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MECHANICAL ANALYSIS ON ROCKET PROPELLANTS

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Abstract

The mechanical properties of solid rocket propellants are very important for good functioning of rocket motors. During use and storage the mechanical properties of rocket propellants are changing, due to chemical and mechanical influences such as thermal reactions, oxidation reactions or vibrations. These influences can result in malfunctioning, leading to an unwanted explosion of the rocket motor.

Most of modern rocket propellants consist of a polymer matrix (i.e. HTPB) filled with a crystalline material (i.e. AP, AN). However, the more conventional double base propellants consist of a solid gel matrix with additives, such as stabilizers. Both materials show a mechanical behaviour, quite similar to that of general polymers. To describe the material behaviour of both propellants a linear visco-elastic theory is often used to describe the mechanical behaviour for small deformations. Because the time-temperature dependency is also valid for these materials a mastercurve can be constituted. With this mastercurve the response properties (stiffness) under extreme conditions can be determined.

At TNO–PML a mastercurve of a double base propellant was constituted using dynamical mechanical analysis (DMA) and compared with a mastercurve reduced from conventional (static) stress relaxation tests. The mechanical properties of this double base propellant determined by DMA were compared with conventional (quasi-static) tensile test results.

Keywords: DMA, mastercurve, polymer, propellant

Introduction

The lifetime of rocket motors is primarily a function of the mechanical properties of the rocket motor propellant, the ageing characteristics of the rocket propellant, the grain design and the environmental conditions endured during operation use. The mechanical properties of solid rocket propellants are very important for the good functioning of rocket motors. An increase in burning surface of the propellant grain due to undesired cracks and voids can result in malfunctioning or, in worst case, explosion of the rocket motor. Ageing of propellants can be caused by a number of different processes:

- chemical (oxidative cross linking)
- physical (migration of plasticizer, humidity)
- mechanical (stress during cyclic cool down, vibrative loads).

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In order to be able to reduce the risk for malfunctioning of the rocket propellant, it is important to assess the propellant behaviour under various conditions. Therefore an extensive propellant characterisation need to be made. In particular by determining the stress and strain capacity and stiffness as a function of time and temperature.

In a conventional method the stiffness properties can be determined in a tensile tester using tensile tests and stress relaxation tests in a broad temperature range. In relaxation tests a dog-bone shaped (JANNAF) test specimen is stretched to a specified strain level with a defined strain rate. The stress response is measured during a certain time period (i.e. 600 sec) and converted into a relaxation modulus. Assuming the thermorheologic behaviour of the propellant, the time-temperature superposition (WLF) principle can be applied. The relaxation test results for different temperatures can be plotted with double logarithmic scale and shifted to form Prony fit, along the time axis. The achieved master curve shows the stiffness properties in a wide range of strain rates.

Using DMA an alternative method can be applied to construct a mastercurve. According to this method a sine-shaped strain is applied on a propellant test specimen at various temperatures and in a broad range of frequencies. The resulting force is measured and calculated into different kind of response properties such as loss modulus and storage modulus. Similar to the relaxation test method the moduli results can be shifted along the frequency axis to construct a master curve. Smaller test samples can be used in this method which is a major advantage when the amount of test-material is limited.

In this report a comparison is made between both test methods. However some dissimilarities in test results were observed, DMA appears to be applicable for propellant characterisation. In particular when knowledge of propellant properties in a wide temperature range are necessary.

Experimental

Generally in mechanical analysis different deformation modes can be applied on a test specimen. In a tensile tester the most common modes are uniaxial tension and compression. In DMA these types of deformation modes can be extended with torsion and shear. In this investigation only tension, compression and torsion were used. A survey of the test conditions can be seen in Table 1.

The difference in heating rate between the DMA experiments on the rectangle (with the Rheometer PL-DTMA) and on the cylinder (with the Seiko TMA/SS-150-C) can be explained by the size difference between both specimens. In order to prevent temperature gradients in the specimen, a lower heating rate was chosen for the larger specimen.

E' and E'' are known as the storage modulus and the loss modulus, respectively. E' represents the elastic properties of a material (the part that springs back in its original form after releasing the stress) and E'' represents the viscous properties (the part that is converted into heat). Tanδ represents the damping of the material (E''/E'). Similar definitions are applicable for G' and G'', however G represents the shear modulus.

