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Study of Mechanical Properties of Naturally Aged Double Base Rocket Propellants

Muhamed SUĆESKA*, Sanja MATEČIĆ MUŠANIĆ
and Ivona FIAMENGO

Brodarski Institute – Marine Research & Advanced Technologies,
Av. V. Holjevca 20, 10020 Zagreb, Croatia
**E-mail: suceska@hrbi.hr*

Sanko BAKIJA

Ministry of Defence of the Republic of Croatia,
Bauera 33, 10000 Zagreb, Croatia

Ante BAKIĆ and Janos KODVANJ

Faculty of Mechanical Engineering and Naval Architecture,
I. Lučića 5, 10000 Zagreb, Croatia

Abstract: Various chemical reactions and physical processes (such as stabilizer consumption, migration and evaporation of nitroglycerine, decomposition of nitroglycerine and nitrocellulose, etc.) take place in double based rocket propellants grains over the time, even under ambient storage conditions. The overall effect of these reactions and processes are changes of physical, chemical, thermal, ballistic and mechanical properties of rocket propellants with storage time, i.e. the reduction of the propellants performances and safe service life.

The aim of this work was to evaluate the mechanical changes of rocket propellants – sustainers, built in in-service antitank guided missiles systems, induced by natural ageing at ambient conditions during up to 35 years of storage. The mechanical and viscoelastic properties were tested using a dynamic mechanical analyser, an uniaxial tensile and compression tester, and a notch toughness tester.

The results have shown that the changes of the studied mechanical and viscoelastic properties are evident, although the results of the tests are rather scattered (as a consequence of measuring uncertainty, different ageing histories of propellants, etc.) or changes of some properties are not too pronounced. For example, after 15 years of storage at ambient conditions the glass transition temperature increases for about 5 °C, the tan δ in the glass transition region decreases for about 5%, the storage and loss modulus at 25 °C increase for about 15%, Young modulus at 23 °C increases up to 30%, the notch toughness at -30 °C decreases up to 15%, etc. Along with these tests, the stabilizer content determination and proving ground ballistic tests were also done.

Keywords: mechanical properties, rocket propellant, natural ageing, dynamic mechanical analysis, tensile test

Introduction

The mechanical properties of solid rocket propellants are very important for proper and safe functioning of rocket motors. Due to chemical reactions and physical processes that take place during the storage time, even under ambient temperature, a number of propellants properties may change [1-10]. The mechanical and viscoelastic properties (such as tensile strength, modulus of elasticity, morphology, temperature of glass transition, etc.) also change during the storage. These changes can result in serious malfunctioning of a rocket motor.

This is the reason why the explosive community is so interested in studying the ageing phenomena of rocket propellants. There are a lot of studies devoted to the artificial ageing at elevated temperatures, but there are much less studies that treat the ageing at ambient storage conditions.

In this paper we tried to fill this gap by presenting the results of a systematic study of the mechanical and viscoelastic properties of naturally aged double base rocket propellants built in antitank guided missiles (ATGM). The study is a part of our lifetime extension program. The main goal of the study was to get the answer to the question: does the present aging state of the ATGM fulfil the requirements for extended life after a very long storage period?

The study was carried out on ATGM manufactured in the period between 1973 and 1990. It should be mentioned that the initial mechanical and viscoelastic properties (i.e. properties immediately after the production), as well as the storages histories of the studied propellants were unknown to us. We assumed that the initial mechanical and viscoelastic properties of the tested propellants were the same (or almost the same); however, there is no doubt that the storage conditions (e.g. storage temperatures) were somewhat different. Also, we assumed that the changes caused by natural ageing during such a long period of time were much more pronounced comparing to the errors caused by different initial properties and different ageing histories.

It should be noted that besides testing of mechanical and viscoelastic properties, some additional tests were carried out also: e.g. visual inspection, chemical stability assessment, internal ballistics tests (static firings of rocket motors and proving ground firings) in order to assess the actual ageing state of ATGM.

