Abstract no. 24031

Ageing Characteristics of Solid Composite Propellants

Eirik Østbye Pedersen, Eirik André Løkke

R&D Department, Nammo Raufoss AS,
P.O. Box 162, NO-2831 Raufoss, Norway
eirik.ostbye.pedersen@nammo.com

Abstract

Nammo Raufoss AS has developed, qualified and manufactured solid composite propellants based on ammonium perchlorate and hydroxyl-terminated polybutadiene since the early 1980s.

For several of these solid composite propellant formulations, ageing studies have been performed; both accelerated ageing at elevated isothermal conditions and natural ageing at ambient conditions, creating a database of ageing data.

Ageing samples were wrapped in foil, then enclosed and vacuum-sealed in anti-static barrier bags and stored at the specified ageing conditions.

The ageing conditions were:

- Elevated isothermal conditions at 71 °C, 60 °C, 50 °C, 40 °C and withdrawal times from 15 days to 720 days.
- Ambient conditions at 21 °C, and withdrawal times from 60 days to 10 years.

The test matrix was:

- Testing of mechanical properties, ballistic properties, thermal characteristics, chemical characteristics, impact- and friction sensitivity.

The paper will give a short description of the solid propellants studied and present ageing data showing solid propellants with excellent ageing characteristics.

Introduction

Nammo Raufoss (Nammo) is a producer of rocket motors for tactical and aerospace applications. Nammo has since the 1970s produced composite propellants at a commercial scale, and since the late 1980s the majority of these have been based on ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB).

Rocket motors with composite propellants generally have an expected service life of 10-20 years so during the development phase of new propellants, extensive accelerated ageing programs are commonly undergone where mechanical-, ballistic-, thermal- and chemical- and sensitivity properties are monitored.

The following paper presents properties obtained through accelerated ageing studies of three AP/HTPB propellant in regular production at Nammo.

Propellant Characteristics

Nammo produces a wide range of > 20 different propellant formulations. A selection of 3 has been made for the purpose of this paper, hereinafter referred to as Propellant A, B and C. All three propellants are AP/HTPB based, are fully qualified and have been in regular production for more than 10 years with between 50 and 300 full-scale batches produced. A rough presentation of propellant characteristics is given in Table 1.

Table 1 - Propellant Characteristics

Propellant	**A**	**B**	**C**
AP distribution	Bimodal	Trimodal	Bimodal
Bonding agent	Tepanol	Tepanol	Epoxy/amine
Burn rate modifier	Iron oxide	-	Iron oxide
Signature	RS	5% Al	RS
Binder	R45M	R45M	R45HTLO
Curing agent	DDI	DDI	IPDI
Burn rate	Medium	Medium	High

Experimental

Sample Preparation and Ageing

All propellant samples were obtained from representative full-scale production batches. They were cast under vacuum directly from the rocket motor casting station into sample buckets, which were then sealed and cured at 60 °C for the same amount of time as their corresponding rocket motors.

Accelerated ageing of bulk propellant was performed by splitting cured buckets in half, vacuum sealing the propellant blocks in ESD proof barrier bags, and ageing iaw. STANAG 4581[1] isothermally at 40, 50, 60 and 71 °C for extraction times ranging from 15 to 720 days.

Propellant blocks were then extracted from the bulk mass of the propellant blocks, removing polymer rich surface regions. Final samples were then prepared by cutting or die punching to desired sample geometry.

Samples for testing of ballistic properties were cast and cured in suitable tooling. The assemblies were bagged and sealed, and subjected to accelerated ageing as described above.

Testing

The test scope on the aged and unaged propellant included the following:

Uniaxial tensile testing was performed iaw. STANAG 4506 [2] using an MTS Alliance RT10, or an Instron 5965 instrument. JANNAF C type specimens were prepared and conditioned prior to testing. For comparison between propellants, only testing at +21 °C with a crosshead speed of 50 mm/min is reported.

Ballistic properties were measured by firing of 2''x4'' model motors iaw. an internal routine based on MIL-STD-286[3]. Motors were conditioned at +63 °C prior to firing.

Thermal characterization was performed both by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) iaw. STANAG 4515 [4]. Tests were performed using a TA Instruments DSC Q1000 V.9.9 and a TA Instruments AutoTGA 2950 HR V6.1A instrument respectively. Heating rates were 10 °C/min.

Chemical quantification of antioxidants were performed by high performance liquid chromatography (HPLC) iaw. STANAG 4581 [1]. Extraction of antioxidants was performed using acetonitrile, and the resulting solution was analysed using HPLC with a 260 nm UV detector. The mobile phase was 80:20% acetonitrile/water with 0,2 g/L ethanolamine added to the acetonitrile. The stationary phase was a LiCrospher 100 RP-18 (5 µm) column and triphenylamine was used as the internal standard.

Impact sensitivity was tested iaw. STANAG 4489 [5] using a BAM impact test machine.

Friction sensitivity was tested iaw. STANAG 4487 [6] using a BAM friction test machine.

Results

Mechanical Properties

The mechanical properties of Propellants A, B and C were investigated after accelerated ageing. Results are presented relative to t_0 values, with t_0 values shown in Table 2

Table 2 – t_0 mechanical properties of Propellants A, B and C.