The DMA experiments were carried out with a Rheometer PL-DTMA Torsion Rheometric System from TNO Industry and a Seiko TMA/SS-150-C from TNO-PML.

Table 1 Survey of test conditions of the mechanical analysis tests

Method	Apparatus	Mode	Temperature/ °C	Type of force	Frequency/ Hz	Measurement	β/ °C min^{-1}	Specimen
DMA	Rheometer PL-DTMA torsion rheometric system	torsion	–100→65	sine	0.1 0.3 1.0 3.0	G', G'', tanδ	0.5	rectangle
DMA	Seiko TMA/SS-150-C	compression	–100→50	sine	0.1	E', E'', tanδ	2.0	cylinder
tensile test	Zwick Z020 tensile tester	tension	–40, –20, 20, 60	quasi static	–	E, $E_{\text{relaxation}}$	–	JANNAF dogbone

The tensile tests and relaxation tests were carried out on a Zwick Z020 Tensile Tester with extensometer for accurate strain determination.

Sample description

Generally, solid propellants can be considered as highly cross-linked, long-chained polymers, highly filled with solid particles. The rubber-like behaviour makes the propellant hard to shape into small specimens. A double base propellant is based on fibrous nitro-cellulose, plasticized with nitro-glycerine. Both propellants contain oxygen and fuel in the same compound. The double base propellant is very homogeneous and more rigid, compared to composite propellants. Therefore it is more easy to machine.

For the mechanical characterisation of a material, specimens have to be machined with very high degree of accuracy, especially when small specimens are used. In comparison to the overall dimensions of a small sample, a relatively minor deviation in length or width might have a significant effect on the measurement results. In addition to that, most propellants are sensitive to impact and friction. Machining can lead easily to ignition of the propellant, causing an exothermic reaction. Therefore, safety is of major concern during preparation of specimens. At TNO-PML a method was developed to prepare specimens by remote control.

The cylindrical samples that are used with the DMA experiments on the Seiko TMA/SS-150-C (Table 1) have a diameter and length of about 3 mm. These specimens were prepared by remote control milling from a propellant block. The specimens for the DMA experiments using the Rheometer PL-DTMA Torsion Rheometric System have a rectangular shape. These specimens were milled out of JANNAF dogbones to the dimensions of 10 mm×6 mm×50 mm, also by remote control. The quasi-static tensile tests were carried out on standard JANNAF dogbone test samples with a 50 mm gauge length.

Results and discussion

DMA testing results in torsion mode

In the DMA experiments storage and loss moduli in shear (G' and G'', respectively) and damping (tanδ) were measured as a function of temperature and frequency. A typical DMA testing result is represented in Fig. 1. This is the result of a DMA temperature scan, in torsion mode at a frequency of 1 Hz.

Figure 1 shows a decrease in storage modulus (G') with increasing temperature. The characteristic damping peaks in the tan δ curve can be attributed to (partial) release of chains in the molecular structure with rising temperature. A transition temperature can be seen at –30°C. At temperatures below approximately –60°C damping is very low, the material responds almost completely elastic. There is hardly any freedom of movement in the chains at these temperatures. In Fig. 2 the storage modulus and damping are represented as a function of temperature and frequency. The transition temperature of –30°C is clearly independent of frequency.