Experimental

The experiments were conducted using double base (nitrocellulose/nitroglycerine) rocket propellants (sustainers) for ATGM. The testing samples for dynamic mechanical and uniaxial tensile and compression tests were prepared by machining rocket grains (grain dimensions were: L = 250 mm, Φ = 65 mm, and mass = 1.5 kg). The samples for DMA tests were of rectangular bar shape (50x10x2.5 mm), while the samples for uniaxial tensile tests were of «dog bone» form (according to JANNAF C). The testing procedure and preparation of the samples were as described in standards [11-17]. All tests were done in the year 2008, i.e. 18 to 35 years after the production.

The DMA tests were carried out using *TA Instruments* DMA, Model 983 in fixed frequency mode, under the following testing conditions:

- fix frequency mode,
- frequency of oscillatory load: 1 Hz,
- heating rate: 2 °C /min,
- amplitude of deformation: ± 0.2 mm,
- length to thickness ratio: (L/T): 10,
- temperature range: -120 °C to +80 °C.

The uniaxial tensile and compression tests and the notch toughness tests were carried out using tensile tester *Alpha 50 – Messphysik Beta 50-5*, and Charpy hammer *Karl Frank Gmb*. The following testing conditions were used:

Tensile and compression tests:

- measuring range: 0 to 50 kN,
- tensile rate: 50 mm/min,
- compression rate: 20 mm/min,
- compression sample dimensions: cylinder 15 mm in radius and 15 mm height,
- temperature range: -40 °C, 25 °C and +50 °C .

Charpy hammer tests:

- measuring range: 0.5 J,
- sample dimensions: 10 x10 x 90 mm,

- distance of supports: 40 mm,
- measuring temperature -30 °C .

The maximum stress and deformation at maximum stress were determined from stress-strain curves dependence, from tension and compression tests, at three different temperatures.

Results and Discussion

Results of dynamic mechanical analysis

A typical DMA thermogram of a double base rocket propellant is shown in Figure 1. It follows from Figure 1 that the storage modulus is almost constant and it reaches maximum value in the region below the glass transition (-120 to -100 °C). Transition from the glassy to the viscoelastic state (onset point on E'-T curve at about -64 °C) has as a consequence a drop of the storage modulus of about 6 times (from 8 GPa at -120 °C to 1.3 GPa at 25 °C). Another distinct change in the storage modulus slope at about 42 °C corresponds to the propellant sample softening.

The loss modulus has a maximum in the glass transition region. The maximum on E''-T curve, at -26.95 °C, is usually taken as the glass transition temperature. At the sample softening region (~ 49.83 °C) the loss modulus decreases rapidly.

The tan δ has a local maximum at the glass transition region. The value of the tan δ increases in the softening region as a consequence of increased mobility of nitrocellulose macromolecules with temperature and increase of dissipative loses of applied energy.

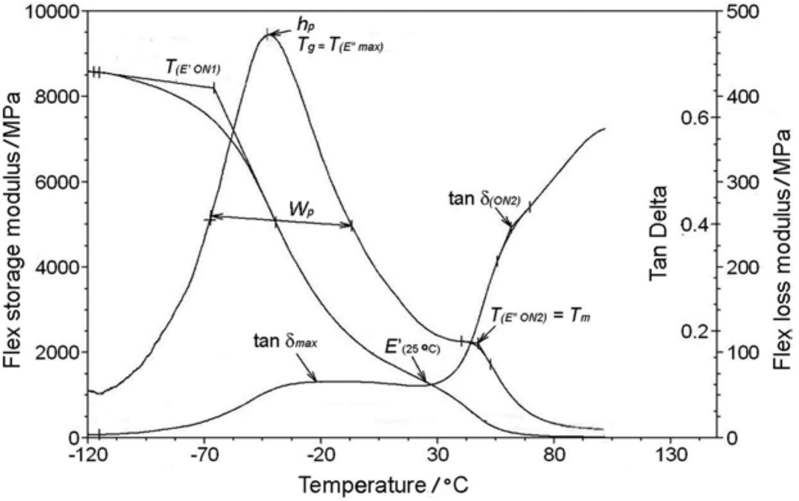

Figure 1. Typical DMA thermogram of DB rocket propellant (storage modulus, loss modulus and tan δ *vs.* temperature).

