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Analysis of the Effect of Mechanical Loading on Energetic Materials by Means of MRI

N. Eisenreich, A. Geißler, E. Geißler, C. Hübner

Fraunhofer ICT, Pfinztal, D

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Norbert Eisenreich, Adam Geißler, Egon Geißler, Christof Hübner

Fraunhofer Institut für Chemische Technologie ICT
Joseph-von-Fraunhofer-Str. 7
76327 Pfinztal, D

Summary

Modern solid propellants are highly filled composite materials. The aging behavior of composite propellants is correlated with a change in mechanical properties. Background of the aging behavior of a composite propellant are micromechanical phenomena. Therefore, the understanding of micromechanical phenomena like matrix filler detachment and micromecanical deformation mechanism is the key to the understanding of aging behavior of composite propellants. In this paper is shown how micromechanical deformation phenomena can be observed by MRI (magnetic resonance imaging). This method can be used for the investigation of the displacement and deformation of the structure.

1. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) stems from the fact that the nuclei of specific isotopes (e. g. of the hydrogen isotope ^{1}H, ^{19}F) possess a magnetic moment (spin) and are precessing under a specific angle with respect to an external magnetic field [1-4]

$$\mathbf{B_O} = B_O\,(0,0,1) \qquad (1)$$

In the case of spin ½ nuclei their components along the field axis ($\mathbf{B_O}$) are either parallel or anti-parallel to $\mathbf{B_O}$. As the parallel orientation is for ^{1}H energetically preferable, this orientation is assumed by a larger number of nuclear spins.

Despite the fact that this phenomenon can be calculated correctly in physically terms only through use of quantum mechanics [5], the macroscopic behavior of the spin ensembles can be described for many of the NMR experiments as a

continuous magnetization vector. In this description, the magnetization vector in the thermal equilibrium points in the direction of the static magnetic field of the magnet. As soon as an RF field is switched, the magnetization vector assumes a component orthogonal to the steady field and begins to precess with the Larmor frequency ω which is proportional to the magnetic field strength

$$\omega = \gamma B_O \qquad (2)$$

where γ is the gyromagnetic ratio of the respective isotope. This NMR principle established a large number of applications in analytical chemistry known collectively as NMR spectroscopy due to the fact that the exact resonance frequency for each nucleus is dependent upon the chemical environment of this nucleus [6]. The resonance frequency of ^{1}H is 42.55 MHz and 40.05 MHz for ^{19}F at B_O=1 Tesla. This means ^{1}H and ^{19}F can be distinguished by means of their resonance frequencies and, therefore, also materials containing ^{1}H or ^{19}F.

In order to determine the solid and fluid concentration it is also possible to use other NMR parameters such as T_1, T_2 or $T_{1\rho}$ to distinguish between the solid and the fluid components [7]. The disadvantage of these solutions is that the local concentration of the solid and the fluid cannot be measured directly, but must be derived by assuming the according relaxation behavior.

In order to derive information concerning the spatial distribution of the spins, and hence of the moisture within the material, the homogeneous magnetic field $\mathbf{B}_O$ must have additional fields derived by defined gradients $\mathbf{G}_x$ (called read-gradient) superimposed on during the excitation and the detection of the NMR signal. As a result, the NMR signal contains spatial information. The resonance frequency varies along the sample in accordance to

$$\omega(\mathbf{r}) = \gamma \cdot (B_O + \mathbf{G}_x \cdot \mathbf{r}) \qquad (3)$$

Another principle which provides spatial information is the use of a gradient $\mathbf{G}_y$ (called phase-gradient) between the excitation and detection. With this process, the signal phases are dependent upon the location in the direction of this second gradient. The excitation must be repeated with a linear variation of the strength of the phase gradient.

The standard imaging experiment consists of applying a read-gradient and then a phase-gradient orthogonal to the direction of the read-gradient. By repeating the experiment under variation of the phase-gradient, a two-dimensional matrix of signals is produced. The image is derived by Fourier transformation in each direction; for this reason, such experiments are entitled 2DFT (two dimensional Fourier transformation). The spatial restriction of the signal in the third direction is usually achieved through use of a slice selection gradient $\mathbf{G}_z$ during the excitation pulse, which produces a slice thickness of $\Delta z = \Delta\omega/\gamma G_z$.

Several imaging strategies have been developed for an effective determination of the spatial distribution of the hydrogen and fluorine density [7,8]. In every MRI-experiment the sample is divided into a matrix of three-dimensional voxels. The size of each voxel is established by the field of view (FOV) selected, which relates to the dimensions of the measuring volume in the magnet as well as to the matrix size (number of voxels according to the relevant spatial dimensions).

2. NMR Imaging of Energetic Materials

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:

- 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.

2. Application of Image Processing on NMR-Images for Displacement Analysis

Using image processing to analyze the displacements between two structures two NMR-images of different loading conditions are necessary. It is possible to compare one image with a reference image by algebraic operations like addition and subtraction of the grey values of the NMR-images. The addition of two images equals double exposure of a film in classical photography. In such an image the movement of filler particles could be tracked.

Crosscorrelation analysis is used in signal processing to compare signals recorded in time domain. This method can also be used to compare coordinate based images. A spatial 2D crosscorrelation is defined by the following equation:

$$K(x',y') = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g(x,y)\cdot f(x-x',y-y')dxdy \qquad (4)$$

The maximum of the crosscorrelation function gives the information of how much the two images have to be shifted that they are similar to each other. In the case of images of structures displaced to each other the values x' and y' describe the displacements. It is possible to correlate the grey values of two images.