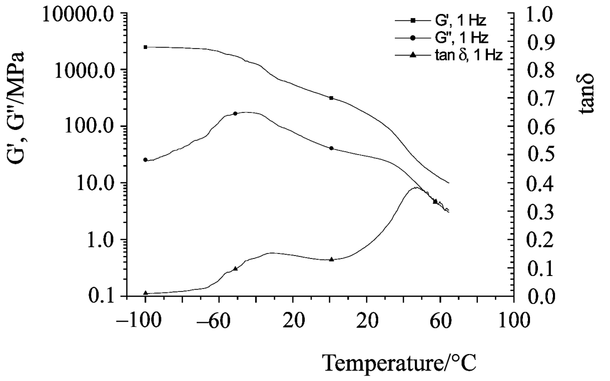

Fig. 1 DMA response of double base propellant, torsion mode, f=1 Hz

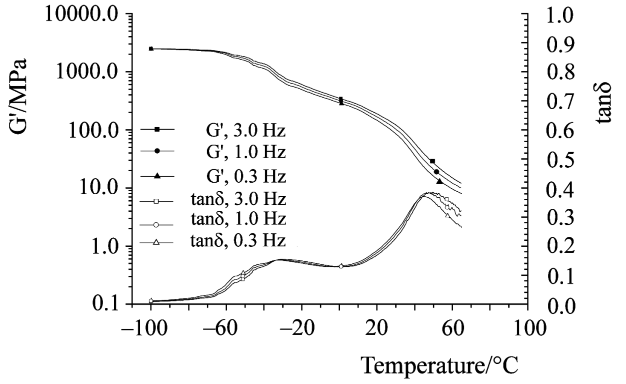

Fig. 2 Frequency dependency of a double base propellant

DMA testing results in compression mode

In the DMA experiments the storage and loss moduli in uniaxial tension and compression mode (E' and E'', respectively) and damping (tanδ) were measured as a function of temperature and frequency. A typical DMA test result is represented in Fig. 3. This is the result of a DMA temperature scan, in compression mode at a frequency of 0.1 Hz.

Figure 3 shows a slight decrease in storage modulus (E') and a slight increase in loss modulus (E'') with increasing temperature. In contrast with the previous DMA measurements, no maximum in tan δ can be seen around –30°C, due to the small deformation at low temperatures.

Correlation of test methods

Initial moduli of elasticity from tensile tests at different temperatures were compared to converted initial moduli from DMA testing results. As a first order assumption the modulus of elasticity are calculated according the following formulas:

The complex moduli were calculated from G' and G'':

$$G=\sqrt{((G')^2+(G'')^2)}$$

and similar from E' and E''. Then G was converted to E-modulus by:

$$E=2G(1+\nu)$$

in which ν is the Poisson ratio, which is assumed being 0.5.

The results of the calculated E-moduli from DMA measurements (torsion and compression), together with the results of the slow tensile tests are represented in Figs 4 and 5, respectively.

In these figures the strain rates of the DMA measurements were determined from the maximum amplitude of the strain and the frequency. The DMA torsion results show same tendency as the initial E-moduli of the STT, however there is a difference in strain rate. The DMA compression results show much lower values than the STT results.

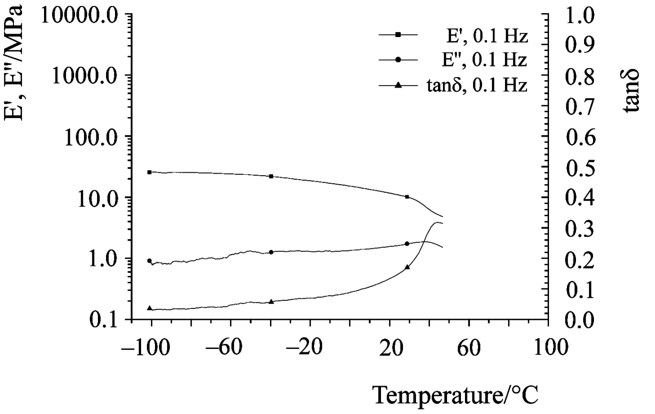

Fig. 3 DMA response of double base propellant, compression mode, f=0.1 Hz, force: 5–10 g

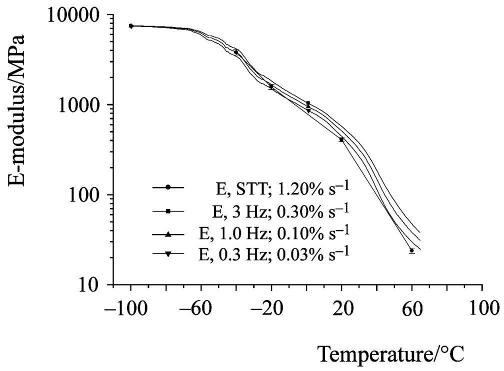

Fig. 4 E-moduli *vs*. temperature, DMA torsion and slow tensile test (STT)