In order to detect and to quantify changes of DMA properties caused by the ageing, several characteristic points/parameters on the *E′-T, E″-T,* and tan δ-*T* curves were selected (as shown in Figure 1). The changes of these parameters versus the year of propellants' production are given in Figures 2-6.

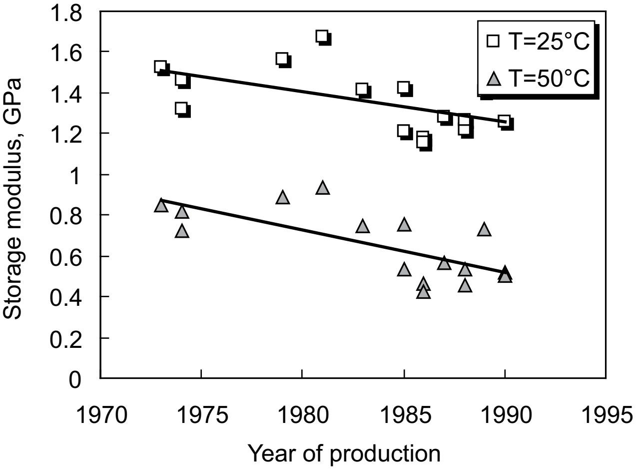

Figure 2. Storages modulus change *vs*. year of production.

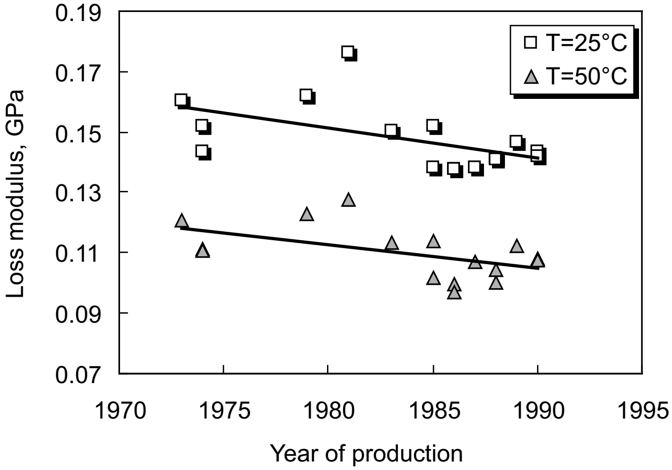

Figure 3. Loss modulus change *vs.* year of production.

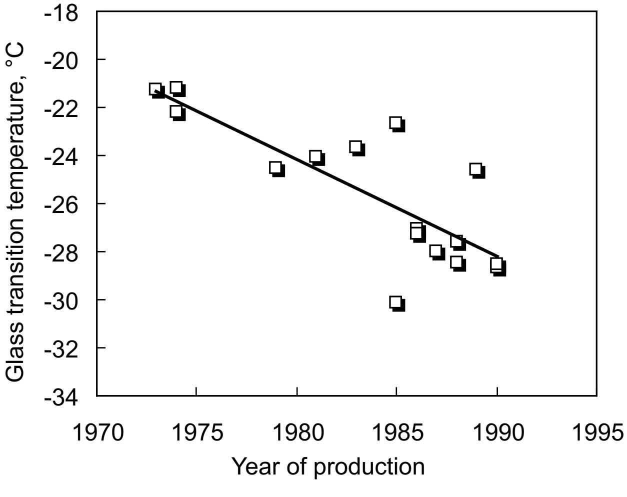

Figure 4. Glass transition temperature *vs.* year of production.

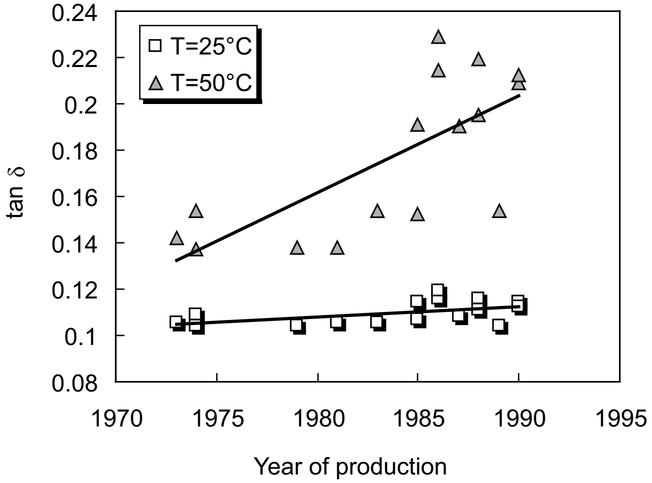

Figure 5. Tan δ *vs*. year of production.

