Analysis of the Effect of Micromechanical Phenomena on Mechanical Properties of Energetic Materials

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Summary

Energetic Materials are explosive agents that generate large amounts of hot gases by an exothermic reaction without the need for atmospheric oxygen. Therefor the oxidizer must be available in form of molecularly bound functional groups or in form of discrete salts (e. g. ammonium perchlorate) containing oxygen. Modern solid propellants are highly filled composite materials consisting of a polymeric binder in which crystalline oxidizers the filler are incorporated in amounts of up to 90 wt.%.

Background of the performance of a composite propellant are micromechanical phenomena. Therefore, the understanding of micromechanical phenomena like matrix filler detachment, distribution of filler, crosslinking, chain scission and micromecanical deformation mechanism is the key to the understanding of the behavior of composite propellants. These micromechanical phenomena influence the sensitivity to impacts during transportation and ignition and the combustion behavior. The performance of composite propellants is correlated with its mechanical properties.

1. Introduction

Modern energetic materials like composite solid propellants, gun powders or special kinds of explosives are composed principally in the same way: relatively hard particles are dispersed in a relatively soft matrix. The matrix material has two main functions: 1st it burns during the service of the propellant and 2nd it gives the mechanical stability of the compound. The particles deliver the necessary oxygen for the burning of the matrix but also contribute to the production of energy by containing combustible substances. Typical rocket propellant formulations are described in [1,2].

Table I Typical formulation of a Polyurethane Binder Composite [2]

Ammonium perchlorate	65.00 wt.%
Aluminum powder	17.00 wt.%
Polyalkylene glycoles	12.73 wt.%
Diisocyanate	2.24 wt.%
Triol	0.43 wt.%
Additives and plasticizer	2.60 wt.%

Modern solid propellants are highly filled composite materials consisting of a polymeric binder in which crystalline oxidizers the filler are incorporated in amounts of up to 90 wt% [1]. Solid propellants have to meet special requirements [3]. The most important properties of solid propellants are listed in Table II.

Table II Requirements for Solid Propellants

Class	Property	Requirements	Purpose
A. Material	1. Mechanical Strength	High strength	To withstand stresses and avoid cracking during operation
	Elasticity	High elasticity	Rough handling and transportation
	2. Thermal Coefficient of expansion	Low	To reduce motion of grain and minimize thermal stresses and cracking during storage

B. Combustion	1. Ignition 2. Pressure limits Lower Limit Upper Limit 3. Temperature Sensitivity Burning Rate	Readily ignitable Above atmosphere pressure High Slow change with temperature	To simplify starting operation; to avoid damage to hard-ware To prevent auto-ignition at ambient Pressure To avoid unstable combustion and explosions To obtain re-producible com-bustion charac-teristics
C. Processing	1. Mixing 2. Viscosity 3. Shrinkage	Not hazardous Adequate in all operations (casting, molding, extruding) Low or insufficient in final stages (curing)	To facilitate manufacture To permit proper processing To control easily final shape

2. Methods for Analysis of Micro- and Mesoscopic Phenomena

2.1 Mechanical Properties

The ability to deform without rupture, and to recover is quite important since any cracks or unbonds which develop would result in additional burning surface and cause an unpredictable chamber pressure during motor operation.

Mechanical Properties are greatly affected by adhesion between the filler and binder. Moisture, frequent temperature variations, and vibration can cause dewetting of the filler from the binder, resulting in a decrease of mechanical properties.

Composite propellants containing ammonium perchlorate possess an extremely chemical stability. Chemical reaction involving the binder affect the mechanical properties.

Cracks can be detected in a standard tensile test due to the weakening of the material. Whether the weakening is really due to cracks has to be determined by

separate methods, which can be very costly. In these cases, the detection of the volume increase of the composite material during tension is a suitable solution. The vacuoles formed by cracks and delaminating lead to a macroscopic observable volume dilatation of the material. With this method, the detection of many cracks distributed in the material is possible, even in these cases, where the detection of the single cracks is not possible with other methods due to their small size.
The measurement of Poisson's Ratio in a standard tensile test can also be used as a method for the determination of the volume dilatation of a sample. Poisson's Ratio is defined as the negative quotient from lateral contraction and elongation:

$$\nu(\varepsilon_l) = -\frac{\varepsilon_q}{\varepsilon_l} \quad (1)$$

Herein, $\varepsilon_q=dq/q_0$ and $\varepsilon_l=dl/l_0$ where q_0 and l_0 are the initial width and length of the sample respectively. The changes of length and width are entitled dl and dq. Besides its capability for the detection of vacuoles in the material, Poisson's Ratio is a necessary parameter for the complete description of the materials mechanical properties in the elastic region.
For the determination of Poisson's Ratio, a non contact laser optical measurement system was developed at Fraunhofer ICT whose function is reported elsewhere [4].
The direct methods for the determination of cracks give a direct information about the presence and the size of cracks or delaminations in the materials [5]. They are not suitable from a statistical point of view, because they allow the observation of only small areas of the material. In order to get a comprehensive picture of the conditions of the material, tomography has to be used, which causes a high instrumentation effort and long measurement times.

