Mechanical and Chemical Analysis of a Composite Rocket Propellant Subjected to Accelerated Ageing

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***Abstract*—Ageing can give rise to many phenomena, which may modify the ageing behavior of composite rocket propellants. For example, i) oxidation of the binder leading to hardening which is generally increased by the presence of air and is therefore greater at the surface than at the center; ii) degradation of the binder by the rupture of chains; iii) migration of species (plasticizer and/or liquid catalyst) towards free surfaces can lead to material hardening and to a higher sensitivity; iv) solid fillers like ammonium perchlorate can undergo various surface phenomena like absorption of moisture, partial dissolution followed by recrystallization or even temperature-based phase transitions. Any of these phenomena could modify the ageing behavior of the composite rocket propellant as a whole. The mechanical methods, like uniaxial stretching test and shore hardness measurement and the chemical methods, such as the soluble fraction measurement, crosslinking density and antioxidant content measurements, make it possible to identify the changes in the key parameters above presented. The measurement of residual antioxidant levels enables a qualitative assessment of the state of binder degradation. The measurement of soluble fraction or crosslinking density enables an assessment of how far the degradation reactions have proceeded either by rupture of chains or increase in crosslink density. There is a direct relationship between these parameters and the propellant mechanical properties. The measurement of tensile mechanical properties enables failure and response properties to be measured at specific temperatures and crosshead rates. The measurement of Shore A hardness allows the change in this property to be determined. The paper presents the results of the mechanical and chemical analysis of a composite rocket propellant based on Ammonium Perchlorate (AP), Aluminum (Al) and Hydroxyl terminated polybutadiene (HTPB), both in environmental conditions and after an accelerated ageing process for 180 days at 60ºC, by different period times within the accelerated ageing. The procedures applied in the field of mechanical and chemical tests, as well as the accelerated ageing protocol developed for evaluation, were according to the standard STANAG 4581/Edition 2, for a rocket propellant type AP/Al/HTPB, with a considerable age, respectively 20 years.**

***Index Terms*—accelerated ageing; composite propellant; reticulation density; antioxidant; plasticizer.**

I. Introduction

In the process of thermochemical degradation of a solid rocket propellant several factors could appear that contribute differently to a possible defect, with effects on the safety and performance of the rocket, such as stabilizer consumption, plasticizer degradation, excessive crosslinking, thermal decomposition, etc. The binder from the propellant composition has a primary effect on the safety in operation and storage of the rocket motor, on the mechanical and thermochemical properties and small changes in the composition can lead to considerable changes in the ageing process of the materials [1].

Measurement of antioxidant levels allows a qualitative assessment of the degradation state of the binder and the formation of cracks can be a direct consequence of the reactions that take place in the binder matrix.

The correct approach involves identifying possible failure modes that may occur during the life cycle and evaluating the effects they may have on the energetic material. Anticipating the loads/stresses due to the environmental, storage, transport, handling or operational conditions to which the product will be subjected during several years of service is a complex activity, which can be at most estimated. Environmental conditions, including transportation, harsh handling, and climatic conditions can cause cracks in energetic materials, increased friability, and damage them. It is the so-called natural ageing, during which slow reactions of physical-chemical degradation can take place, which can irreversibly modify its initial properties.

Therefore, a need to identify an evaluation mechanism arises which, on the basis of a process of accelerated ageing of energetic materials over a reasonable period of time, can simulate, with good accuracy, their natural ageing process over a long period of time and lead to sufficiently reliable predictions of actual operating life.

This paper presents the procedures applied in the field of chemical and mechanical tests as well as the accelerated ageing

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protocol developed for evaluation, according to the standard STANAG 4581/Edition 2, for a rocket propellant type AP/Al/HTPB, with a considerable age, respectively 20 for years.

II. Chemical Tests

The chemical tests performed have the role of highlighting the composition of the propellant and how it changes during the ageing process. By using chemical methods, changes in the chemical structure of the polymer matrix as well as physical and chemical changes in the fraction of soluble can be observed (antioxidants and plasticizers).