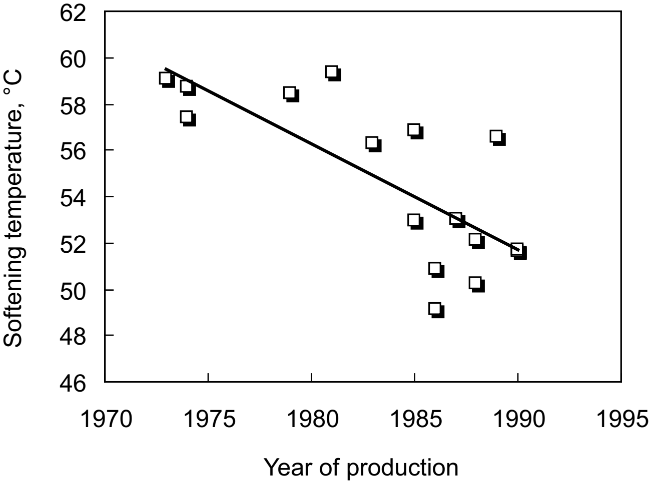

Figure 6. Softening temperature *vs*. year of production.

It is obvious from Figures 2-6 that the scattering of the results is considerable. Such scattering of the results is not only the consequence of measuring uncertainty but also the consequence of the fact that the ageing histories of the tested propellants were considerably different.

However, in spite of such scattering of the results and the fact that changes of some parameters were not too pronounced, it is obvious that ageing at the ambient storage conditions for a long period of time caused significant changes of DMA parameters: the storage modulus, the loss modulus, the glass transition temperature, and the softening temperature increased with the ageing, while the tan δ decreased.

If we suppose a linear change of the studied DMA parameters with the ageing time, we can conclude as follows. The glass transition temperature (Figure 4) equals -28 °C for the propellant produced in 1990, while for the propellants produced in 1973 it equals about -21 °C – this means that the difference is 7 °C. In other word, in this time period the glass transition temperature increased for about 0.4 °C every year. Similarly, the softening temperature increased in the same time period for about 8 °C. Furthermore, the storage modulus at 25 °C, during the same period, increased from 1.25 to 1.52 GPa, while the loss modulus increased slightly - from 0.14 to 0.16 GPa. A significant change of the tan d value at 50 °C is visible from Figure 5 – in 17 years of ageing the tan δ decreased from 0.20 to 0.13.

Such results are in accordance with our results obtained under conditions of artificial ageing at elevated temperatures [18], and can be explained in the following way. The increase of the storage modulus is connected with the reduction of mobility of macromolecules**.** On the other hand, the reduction of the mobility of nitrocellulose macromolecules is a consequence of the decrease of nitroglycerine amount (due to its migration from the propellant grain centre to the surface, and its vaporization and decomposition). A combined effect of these physical processes and chemical decomposition reactions is a shortening of the distance between nitrocellulose macromolecules and an increase of intermolecular interactions. Consequently, the mobility of the nitrocellulose chain units decreases.

The decrease of the tan δ (a parameter very sensitive to the motion of chain units of macromolecular chain), as well as the increase of the softening and glass transition temperatures confirm also the statement that the ageing causes the reduction of mobility of nitrocellulose chain, primarily due to decrease of the plasticizer (i.e. nitroglycerine) amount.

Results of uniaxial and toughness tests

The results of the propellants testing by the tensile tester machine and Charpy hammer are shown in Figures 7 to 11. The following parameters were analysed: Young’s modulus, the stress at maximum load, the strain at maximum load, and the notch toughness at -30 °C .