Propellant	Test T [°C]	Stress [MPa] Max.	Stress [MPa] At rupture	Strain [%] At max. stress	Strain [%] At rupture	Modulus [MPa]
A[1]	+21	1,12	1,08	59,7	61,5	3,58
A[1]	-54	5,11	4,98	55,9	57,8	58,50
A[1]	+63	0,86	0,83	55,8	57,0	2,58
B[1]	+21	0,78	0,73	44,2	49,3	3,43
C[2]	+21	1,43	1,40	28,2	29,3	7,21

[1)] Results corrected iaw. STANAG 4506, [2)] Engineering values

Propellant A

The mechanical properties of Propellant A were investigated after accelerated ageing at 50, 60 and 71 °C as well as after natural ageing at 21 °C. Results are shown in Figure 1 and Figure 2 relative to t_0 values. Only results corrected iaw. STANAG 4506 are reported.

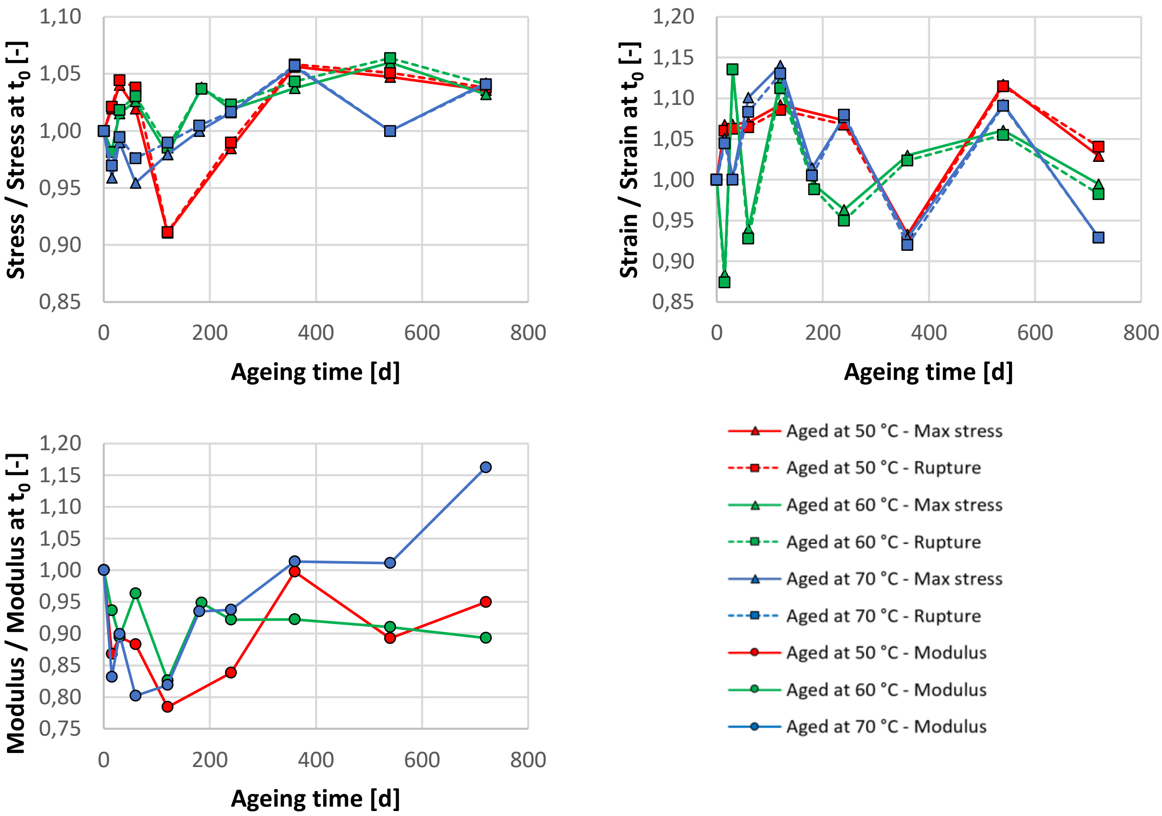

Figure 1 - Uniaxial tensile testing at 21 °C of Propellant A.