The chemical tests performed on the material under analysis were:

- the soluble fraction measurement;
- crosslinking density measurement;
- antioxidant content measurement.

A. The soluble fraction measurement

The soluble fraction measurement in a crosslinked polymer allows the determination of crosslinking limits within the polymer structure. The higher the non-crosslinked polymer fraction, the higher the soluble content.

Experimentally, it has been shown that the mechanical deformation at maximum strain (Ɛ max) is a function of the soluble fraction. The soluble fraction may be determined by extraction at ambient temperature or by heating under reflux with solvents. It can be used in the modified Charlesby-Pinner equation to evaluate the crosslinking density. The extraction is carried out for several days, on a mass of propellant introduced in toluene or dichloromethane, at ambient temperature until a stable state of swelling is obtained. The gelified fraction is then separated from the solvent phase and evaluated. In the first phase, a portion (W_i) with a mass of 1 to 2 g of composite propellant is introduced into a large-volume glass beaker containing about 100 ml of toluene or dichloromethane. This mass of solvent changes after 24, 48 and 72 hours at ambient temperature. At the end of the extraction phase, the gelified fraction is dried in an oven at 50°C to remove the solvent until a constant mass (W_S) is obtained. The calculation of the soluble fraction is calculated by (1):

$$S = \frac{W_i - W_S}{W_i} * 100(\%) \tag{1}$$

where W_i – sample mass before swelling (g), W_S – dried sample mass after extraction (g).

B. Crosslinking density measurement

The crosslinking density is a useful parameter for determining the physical properties of a composite propellant. In fact, this parameter evolves depending on the degree of ageing of the material. Consequently, it can be used to assess the degradation state of the material. The method involves introducing a given volume of solid propellant in toluene for several days at a given constant temperature (ideally room temperature). Compression measurements are performed once the steady state of swelling has been reached (usually after one week).

Propellant samples are cut into discs. Their height and diameters are measured accurately with a micrometer (usually 1.5 cm high and 2.5 cm in diameter). Each sample is placed in a glass beaker and about 60–100 ml of toluene is added. The sample should always remain completely immersed in toluene throughout the experiment so that the swelling process is not disturbed.

The sample is introduced into toluene until equilibrium is established. To determine if this equilibrium has been reached, the sample is weighed every 30 s for 5 min. Moment zero is the time when the sample is removed from the solvent. Then a curve is drawn for the mass measurements as a function of time, the shape of which will be a straight line, which by extrapolation will allow to evaluate the mass at time zero. Equilibrium is reached when the mass of the swollen sample, at time zero, is constant (usually after one week).

Each swollen sample is placed on the plate of an apparatus for determining the compression modulus, as shown in Fig. 1. The dial of the device is set to zero. Compression measurements are immediately performed by adding various weights with known mass (between 40 and 400 g). Longitudinal deformation is recorded for each weight added.

After each deformation measurement, the weight is withdrawn for 2–5 min to allow the sample to return to its initial steady state in the solvent.

It may be necessary to adjust to zero again, in particular for the heaviest weights, at the end of the experiments. Measurements are discontinued once an acceptable curve is obtained (generally after about 10 measurements. The weight curve (kg) as a function of deformation (m) is then drawn and its slope determined.

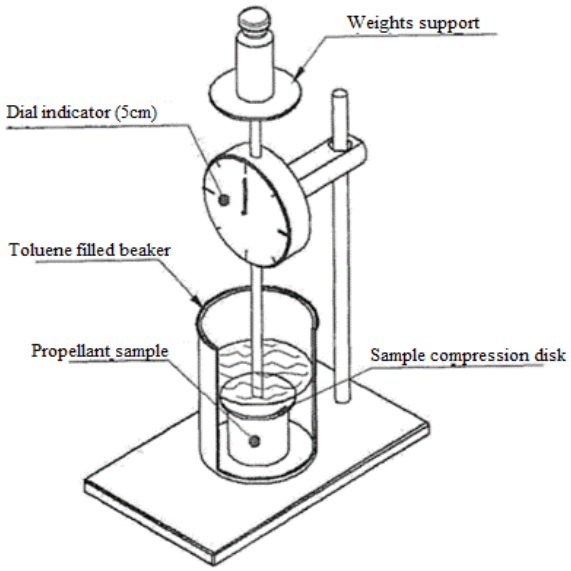

Figure 1. Crosslinking density measurement stand [2]

