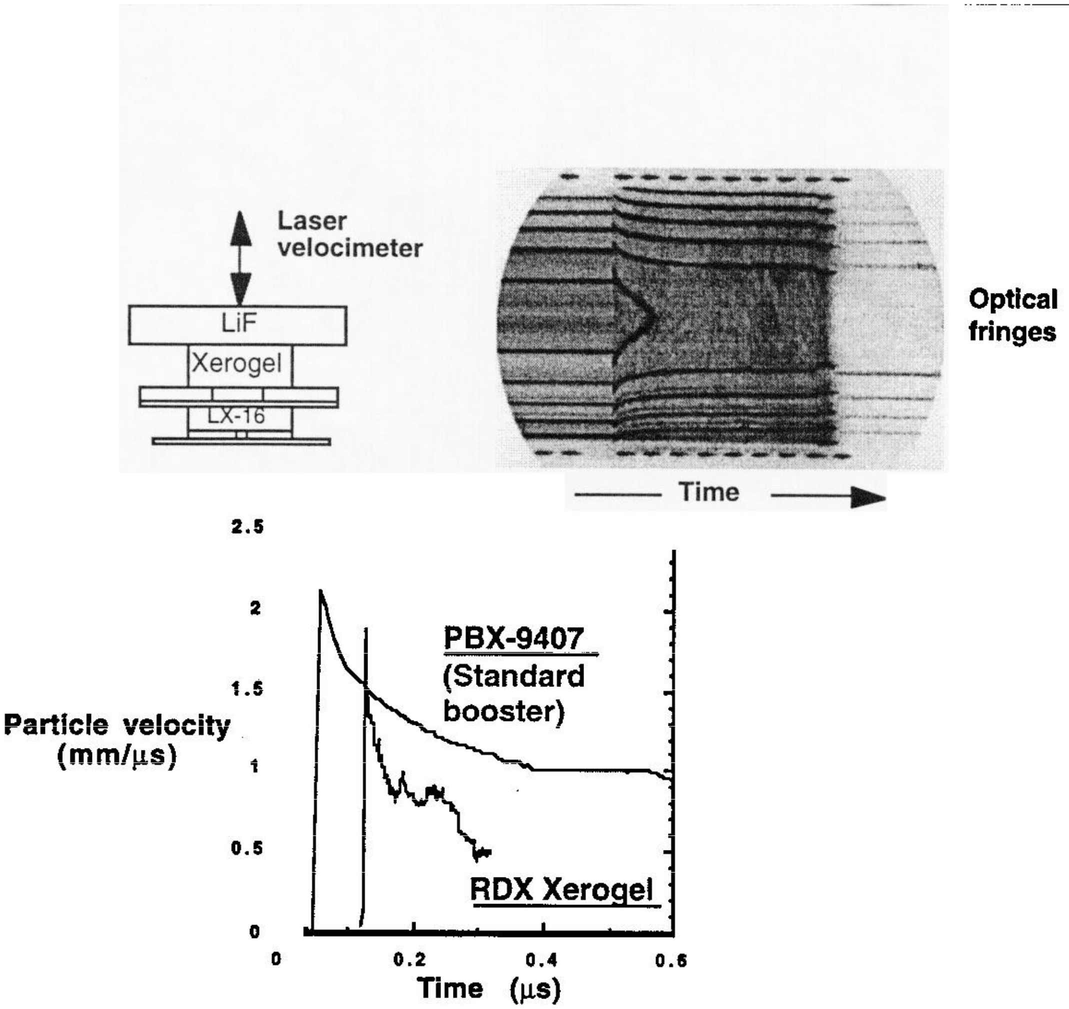
Laser velocimeter
LiF
Xerogel
LX-16
Optical fringes
Time
2.5
2
1.5
1
0.5
0
Particle velocity (mm/μs)
0
0.2
0.4
0.6
Time (μs)
PBX-9407
(Standard booster)
RDX Xerogel

Figure 5

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