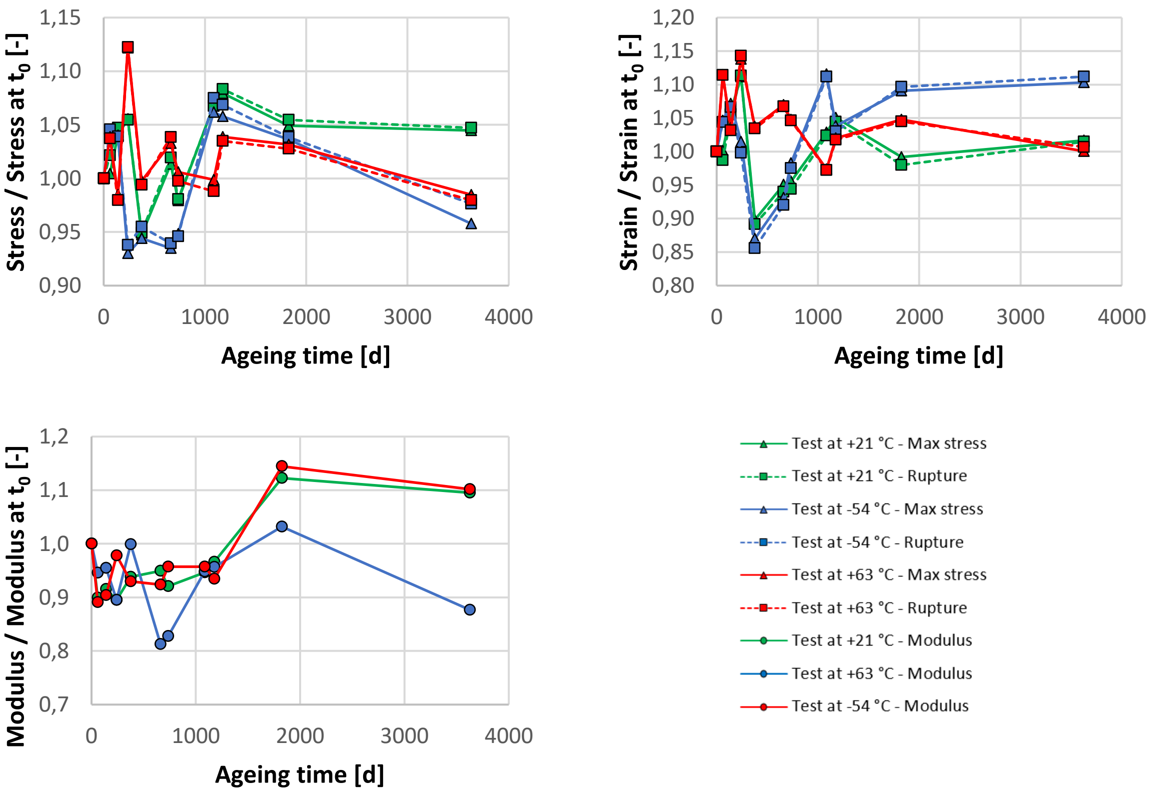

Figure 2 – Uniaxial tensile of Propellant A aged naturally at 21 °C.

Accelerated ageing of Propellant A shows limited effect on the mechanical properties of the propellant. The noise-to-response ratio is high, especially at lower ageing times, and attempts at fitting ageing models and estimating activation energy were unable to yield satisfactory results.

No clear trends can be discerned. The average of all aged stress values is less than 0,5 % from the respective t_0 values. For strain, it is observed an average 3 % increase and for modulus an average loss of 7 % is observed. No clear differences can be observed between the different ageing temperatures.

The same general trends can be observed for the natural ageing for accelerated ageing – limited response with ageing, and high noise to response ratio. Cold- or warm conditioned testing does also not appear to give any different trends than the ambient conditioned tests.

Propellant B

The mechanical properties of Propellant B were investigated after accelerated ageing at 40, 60 and 71 °C. Results are shown in Figure 3 relative to t_0 values. Only results corrected iaw. STANAG 4506 are reported.