The crosslinking density is calculated using (2):

$$c = \frac{h_0 S}{3 A_0 R T}, \tag{2}$$

where: h_0 – height sample (m); A_0 – effective section area (eg. circular face) (m^2); R – universal gas constant (8.315 J/mol*K); T – temperature (K); S – slope × 9.807 m/s^2 (N/m); C – crosslinking density (mol/m^3).

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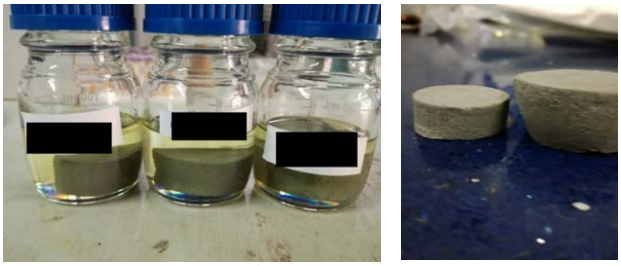

Figure 2. Propellant samples for crosslinking density determination

C. Antioxidant content measurement

This type of measurement depends on the nature of the antioxidant used. The method described below is valid for 2,2-Methylene-bis- (4-methyl-6-tert-butyl-phenol) under the trade name CALCO, AO-2246 or MBP5 or 2,6-Di-tert-butyl-phenol p-cresol, with the trade name IONOL. However, the method may be used for other types of antioxidants if it is demonstrated that the application of the method does not alter the chemical composition of the antioxidant analyzed [3].

The method uses solutions obtained after extraction of the propellant in a solvent adapted to the composition. Determination of the antioxidant content is performed by liquid phase chromatography, requiring calibration with standard solutions and preparation of samples by ultrasonic extraction in solvent for 30 minutes.

First, 10 mg of antioxidant and approximately 10 mg of internal reference material are dissolved in a vial, previously weighed to the nearest 0.1 mg, in 50 ml of methanol or any other suitable solvent. Dissolution at a higher volume is acceptable, provided that the mass-volume ratio remains constant. About 5 g of propellant (cut to size 2 to 3 mm) are extracted and about 10 mg of internal reference material in 50 ml of methanol or other suitable solvent. The samples are shaken for at least 6 h. Then they are allowed to stand for a few minutes before sampling 10 ml to 15 ml of the solution. The samples are centrifugated to give a perfectly clear solution or are filtered (3 µm) before injection.

The solution to be analyzed (3 µl) is injected into the liquid chromatograph with UV detector. Injections with standard solutions and solutions to be analyzed must be performed under the same operating conditions. The determination is made by calculating the areas of the peaks. The results are expressed as a percentage of antioxidants present in the material as a result of an internal calibration method.

HPLC Finnigan Surveyor Plus High-Performance Liquid Chromatograph, Thermo Scientific, Quadrupole Pump - LC Pump Plus, UV VIS Diode Detector - PDA Plus Refractive Index Detector and Detector and Autosampler - Autosampler Plus. Capillary column: Hypersil Green PAH 150 mm × 4.6 mm × 5 µm.

Operating parameters: PDA PLUS detector; wavelength: 280 nm; operating pressure: 120 bar; mobile phase: acetonitrile and water, 80:20%, isocratic; mobile phase flow rate of 3 ml/min; injection volume: 1 µl; autosampler temperature: 30°C; column temperature: 30°C.

