Investigation of properties of heterogeneous solid rocket propellants after accelerated aging

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Introduction

Heterogeneous solid rocket propellant (HSRP) is a high-energetic material, from which in technological process are obtained loads of propulsion rocket for various purposes. Loads of this type are made from the slurry of composition (highly filled suspension), which is the propellant in initial process and which liquid phase is mainly a synthetic butadiene rubber with functional groups (such as HTPB), the filler is a solid oxidant (ammonium perchlorate) and aluminium powder – after curing. The geometrical dimensions and shape of the load and its composition affects the basic characteristics and working conditions of a rocket motor.

Heterogeneous solid rocket propellant should provide :

– required energy efficiency,
– operating reliability,
– high chemical and physical stability upon storage at different conditions,
– ability to steady combustion,
– homogeneity of the physicochemical, physicomechanical and ballistic properties.

The most important main characteristics of the propellant load made of HSRP are:

– **specific impulse** (as determined by the composition, imposed by the constructor),
– **burn rate** (adapted to the requirements),
– **physicochemical properties**,
– **mechanical properties**,
– **shelf life**.

Rocket motors with HSRP are characterized strictly by temporary storage time, which depends primarily on the changeability of physicochemical and mechanical properties HSRP due to time. This time is determined on the basis of accelerated aging test at higher temperatures than ambient, which allow to predict the shelf life of exploatation of loads. HSRP characteristics depend basically on the mechanism of oxidation of crosslinked rubber HTPB (binder), which affects the mechanical parameters of fuel according to empirical kinetic model proposed by Layton [1] expressed in the form of equation (1)

$$P(T,t) = P_0(T,t_0) + k(T) \cdot \lg(t) \quad (1)$$

where P(T, t), $P_0(t_0)$ – studied mechanical parameter for specific temperature and time of aging (t) and the initial time (t_0), k(T)- constant rate of aging, temperature dependent.

Assuming that the same mechanisms occur both during accelerated aging and natural aging rate constant is a function of temperature, which in accordance with the Arrhenius equation has the form

$$k(T) = A \cdot e^{\left(-E_a/R \cdot T\right)} \quad (2)$$

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where: A – constant reaction rate of aging; E_a – activation energy; R = 8,314 [J mol^{-1} K^{-1}] – gas constant, T – absolute temperature.

Aging changes the physical and chemical properties of HSRP as a result of occurring chemical and physical processes, namely:

a) Oxidation of the binder leading to hardening of the propellant. Hardening of propellant generally increases due to the presence of air. The hardness of the propellant is higher at/on the surface than in the middle of the propellant.
b) Degradation of the adhesive due to bursting/decay chains.
c) Migration of plasticizers and/or liquid catalyst in the direction of the free surfaces causing hardening of the propellant and increase its sensitivity to friction.
d) Surface changes of ammonium perchlorate as a result of moisture absorption, partially dissolved, after which recrystallization occurs.

Characteristics of aging research

Aging studies are mainly measurement of: the content of antioxidant remaining in the propellant, the content of the solubilized fraction and the crosslink density, the content of plasticizer in different parts of the propellant and to determine the viscoelastic properties, and mechanical strength of the propellant [2 – 4]. It follows that:

1. Measurement of antioxidant remaining in HSRP provides a quantitative assessment of the state of degradation of the binder.
2. Measurement of the solubilized fraction (sol) or the crosslink density can evaluates how far developed HSPR degradation reactions, both as a result of crack chains and reduction of the crosslink density.
3. Measurement of the plasticizer and burning rate modifier in HSPR will determine its rate of migration of the propellant.
4. Measurement of mechanical strength of monoaxial stretching allows the measurement of mechanical properties of the propellant and respond to its destruction in the data at the specified temperatures and speeds of travel traverse extending propellant sample.
5. The application of dynamic-mechanical analysis (DMA) allows an assessment of the viscoelastic properties of the propellant.
6. The hardness measurement by Shore A method makes it possible to determine changes in hardness of propellant.