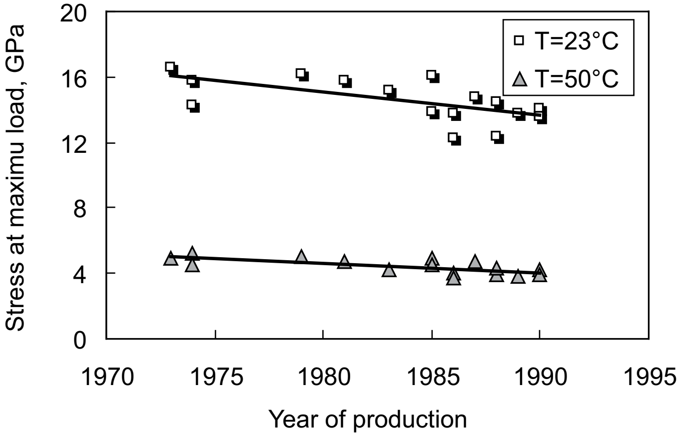

Figure 7. Stress at maximum load (tensile) *vs.* year of production.

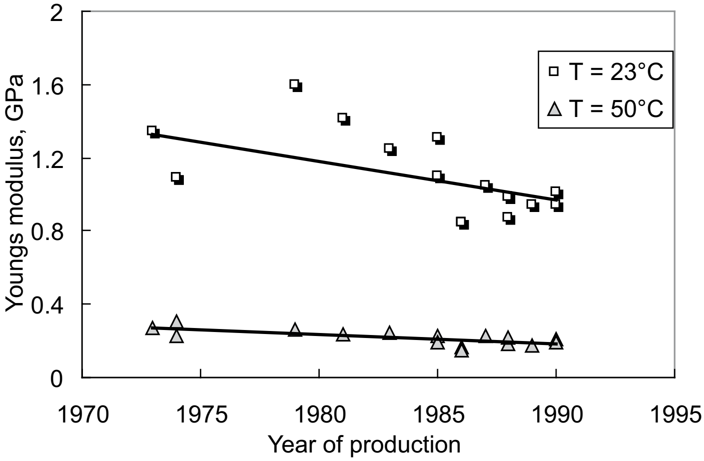

Figure 8. Young's modulus (tensile) *vs.* year of production.

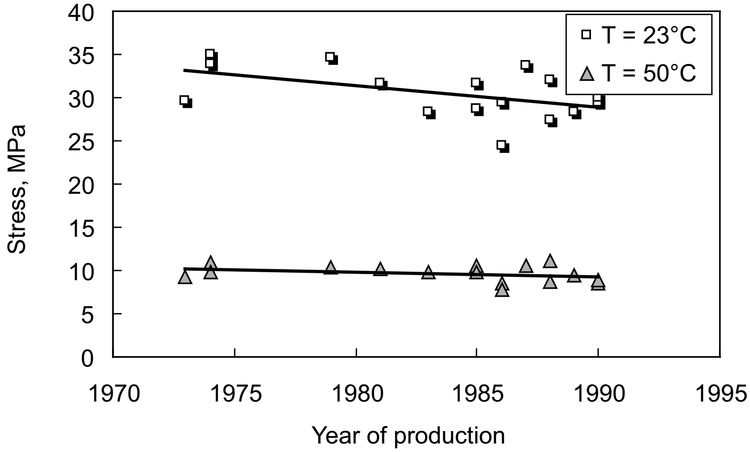

Figure 9. Stress at maximum load (compressive) *vs.* year of production.

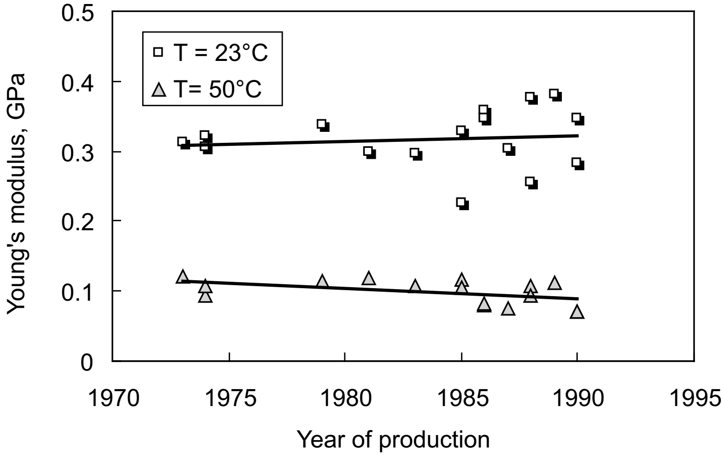

Figure 10. Young's modulus (compressive) *vs.* year of production.