III. MECHANICAL TESTS

Rocket propellants are designed to meet a variety of applications, which require an increased demanding on the structural capabilities of fuel grain. It is generally accepted that the specific service life of a rocket propellant cannot be assessed without knowing the destination of the rocket for which it was designed. When a solid propellant rocket engine suffers a catastrophic failure, it is generally due to a structural problem such as a crack or a failure to adhere to the combustion chamber. The methods used to determine the service life of solid composite rocket propellant grains are therefore based on the measurement of their mechanical properties and their prediction. Measurement of mechanical properties during uniaxial tensile tests and dynamic mechanical analysis allow an assessment of the propellant status [3, 4]. It is possible to predict the life of the rocket engine if the degradation of mechanical properties and structural analysis by the finite element method are taken into account.

The mechanical tests undertaken in this study are:

- uniaxial stretching test;
- shore hardness measurement.

A. Uniaxial stretching test

The samples, dumbbell-shaped, were taken from the center of the solid propellant grain by cutting with a band saw. The dumbbell-shaped specimens were then cut using the punch (Fig. 3) made to the dimensions shown in Table 1.

The samples were preconditioned in an air-conditioned room at a relative humidity of 30% for 48 h at a temperature of 23°C. The uniaxial tensile tests were performed with the James Heall dynamometer, model TITAN 710. The temperature in the working chamber was 23°C. Traction rate was 500 mm/min.

TABLE 1. SIZE OF THE SAMPLES

Size	[mm]
A Total length (minimum)	75
B Head width	12.5±1.0
C Narrow straight side length	25.0±1.0
D The width of the straight narrow part	4.0±0.1
E Outer radius of curvature	8.0±0.5
F Inner radius of curvature	12.5±1.0

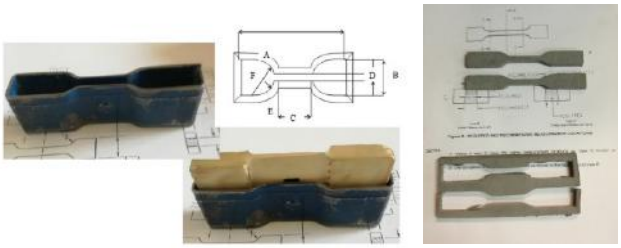

Figure 3. Dumbbell-shaped test samples

B. Shore A hardness measurement

A number of 3 samples were cut with a width of at least 6 mm, allowing a diameter of at least 35 mm and with a uniform and smooth surface. The samples were cut using a metal band saw. Hardness tests were performed using a PHPSA Shore A durometer with the following characteristics:

- penetrator: conical 350, diameter 1.25 mm;
- penetration footprint: 0 – 2.5 mm;
- measuring range: 10 - 90 HA;

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- accuracy: ± 1;
- measuring dial: 1 – 900;
- spring force: 0.55 – 8.065 N;
- force applied: approx. 12.5 N;
- scale diameter: 54 mm.

The device has been carefully placed in direct contact with the sample, avoiding any form of impact. Were made 6 measurements for each sample, at a distance of at least 5 mm from each other and at a distance of at least 13 mm from the edges. Shore A hardness was read on the machine after 3 s by three independent operators.

Figure 4. Propellant sample (left) and the Shore A durometer

IV. Accelerated Ageing Program

Three samples of solid rocket propellant in block form were pre-tempered at ambient temperature for a period of 2 weeks and then tempered in an airtight chamber, under nitrogen gas atmosphere and artificially aged at a temperature of 60° C, relative humidity 15%, for a period of 3 months. The solid rocket propellant blocks and their packaging for tempering in the climate chamber are shown in Fig. 5.

From the solid rocket propellant block were taken:

- 4 samples for the soluble fraction measurement test;
- 4 test specimens for the tensile test;
- 4 disks for the crosslinking density measurement test;
- 3 discs for the Shore A hardness test.

The remaining material was used in chemical tests (soluble content, antioxidant content). Prior to sampling, a 3 mm thick layer was removed from all surfaces of the block samples.