3. Results of the NMR-Experiments

In a Bruker 4,7 Tesla (200 MHz) MRI-system the experiments have been conducted with a probe-head with 25 mm diameter (Fig. 1). NMR-images are recorded with a MSME-sequence. The size of the field of view (FOV) has been 25x25 mm^2 and the voxel size was about 0,1 mm.

In MRI the measured values for every pixel are stored in a matrx. Gray-scale images typically contain values in the range from 0 to 255. Fig. 2 shows the pore

structure of a foam in two different displacement situations. The probes were against each other shifted 0,5 mm.

Fig. 2.3 shows the sum of the NMR-values of the reference stucture A and the shifted structure B. The image of the sum of the NMR-values discribe the displacements like a double exposed film.

Shifts are computed with the cross-correlation function of the NMR-values. Fig. 3 shows the NMR-intensities along a line in structure A and B. The position of the characteristic maxima of the intensity function gives information of the displacement between the probes.

For the calculation of the displacements the two intensity functions are correlated by crosscorrelation (Fig. 4). The position of the maxima of the crosscorrelation function discribes the describes the shifts of the two probes towards each other.

4. Conclusion

With MRI it is possible to detect the deformations in the interior of the structure. By cross-correlation displacement profiles can be derived from two images like in figure 2.

Fig. 1.1: MRI-system

Fig. 1.2: Probe heads

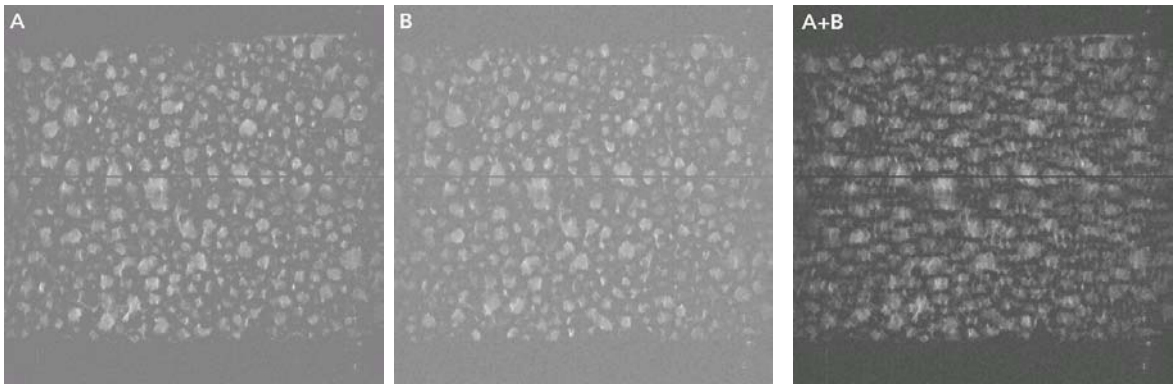

Fig. 2.1: NMR-Image of Reference structure (MSME-Sequence, 256x256, FOV= 25 mm)

Fig. 2.2: NMR-Image of displaced structure (MSME-Sequence, 256x256, FOV= 25 mm)

Fig. 2.3: Image (A) +Image (B)

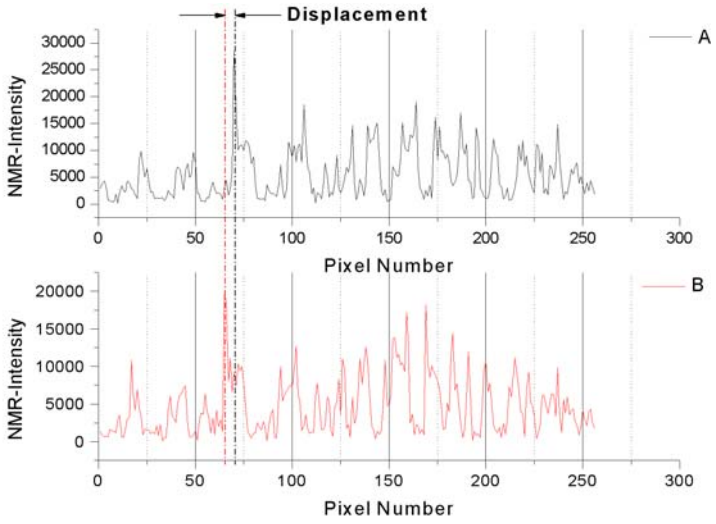

Fig. 3: NMR-Intensity along a line in image (A) and image (B)

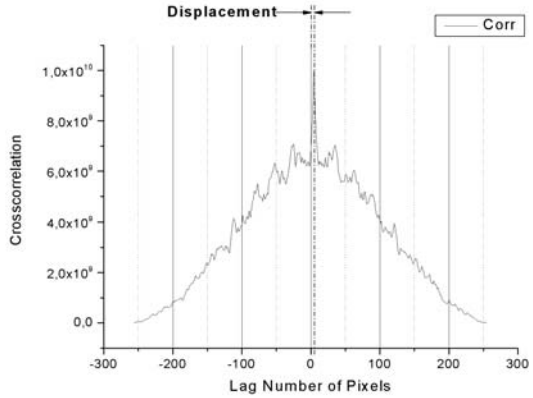

Fig. 4: Crosscorrelation function

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