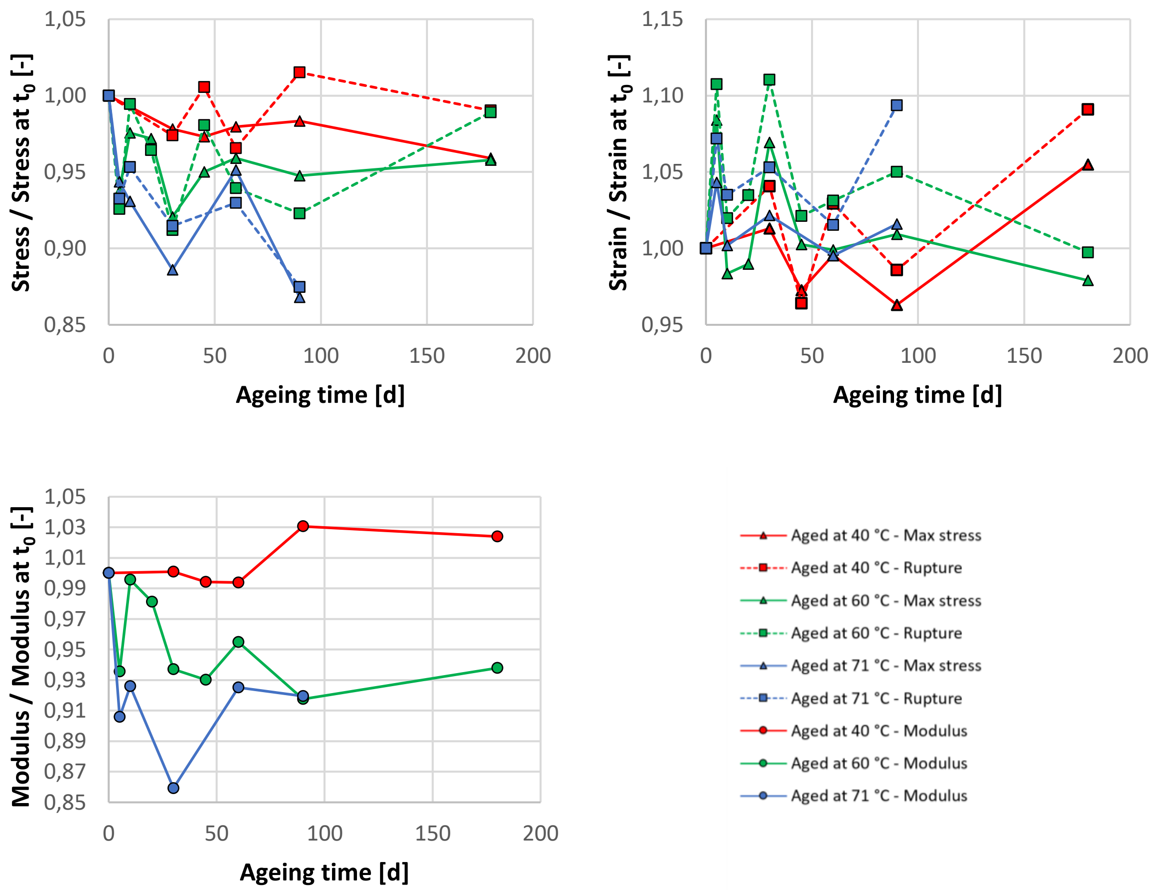

Figure 3 – Uniaxial tensile testing at +21 °C of Propellant B.

Similar trends are observed for Propellant B as for Propellant A with limited responses from ageing, high noise to response ratio and no clear discernable trends. The temperature sensitivity is slightly more apparent for Propellant B, with stress lowering by an average of 2, 5 and 8 % for 40, 60 and 71 °C respectively. Strain capacity increases by 1, 3 and 3,5 % on average, and modulus is lowered by 0, 5 and 10 %.

Propellant C

The mechanical properties of Propellant C were investigated after accelerated ageing at 40, 60 and 71 °C as well as after natural ageing at +21 °C. Results are shown in Figure 4 relative to t_0 values. Engineering values are reported.

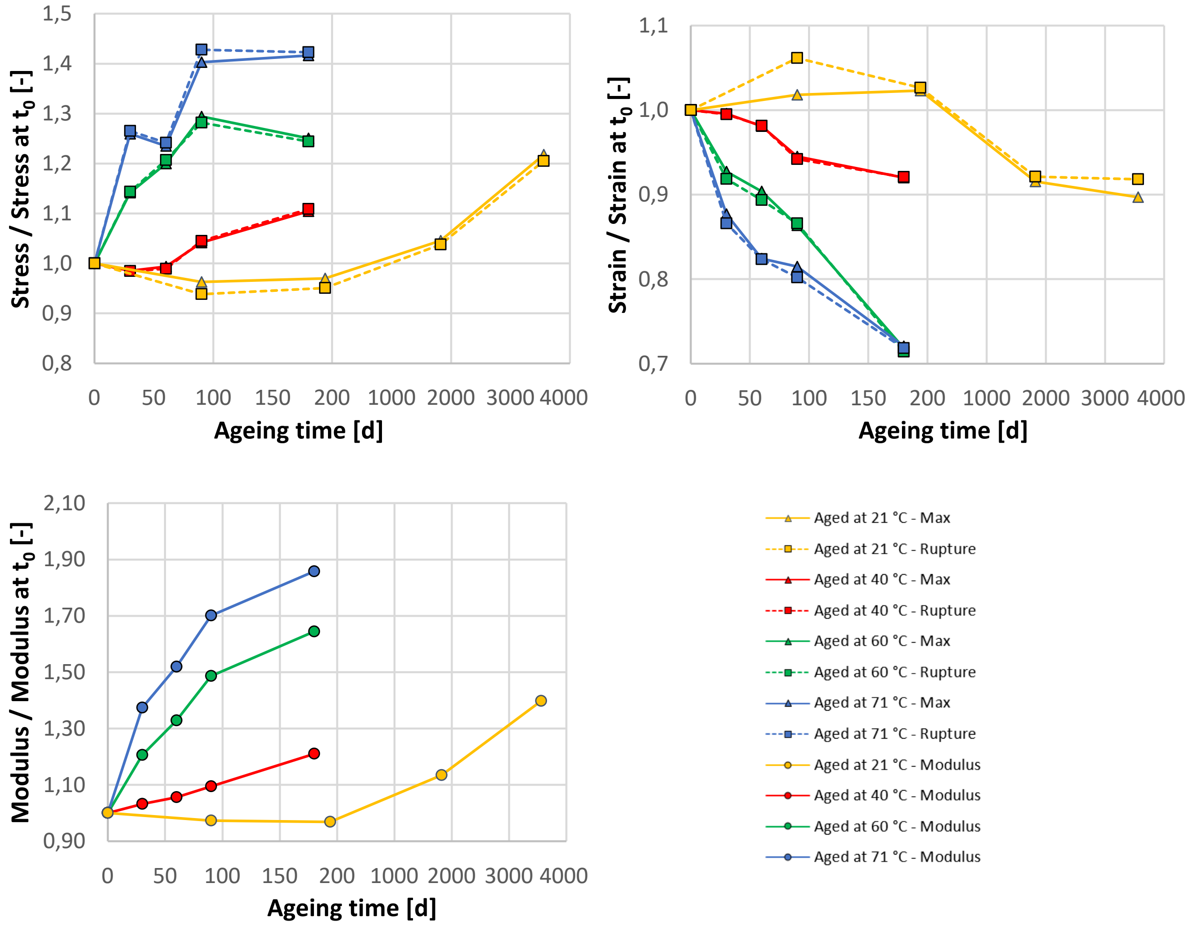

Figure 4 – Uniaxial tensile testing at +21 °C of Propellant C. Note the non-linear time scale at ageing beyond 200 d.