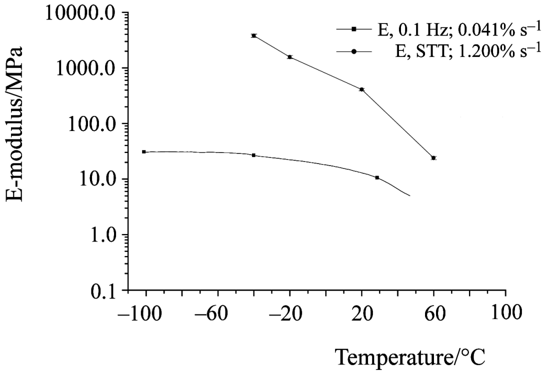

Fig. 5 *E*-moduli *vs*. temperature, DMA compression and slow tensile test (STT)

Correlation of torsion tests with relaxation tests

The time-temperature dependency was applied to the DMA test results in the torsion mode. The data from Fig. 6 was therefore shifted horizontally and reduced to the mastercurve, shown in Fig. 7.

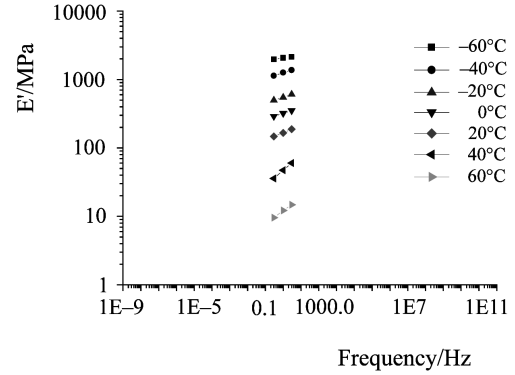

Fig. 6 Storage modulus *vs*. frequency of a double base propellant

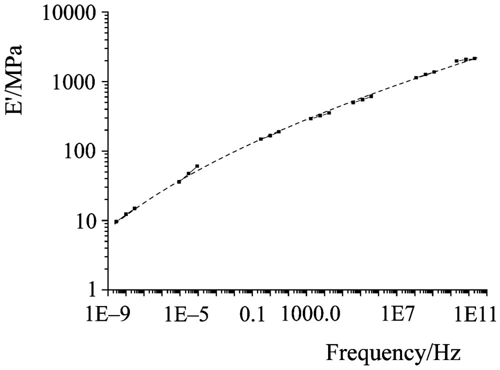

Fig. 7 Mastercurve of a double base propellant, T_{ref}=20°C

In Table 2 the applied shiftfactors of the relaxation tests and the DMA test results (torsion mode) are represented.

Table 2 Shiftfactors of double base propellant

Temperature/°C	Shiftfactors [–]	
	Relaxation results	DMA (torsion) results
–60	–	10.8
–40	10	8.6
–20	7	5.1
0	–	2.8
20	0	0.0
40	–	–4.5
60	–8	–8.0

The number of shiftfactors that can be compared are limited because the relaxation tests were carried out at only 4 temperatures. It appears that the difference is larger at lower temperatures. The results of the slow tensile tests however, are similar at lower temperatures. This could be explained by inaccuracies in horizontal shift as a consequence of the relatively low number of data points since measurements were only performed at three frequencies.

Conclusions

From this study the following conclusions could be drawn:

- DMA techniques could be applicable to determine the mechanical properties of solid rocket propellants.
- Results from DMA provide important information about fast changes in mechanical properties due to temperature changes.
- Considerable differences in propellant stiffness were observed by comparison of DMA results with conventional mechanical test methods.
- The sample dimensions in DMA tests have to be taken into account, when the mechanical properties are determined over a broad test range.
- In order to determine the time-temperature superposition principle, an isothermal frequency scan mode should be applied, instead of temperature scan mode.

List of abbreviations

AN	Ammonium nitrate
AP	Ammonium perchlorate
DMA	Dynamical mechanical analysis

E	Elasticity modulus
G	Shear modulus
HTPB	Hydroxy-terminated polybutadiene
JANNAF	Joint Army, Navy, NASA, Air Force
STT	Slow tensile test
TMA/SS	Thermal mechanical analysis/stress strain
ν	Poisson ratio

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