2.2. Microscopy

Microscopy is a classic method for the detection of cracks in composite materials. The materials must be prepared for the detection of the failures which in many cases causes artifacts. Especially in the case of elastomeric materials, cracks which occurred between filler and matrix during loading can close again when the material is unloaded again. Furthermore in most cases, the investigation is only possible on the surface of the material.

2.3. NMR Imaging

MRI allows an insight into the interior of even opaque materials. MRI, therefore, enables the non-destructive characterization of energetic materials. By the use of NMR different information about the material properties are available [6,7]:

- chemical information
- physical information
- spatial information

The application of MRI provides an insight to the molecular structure and build-up of macromolecules. Thus, chemical information like aging-induced changes in the molecule structure of energetic materials could be achieved by NMR.
Physical information describing the mobility of molecules could be delivered by NMR. It is possible to observe influence parameter of energetic materials on molecular mobility like crystality, crosslink density and molecular weight. During aging the molecular weight decreases and the crosslink density changes. NMR offers a useful method to analyze aging processes. Magnetic resonance imaging enables the spatial resolution of material properties. It is possible to image structures like cracks, pores and the distribution of fillers.

3. Conclusion

The measurement of material properties is a quick simple and valuable method to examine the aging behavior of energetic materials. Especially the determination of Poisson’s Ratio is a powerful method for the determination of dewetting in energetic materials. It is relatively simple to perform and gives additional information for the use of FEM methods for the development of energetic systems.

With MRI it is possible to detect the deformations in the interior of the paste for examples of hollows or agglomerates of filler material. The homogeneity of a specimen can be tested by distribution of the solid concentration.

NMR imaging provides valuable information about the morphology of energetic material during aging, the extrusion in a piston extruder and after mixing.

Especially, NMR imaging offers new aspects of examining aging behavior. With this method the different aging mechanism like change in crosslinking density and molecular degradation could be separated and qualified by the determination of the local molecular mobility.

Figure 1: Light microscopy – Matrix-filler detachment

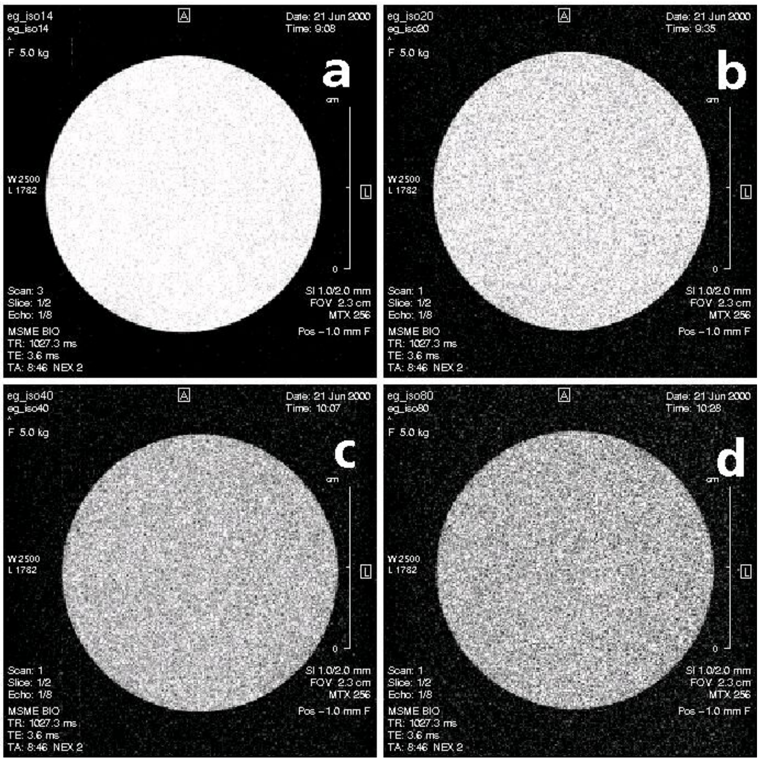

Figure 2: NMR-images of polyurethane with different isocyanate index
(Diameter of specimen 20 mm, MSME-Sequence)
a) 12.5 isocyanate index
b) 25 isocyanate index
c) 50 isocyanate index
d) 100 isocyanate index

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