However may be also carried out other measurements such as: determination of thermochemical properties by DSC or DTA (STANAG 4515), sensitivity to impact, friction, electrostatic, thermal sensitivity (STANAGs: 4489, 4487, 4490, 4491); analysis of the content of transition metal compounds by plasma atomic emission spectrometry using argon or by any other suitable method. Some of them will be discussed below.

Aging of samples at elevated temperatures HSPR

Heterogeneous solid rocket propellant samples aging at elevated temperatures is intended to simulate spontaneous aging processes

in less time that we face during the actual storage devices containing HSPR in operating conditions. They are made in many ways, both in a selected temperature or in several. In the case of a temperature of 60°C tests are carried out for 3 and 6 months [2]. After completion of the accelerated aging propellant samples are removed and cooled to ambient temperature. While accelerated aging may occur destructive effects of a propellant sample such as cracks, holes, cavities, which should be recorded. Most propellant samples are conditioned in all the blocks, since this can be several kinds of samples for specific tests. Blocks are placed in a suitable container or carton so as to obtain the seal. Samples aged in the thermostat may have altered the surface, which also should pay attention when they are removed. Therefore, some of the top layer of the propellant block should be removed, and only collect adequate samples of propellant from the block. Removed layer can be useful for studies related to the processes occurring near the surface of the propellant. According to [2] is prepared from such a block of five samples JANNAF C uniaxial tensile test, three rods DMA and four disks for testing Shore hardness (Fig. 1). The residue of the propellant can be used for analysis of physicochemical, thermal properties etc.

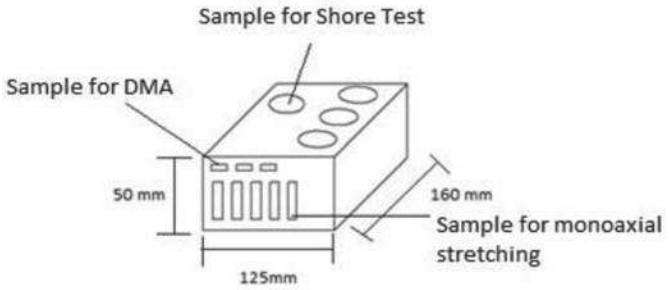

Fig. 1. The location of the samples in block propellant [2]

Determination of the soluble fraction – sol in propellant

This parameter is important because the fraction dissolved allows us to specify so called cross-link density of the propellant. There are two methods to determine this. The first is to swell a certain quantity of propellant in dichloromethane or toluene for a suitable time, separating the solvent from the gel fraction. For this purpose, an appropriate weight of propellant is placed in a beaker with the solvent (100 ml 1–2 g of propellant) and allowed to stand at ambient temperature for swelling the sample of propellant. A swelling time of the samples is around 4 days, after which the fraction is separated and the gel is dried in a thermostat to a constant weight. Soluble fraction (S) is calculated from the formula:

$$S = (W_i - W_s)/W_i \quad (3)$$

where: W_i – weight of unswollen sample[g], W_s – sample weight after extraction [g].

In the second method, the extraction is carried out using a set of the Soxhlet. In this case, as a solvent, dichloromethane is used. The sample is extracted for at least 16 h. After extraction thimble is dried and weighed again. Sol fraction of the sample is equal to the depletion weight of the core, divided by initial weight of the sample of propellant. The content of the dissolved fraction was calculated from equation (4):

$$S = (W_2 - W_3)/(W_2 - W_1) \quad (4)$$

where: W_1 – weight of dry thimble, W_2 – weight of thimble + sample before extraction, W_3 – weight of thimble + sample after extraction.

The content of soluble fraction allows us to specify the change of parameter called cross-linking density, which indicates the state of degradation of the propellant. This parameter can be evaluated with a modified equation of Charlesby-Pinner (5)

$$\text{Cross-linking density} = (1\text{-}S)(S + S^{1/2})/(S + S^{1/2}) \quad (5)$$

where: S – soluble fraction.