Ageing appears to affect the mechanical properties of Propellant C significantly more than Propellants A and B. Significant increases to stress and modulus as well as decreased strain capacities are observed at roughly a factor 5 compared to the other propellants. The main difference that may affect ageing degradation of mechanical properties is that Propellant C has an epoxy/amine based bonding agent and IPDI as a curing agent, whereas Propellants A and B employ Tepanol as the bonding agent and DDI as the curing agent.

A clear temperature dependency is also observed, with the ageing effects intensifying with increased ageing temperature.

Linear (1) and logarithmic (2) ageing models were used to estimate rate constants by linear data fitting.

$$P = P_0 + k \cdot t \tag{1}$$

$$P = P_0 + k \cdot \ln\left(\frac{t}{t_0}\right) \tag{2}$$

Estimated rate constants are shown in Table 3. It can be seen that the logarithmic ageing model produces the best fits at high temperatures, but fails at 21-40 °C and the linear ageing model produces the better fits in the low temperature region, suggesting a shift of ageing regime over the investigated temperature range.

Table 3 - Ageing rate constant – Linear fit estimates

	Max stress				Strain at max				Modulus			
Ageing T [°C]	**k_{lin} [10^{-3} MPa/d]**	**R^2**	**k_{log} [10^{-1} MPa]**	**R^2**	**k_{lin} [10^{-2} %/d]**	**R^2**	**k_{log} [%]**	**R^2**	**k_{lin} [10^{-2} MPa/d]**	**R^2**	**k_{log} [MPa]**	**R^2**
71	4.241	0.86	1.803	0.98	5.078	0.93	2.093	0.99	4.162	0.92	1.724	0.99
60	2.798	0.82	1.215	0.97	4.438	0.99	1.689	0.91	2.972	0.95	1.195	0.98
40	0.694	0.81	0.219	0.51	1.013	0.96	0.475	0.83	0.812	1.00	0.299	0.85
21	0.076	0.87	0.399	0.43	0.090	0.89	0.514	0.59	0.074	0.96	0.385	0.59

The estimated rate constants were used to estimate activation energies assuming Arrhenius type ageing kinetics. Arrhenius Plots are shown in Figure 5. Here data from 21-60 °C is used to estimate activation energy in the linear ageing model, and data from 40-71 is used in the logarithmic model.

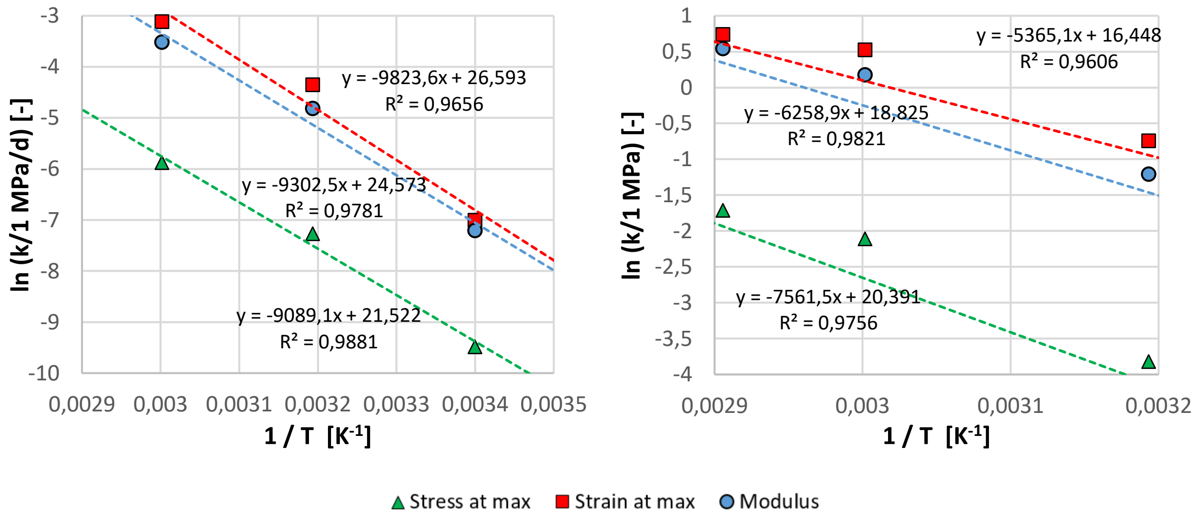

Figure 5 – Arrhenius plots for activation energy estimation of ageing of Propellant C. Linear ageing model (left) and logarithmic ageing model (right).

Activation energies are estimated from in the range 40 – 80 kJ/mol, shown in Table 4, which is in the expected range for propellant ageing [7] . Activation energies are estimated lower between 21 and 60 °C than for at lower temperature that for higher temperatures indicating a change in ageing regime over the investigated temperature range.

Table 4 –Estimated ageing activation energies

			E_A [kJ/mol]	
T range	**Model**	**Stress at max**	**Strain at max**	**Modulus**
21 – 60 °C	Linear	74	80	76
40 – 71 °C	Logarithmic	61	44	51

Ballistic Properties

The effect of accelerated ageing at 60 °C on ballistic properties was investigated for Propellant A. Burn rates were evaluated between 11 and 20 MPa, and results are shown in Figure 6, relative to burn rate at t_0, which is here defined as the burn rate at 15 MPa.