Figure 5. Preparation of propellant sample vessels for the ageing process

V. Results

The results obtained are presented comparatively for the samples aged naturally (3 months at atmospheric temperature) and for the samples artificially aged (3 months at 60°C). The results of the chemical and mechanical tests are presented both in detail for each sample and in the form of the calculated average value, showing the standard deviation.

A. The soluble fraction measurement

The working procedure was the same for both the non-aged samples and the aged samples. The environmental conditions were similar. The results obtained for the samples of material aged at ambient temperature as well as at 60°C are presented in Table 2.

Table 2. Results Obtained for the Soluble Fraction

Sample code	Non-Aged sample [%]	Aged sample [%]
1	5.49	5.58
2	5.78	5.73
3	5.71	5.64
4	6.00	6.00
Average	5.74	5.73
Standard deviation	0.18	0.16

B. Crosslinking density measurement

The comparative results are presented in Table 3 for the crosslinking density measurement test for the solid rocket propellant samples analyzed under normal climatic conditions and after a 60°C accelerated ageing program for 3 months.

Table 3. Results Obtained for Crosslinking Density

Sample code	Non-Aged sample [mole /m^3]	Aged sample [mole /m^3]
1	8.423	9.016
2	9.185	8.689
3	8.540	9.609
4	8.263	9.453
Average	8.603	9.192
Standard deviation	0.350	0.363

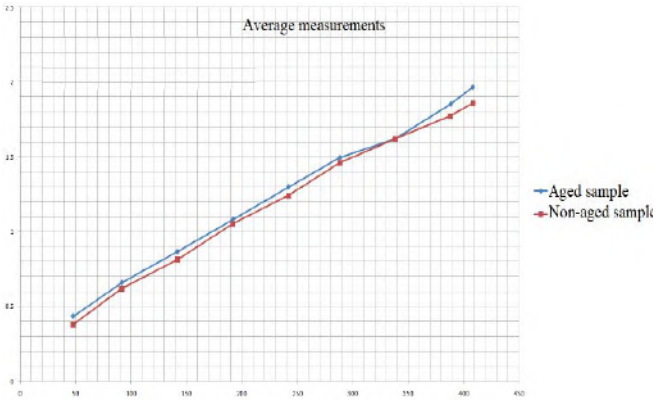

Figure 6. Applied weight (g) vs. deformation (mm) (average values) for non-aged and aged solid rocket propellant samples

C. Antioxidant content measurement

The results for the antioxidant content of solid rocket propellant samples analyzed under normal climatic conditions and after a 60°C accelerated ageing program for 3 months are presented comparatively in Table 4.

Table 4. Results Obtained for Antioxidant Content

Sample code	Non-Aged sample [%]	Aged sample [%]
1	0.163	0.171
2	0.168	0.171
3	0.174	0.163
4	0.175	0.174
5	0.170	0.171
Average	0.1700	0.1700
Standard deviation	0.0043	0.0036

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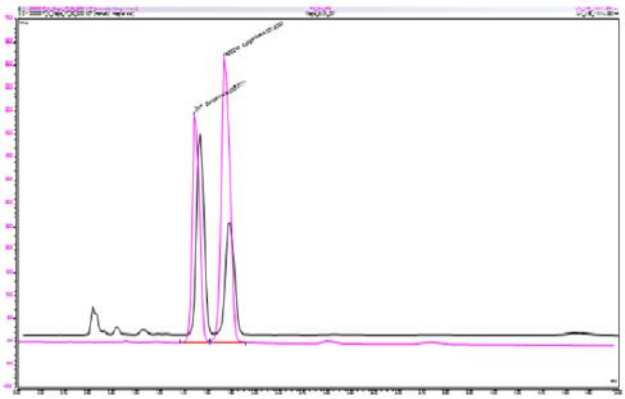

Figure 7. HPLC chromatogram for fuel sample (purple curve), and reference substances mix (2,6-Di-tert-butyl-p-cresol (A1) and 2,2-Methylene-bis- (4-methyl-6-tert) -butyl-phenol) (A2)) - black curve

D. Uniaxial tensile test

Table 5 and Fig. 8 show the results of the uniaxial tensile test for solid rocket propellant samples analyzed under normal climatic conditions and after an accelerated ageing program at 60°C for 3 months.