Figure 11. Toughness changes *vs.* year of production.

The results given in Figures 7 to 11 are also rather scattered due to the same reasons as mentioned in the case of DMA tests. However, generally spoken one can observe a good agreement between these results and the results of DMA tests.

For example, the stress at maximum load slightly increases (tensile stress at 23 °C for the propellants produced in 1999 equals 13.6 MPa, while for propellants produced in 1973 it equals 16.6 MPa; the compressive stress for the propellants produced in 1999 equals 28.2 and it is 33.8 MPa for the propellants produced in 1973), Young's modulus slightly increases (Young's modulus obtained by tensile tests at 23 °C equals 0.94 GPa for the propellants produced in 1999, and 1.34 GPa for the propellants produced in 1973, while Young's modulus obtained from the compressive tests at 23 °C remains almost constant during this ageing period, but slightly increases at 50 °C).

The results of notch toughness at -30 °C are very scattered (probably due to the fact that the tests were carried out at the temperature close to the glass transition temperatures at which small changes in temperature may cause significant changes in toughness), but it seems that there is a trend of its decrease with the aging time.

The main reason for an increase of the storage modulus and Young's modulus, and also for an increase of the glass transition and the softening temperature, and a decrease of the tan δ and notch toughness with the ageing time is the reduction of NC macromolecules mobility due to the nitroglycerine (which acts also as a plasticiser) amount reduction.

In addition to the DMA and the tensile and compression tests results, additional tests were done in order to fully characterise the actual ageing state of the studied propellants; e.g. visual inspection, stabilizer concentration, ballistic tests (rocket motor static firing test and proving ground firing tests). The visual inspection has shown that there are no cracks, flaws or other failure on the surface of the propellant grains. It is interesting to note that the stabilizer concentration tests, done by HPLC [16, 17], have shown that the initial stabilizer (ethyl centralite) was completely consumed and only its nitro and nitroso derivatives were detected.

The static firing tests of rocket motors in the temperature range -50 °C to +50 °C have shown proper functioning of the motors, without any malfunction caused by the propellant charge (however, malfunctions of igniter charges happened). The firing tests on the proving ground, i.e. in the real conditions, also did not show any malfunctions or failures connected with the propellant charges – neither boosters nor sustainers.

Conclusions

The mechanical and viscoelastic properties of double base propellants built in small calibre antitank guided missiles (ATGM), and aged at ambient storage conditions for a long period of time (up to 35 years) were studied in this paper.

The results have shown that some considerable changes of the mechanical and viscoelastic properties of the propellants happened during the ageing. For example, an increase of the modulus of elasticity and Young's modulus, an increase of the glass transition and the softening temperatures, and a decrease of the toughness and the tan δ were observed. The observed changes are connected with a decrease of nitrocellulose macromolecules chains mobility due to the plasticiser amount decrease and due to chemical degradation of energetic constituents, nitrocellulose and nitroglycerine.

The results of these tests, together with stabilizer concentration tests, static firing tests of rocket motor, and proving ground ballistic tests, have shown that the changes of the mechanical and viscoelastic properties of the propellants after 35 years of ageing are still not of such extent to cause malfunctioning of the rocket motors, although some of them are significant.

Furthermore, according to the common stabilizer concentration criteria [16, 17] all propellants are assigned as "unstable" (since the original stabiliser was completely consumed, i.e. not detected at all), but from the mechanical and ballistic point of view they were still safe to use. Static and ballistic tests on the proving ground did not show any critical malfunction of the rocket motors due to the propellant charge.

The other tests carried out in this study have shown that some other parts of the ATGM were more critical in terms of safe service life than the propellant charges (e.g. electronic components, igniter charges, some metal parts, etc.).

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