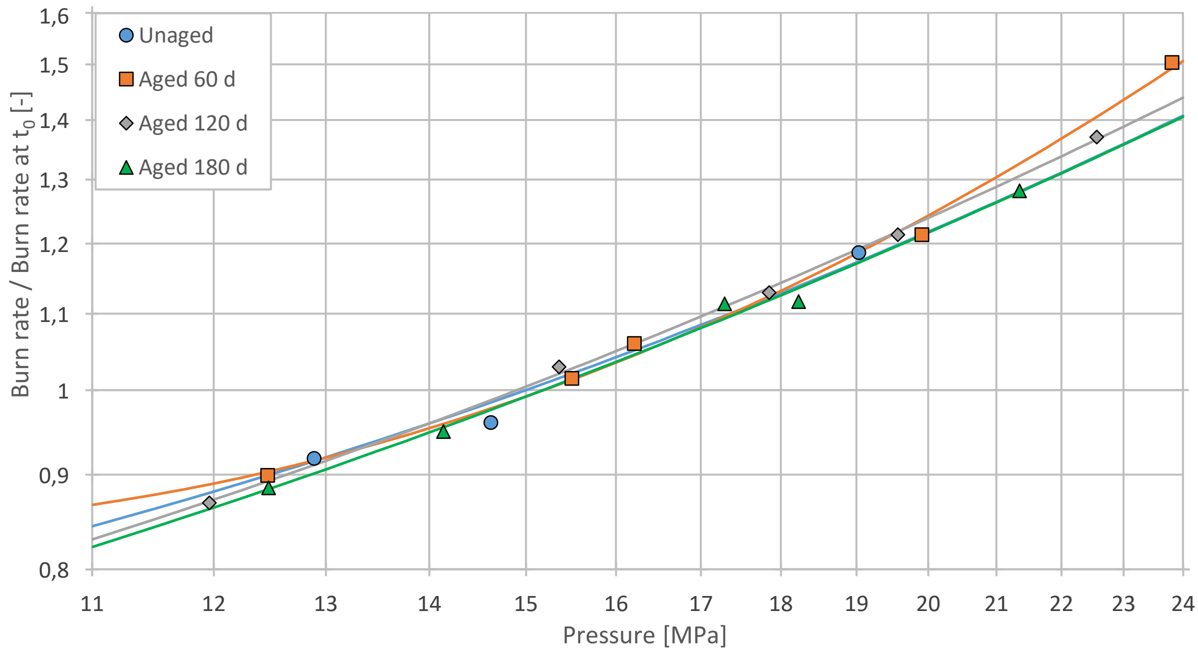

Figure 6 – Effect of accelerated ageing on ballistic properties for Propellant A. Log-log scale.

The ballistic results display no directional trend and vary within a ±2 % range. The results give no indication of accelerated ageing having any effect on ballistic properties.

Thermal Properties

The effect of accelerated ageing on thermal properties were investigated for Propellant A. For DSC, exothermic onset, and exothermic peak temperatures were registered. For TGA, temperature of maximum weight loss and end weight loss were recorded, as shown in the example thermograms in Figure 7. Results are shown in Figure 8.

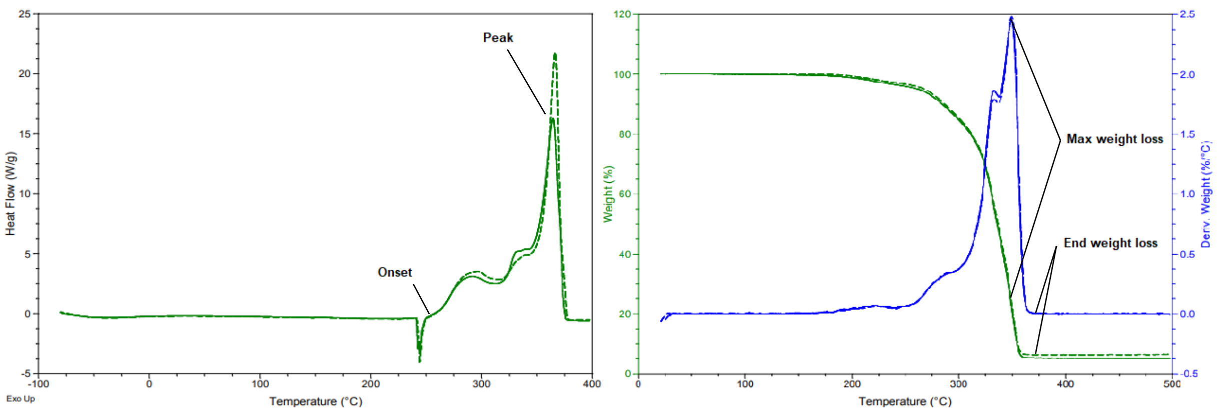

Figure 7 - Example DSC-(left) and TGA (right) thermograms.