Determination of crosslinking density

Crosslinking density is a parameter which allows to determine the physical properties of HSRP, because during the aging this parameter changes and allows to estimate the state of degradation of the propellant as a result of the processes of its aging. The test method involves swelling in toluene particular sample HSPR for several days (approximately one week) at room temperature until a stable swollen state. The sample in the shape of a cylinder with a diameter of 2.5 cm and a height of 1.5 cm is subjected to a compression weights of known mass. The results are presented in the form of a graph of the weight loading, depending on the deflection of propellant samples for each aging time. The density of cross-linking (C) is estimated from the equation (6)

$$C = h_0 S/(3A_0 RT) \quad (6)$$

where: h_0 – the amount of sample A_0 – cross-sectional area of the specimen, R – gas constant (8.315 J/(mol K)), T – temperature, S – the slope × 9,807 m/s^2 (N/m), C – crosslinking density (mol/m^3) [2]. Figure 2 shows graphs illustrating methods of changing sol contain during aging at 60°C for HTPB and CTPB based propellants.

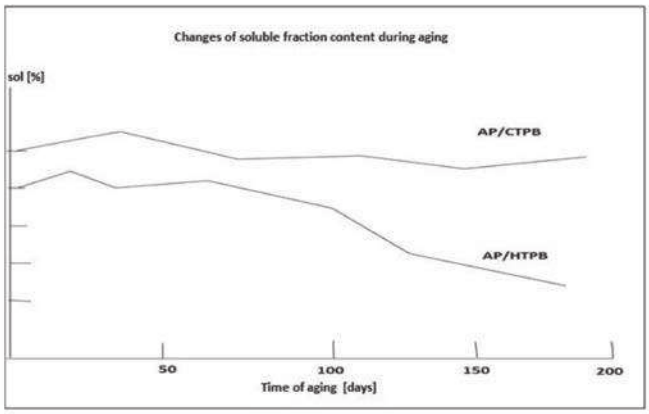

Fig. 2. Changes of the soluble fraction as a function of aging time [4]

Determination of antioxidant content in rocket propellant

The content of antioxidant in the HSRP prevents the degradation processes of the binder by oxidation cross-linked rubber HTPB time. From this point of view, to determine its content of the propellant is at high importance. To determine the amount of antioxidant in HSRP is used high performance liquid chromatography (HPLC) with a suitable internal standard. The sample of propellant about weight of 5 g is cut into small pieces measuring about 2–3 mm, and extracted with methanol. Agitation should last about six hours. Then, using centrifuges and filtration, a clear solution is injected into the HPLC system. As a standard solution is used triphenylamine. From obtained in the measurement- chromatogram is determined by calculating the amount of antioxidant chromatography peak areas. Figure 3 shows a chromatogram obtained when tested separated antioxidants: 2,2'-methylene-bis(4-methylene-6-tert-butylphenol) (commercial name: MBP5), 2,6-di-tert-butyl-p-cresol (commercial name: IONOL) triphenyloamine.

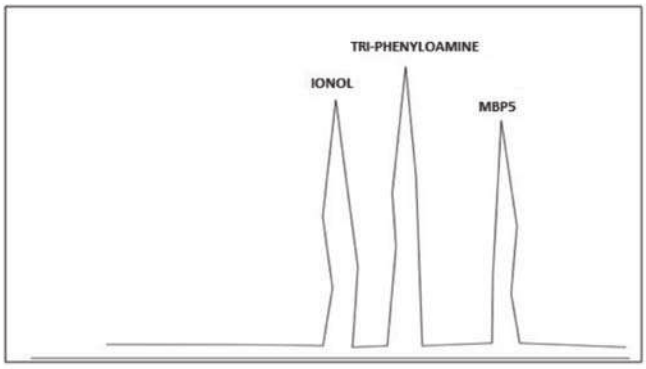

Fig. 3. The chromatogram analysis of antioxidant [2]

Determination of antioxidant in the propellant is not always possible due to the fact that certain antioxidants (ex. 2,5-di-tert-butyl-hydroquinone) are highly reactive with isocyanates used to cure the propellant and it is attaching to the end of molecular chain to form HTPB covalent bond. As the effect this kind of antioxidants can not be extracted and therefore it is not possible to determine their amount in the propellant.