TABLE 5. RESULTS OBTAINED FOR THE UNIAXIAL TENSILE TEST (%)

	Non-Aged sample		Aged sample	
Sample code	Breaking stress [MPa]	Strain [%]	Breaking stress [MPa]	Strain [%]
1	1.110821	7.169	0.795606	6.847
2	1.088931	6.668	0.746873	6.555
3	1.064726	7.262	0.778145	6.995
4	1.118643	6.923	0.756501	6.555
Average	1.095780	7.006	0.769281	6.738
Standard deviation	0.020977	0.230	0.018954	0.190

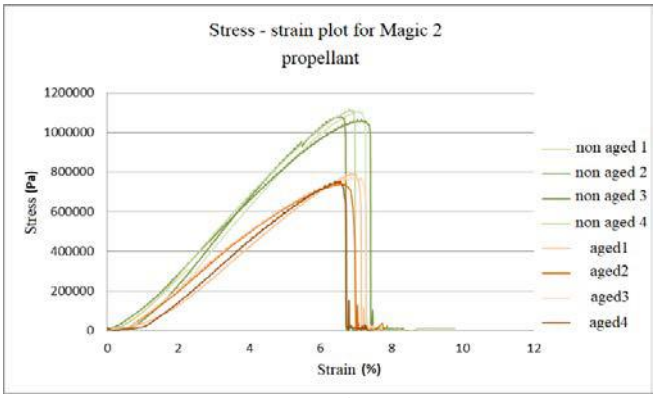

Figure 8. Stress(Pa)-strain(%) graph of non-aged and aged solid rocket propellant MAGIC-2

E. Shore A hardness measurement

The results for the Shore A hardness measurement test for solid rocket propellant samples analyzed under normal climatic conditions and after a 60°C accelerated ageing program for 3 months are presented comparatively in Table 6.

TABLE 6. RESULTS OBTAINED FOR SHORE A HARDNESS

Sample code	Non-Aged sample	Aged sample
1	75.3	77.,3
2	76.7	77.5
3	75.3	77.0
Average	75.7	77.2
Standard deviation	(+) 1.98	

F. Overall evaluation

The results obtained in the physical-chemical and mechanical tests performed on samples of non-aged and aged solid rocket propellant are summarized in Table 7. The differences in the measured parameters are presented as a percentage in relation to the initial measured value.

TABLE 7. COMPARATIVE RESULTS OF TESTS PERFORMED

Sample/ tests performed	Soluble fraction [%]	Crosslinking density [mole/m^3]	Antioxidant content [%]	Uniaxial tensile tests		Shore A Hardness
				Breaking stress [MPa]	Strain [%]	
Naturally aged	0.0575	8.603	0.170	1.095780	7.006	75.7
Accelerated ageing	0.0574	9.192	0.170	0.769281	6.738	77.2
Absolute difference	-0.0001	0.589	0.000	-0.326498	-0.268	1.5
Relative difference [%]	(-) 0.13	(+) 6.85	-	(-) 29.80	(-) 3.82	(+) 1.98

VI. CONCLUSIONS

The soluble fraction and the antioxidant content are constant, which doesn't support the idea of a binder oxidation process (HTPB) taking place.

The increase in crosslinking density by 6.9% indicates a hardening of the material due to excessive crosslinking during the ageing process. This effect is also visible in terms of Shore A hardness of the material, which increases by 2%. The hardening of the material is also revealed by the depreciation of the uniaxial tensile strength, the breaking stress being lower by 30%.

There is a significant deterioration in the mechanical strength of the solid fuel, but not critical to the operation, in ambient climatic conditions, of the rocket engine, as evidenced by the fact that it has retained the characteristics of maximum relative elongation (about 7%).

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