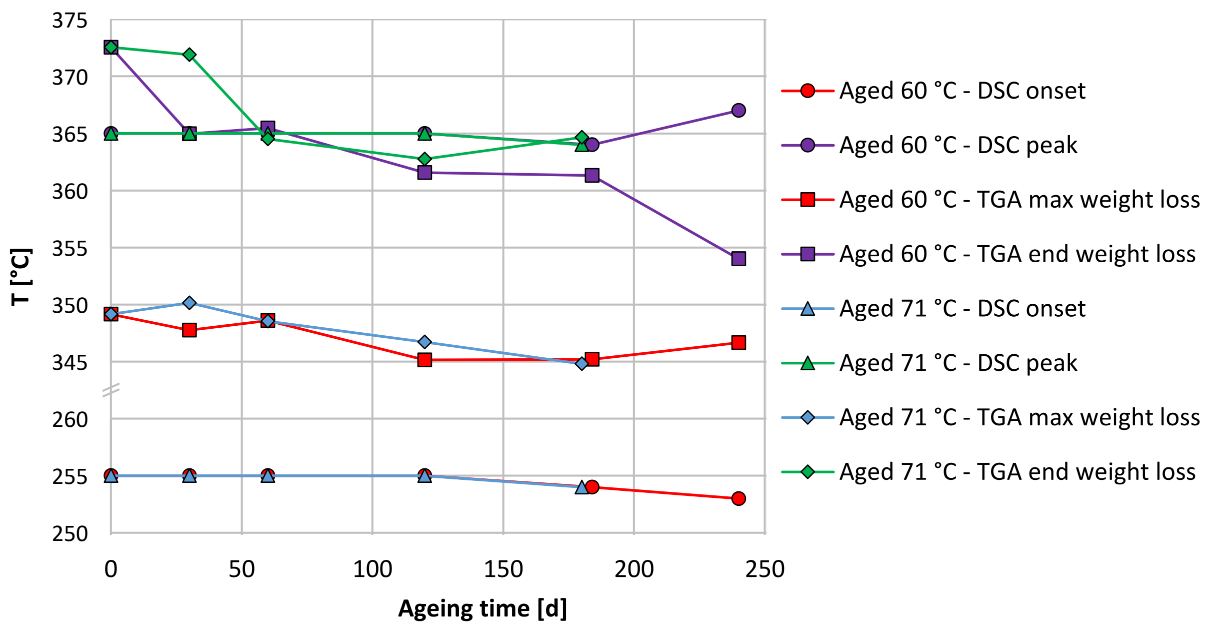

Figure 8 – Effect of accelerated ageing on DSC and TGA measured thermal properties for Propellant A.

From the DSC results, all samples show a exothermic onset temperature of 256 ± 1 °C and an exothermic peak temperature of 365 ± 2 °C. The variation can be considered well within expected experimental uncertainty and thus, no effect ageing can be discerned, independent on ageing temperature.

From the TGA results, no effect of ageing can be discerned on the temperature of maximum weight loss. The temperatures of end of weight loss can be seen to slightly decrease with increased ageing time. The effect appears independent on ageing temperature.

Chemical Quantification

The effect of accelerated ageing on antioxidant levels were investigated for Propellant A. Results are shown in Figure 9 relative to the nominal antioxidant level in the propellant. There are two different antioxidants in Propellant A, one of which proved to be in-extractable with the method applied. The other was partially extractable with about ~50 % of the nominal antioxidant level being measured at t_0. No significant effect of ageing can be discerned on the level of extractable antioxidants.

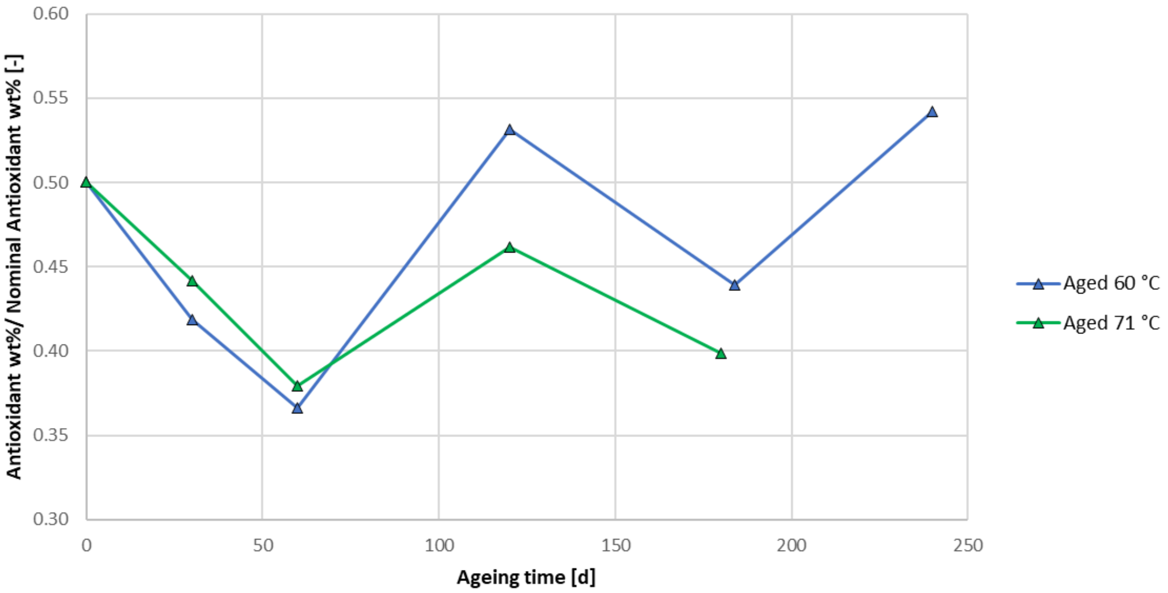

Figure 9 – Effect of accelerated ageing on antioxidant levels for Propellant A.