Measurement of plasticizer content

The most commonly used HSRP plasticizers include: dioctyl adipate ($[C_8H_{17}OOC\ (CH_2)_2]_2$), isodecyl pelargonate ($CH_3(CH_2)_7COO(CH_2)_7CH(CH_3)_2$), trioctylphosphate ($(C_8H_{17}O)_3PO$) [5]. Determination of plasticizer in HSPR carried out by gas chromatography (GC) using a flame ionization detector (FID) and mass spectrometer (MS). It should be emphasised that this method is associated with the method for determining the sol, because part of the fraction prepared during first mentioned technique is spent on measuring of the amount of plasticizer. So both can be combined and this reduce the time to re-prepare samples and perform them simultaneously. Before the actual measurement, it is necessary to prepare four standard solutions, which are most often a mixture of acetonitrile and acetone in a volume ratio of 80/20. The solutions of samples are evaporated for about six hours under an efficient fume hood. It is also used vacuum oven for about two hours at 50°C. After this time there is visible a distinct solid residue to which is added a mixture of standard solution. The upper layer of liquid contains plasticizer and is filtered out before the measurement using a gas chromatograph. It is important for the final calculation to take into account that some of the plasticizers consist of a mixture of isomers. Accordingly, the total area of the peaks corresponding to component isomers is necessary to integrate. It is also needed to know the initial weight of the sample before the extraction and the volume of diluted extract. As a result is obtained the percentage of plasticizer content in the propellant, allowing for the control and observation of the loss of this substance during aging processes [2].

Mechanical Tests

Accelerated aging of HSRP cause changes of the mechanical properties of propellant, especially to the elastic modulus (Young's modulus, E_a), the maximum amount of stress (σ_m) and deformation (ε_m) at maximum stress; the viscoelastic properties of the fuel (the loss modulus, damping coefficient) and the hardness of the propellant. To study this type of changes in mechanical parameters are used procedures described in STANAG-4506, concerned about monoaxial stretching. For testing the viscoelastic properties is used for dynamic mechanical analysis (DMA) according to the procedure described in STANAG 4540. Shore hardness type A of the propellant, by contrast, is determined according to the test procedure described in ASTM D2240–00 [2].

As a result of uniaxial tensile tests is obtained graph of the stress (in MPa) in function of elongation (%) of the sample (Fig. 4). It is important from the point of view of the accuracy of the results obtained to examine several samples non aged propellant and the aged ensuring identical conditions.

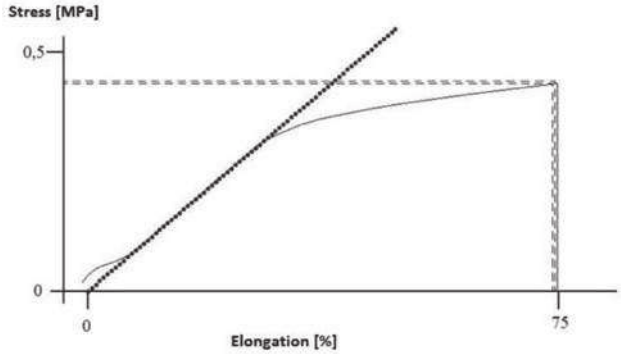

Fig. 4. Relationship between elongation of the sample of the applied stress [6]

Reduction of elongation below 50% is taken as a criterion for the end of the shelf life of the propellant [7]. DMA analysis determines viscoelastic properties of the aged HSPR in wide range of temperatures and frequencies of vibration. The results of these tests are obtained in the form of plots of elastic modulus (G', E'), loss modulus (G", E") and damping coefficient ($tg\sigma = G"/G'$) according to temperature (Fig. 5), which show a downward trend with increasing temperature.

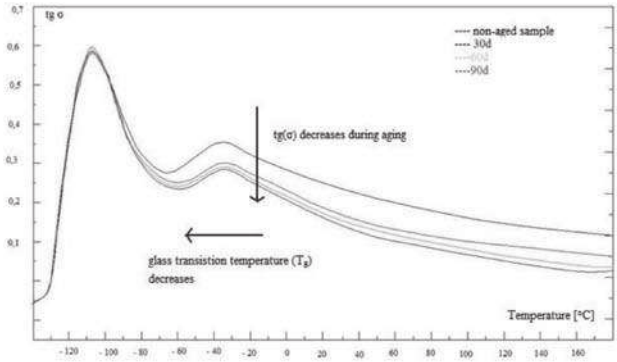

Fig. 5. DMA curve for non-aged propellant, aged 30, 60 and 90 days; Source: own study based on [8]

It should be noted that the graph DMA peak $tg\sigma$ in low temperature corresponds to the glass transition temperature HSPR, which is a measure of the transition of propellant from the glassy state in the plastic state. The advantage of this method is also the fact that a series of studies have shown a gradual change rather than sharp, which reduces the need of repeating the tests. All tests DMA for both non aged and aged HSPR samples should be carried out under identical operating conditions.

As mentioned above, during aging HSPR also exist the change in hardness of propellant and according to it there are measurements of this parameter during accelerated aging by Shore's method, type A. This method measures the penetration depth of the indenter into the test material. During the test, the indenter is loaded with a fixed spring characteristics. The higher is the hardness of the test material, the smaller is the depth of the recess and the greater the indentation. According to the standard test sample must be properly prepared, it is necessary to even the surface to have a thickness of approx. 6 mm and a diameter of at least 35 mm. The results are read directly from the instrument. All data on propellant examined, and information about aging parameters are essential for correct analysis of the results.

The supplementary methods in propellant research

In addition to the above-mentioned test methods can be carried out other tests of HSPR, namely: thermal properties by DSC or DTA (STANAG 4515); sensitiveness to impact, friction, heat and electrostatic discharge (STANAGs: 4489, 4487, 4490, 4491).

Factors influencing the outcome of research

The correct analysis and interpretation of research results depends primarily on the accuracy of testing in accordance with the applicable methodologies. Already in the planning stages of research it is needed to precisely define their terms. All this information is collected in the form of reports, so that after a certain time to be able to go back to the data and to compare them or combined with each other. First of all, the results are affected by the composition of the propellant examined, test conditions and their environment, methods of sample preparation before measurement and conditioning time, the parameters of the instrument. For a given series of tests, all these elements should be reproducible and as close as possible to each other. It should be clearly defined when the starting point of measurement and ending point is, which is mostly agreed on. To have the full spectrum of the analysis it is indispensable to perform the test in a variety of environments, in this way the group of tests can be usable for a particular group of propellants for certain applications. Choosing the appropriate method is often dictated by fuel producers or users, who want to specify a particular parameter of propellant. The factor that still makes difficulties in assessing the aging phenomena is their mechanism, often complicated to define and ambiguous.

Summary

Based on the study of aging and changes in selected parameters HSPR in time, it is possible to define the time period in years of safe storage of products containing HSPR for a given storage temperature of empirical formula (7), concerning the aging process based on a chemical reaction

$$t_E = \frac{t_T F^{\frac{(T_T - T_E)}{\Delta T_F}}}{365{,}25} \qquad (7)$$

where: t_E – time in years for the temperature, T_E – operating temperature storage, t_T – time of aging test in days for the T_T – temperature (temperature of accelerated aging), F – the rate of change of 10°C response to changes in temperature, F = 2–5 (rate of change rate of reaction), ΔT_F = 10°C , T_T and T_E°C . The factor F is a function of activation energy (E_a) during the aging process for the activation energies in the field E_a = 80–120 kJ/mol and temperature T_T = 20–90°C, coefficient F = 3 [9].

With this kind of research should be given particular attention to every detail, as even the appearance of the propellant surface shows some stage of degradation or destruction under the influence of external factors. All these aspects must be analyzed together, because only in this way it is possible to properly forecasting continuous relevance HSRP both for safe storage and use.

The combination of knowledge about mechanical degradation rate of the propellant with the results of structural analyzes should allow forecasting during the safe operation of the propulsion system, providing accurate, reliable performance of rocket motors for HSRP.

Aging tests are also important from the point of view of environmental safety because they prevent:

- uncontrolled combustion of the propellant storage site,
- destruction or self-ignition in rocket motors during operation,
- use of propellant with lower ballistic characteristics,
- health and life risk of persons employed in the defense industry plants associated with the production of HSRP.

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