Sensitivity Properties

The effect of accelerated ageing on impact- and friction sensitivity was investigated for Propellant A. Results are shown in Figure 10.

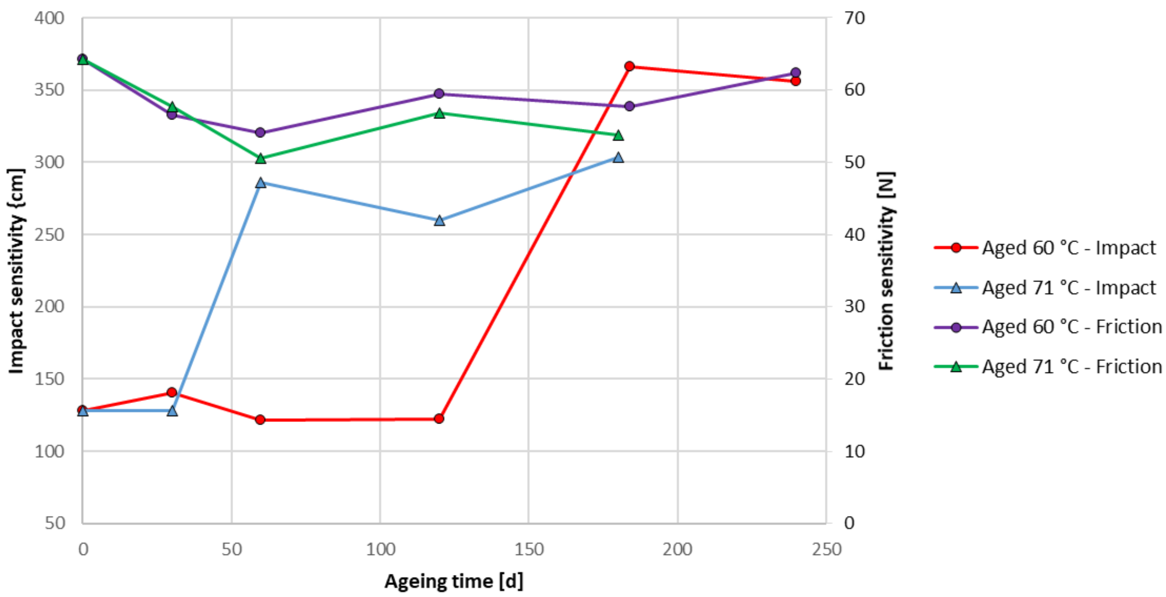

Figure 10 – Effect of accelerated ageing on impact- and friction sensitivity for Propellant A.

The results indicate that the propellant becomes less sensitive to impact as a result of accelerated ageing with the necessary impact energy required for reaction doubling between 120 and 180 d of accelerated ageing at 60 °C. The onset of the loss of impact sensitivity incurs earlier, between 30 and 60 d, when ageing at 71 °C.

No discernible effect of accelerated ageing can be seen on friction sensitivity, independent on ageing temperature.

Conclusion

Nammo Raufoss has conducted an accelerated ageing study of three AP/HTPB-based propellants in regular production at their facility. Propellant A has been thoroughly characterized of mechanical properties, ballistic properties, thermal characteristics, chemical characteristics, impact- and friction sensitivity, and Propellants B and C have been characterized for mechanical properties.

Propellant A displays excellent ageing characteristics, showing no significant change to ballistic properties, highly limited change on thermal characteristics, no significant change in antioxidant level, no significant change to friction sensitivity and a lowered impact sensitivity with ageing ranging from 180 d at 60 °C to 240 d at 71 °C. The mechanical properties of Propellant A show no clear degradation, but vary with approximately ±10 % over the ageing time investigated.

Propellant B displays similar ageing characteristics as Propellant A, with limited effects on mechanical properties from accelerated ageing.

Propellant C displays a significantly more severe degradation of propellant properties with accelerated ageing, likely due to its epoxy/amine-based, rather than Tepanol bonding agent, or its IPDI rather than DDI curing agent. Activation energies for ageing degradation of mechanical properties were estimated to between 40 and 80 kJ/mol. Activation energy was found to be dependent on temperature and differed between stress, strain and modulus.

References

[1] STANAG 4581, Explosives; Assessment of Ageing Characteristics of Composite Propellant Containing an Inert Binder

[2] STANAG 4506, Explosive Materials, Physical/Mechanical Properties Uniaxial Tensile Test

[3] MIL-STD-286, MILITARY STANDARD: PROPELLANTS, SOLID: SAMPLING, EXAMINATION AND TESTING

[4] STANAG 4515, EXPLOSIVES. THERMAL ANALYSIS USING DIFFERENTIAL THERMAL ANALYSIS (DTA). DIFFERENTIAL SCANNING CALORIMETRY (DSC), HEAT FLOW CALORIMETRY (HFC), AND THERMOGRAVIMETRIC ANALYSIS (TGA)

[5] STANAG 4489, EXPLOSIVES, IMPACT SENSITIVITY TESTS

[6] STANAG 4487, EXPLOSIVE, FRICTION SENSITIVITY TESTS

[7] AOP-46, THE SCIENTIFIC BASIS FOR THE WHOLE LIFE ASSESSMENT OF MUNITIONS