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The EDA-project Insensitive Munitions & Ageing

Results from WP2 and WP3

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Sammanfattning

EDA-IMA är ett EDA-projekt där åldringsegenskaperna för lågkänsliga energetiska material som ingår i IM studeras. Syftet med projektet är att vid behov utveckla analysmetoder för att kontinuerligt kontrollera effekten av åldring för dessa energetiska material och föreslå en metodik för att uppskatta hur lång tid IM-egenskaperna för ammunitionen kan förväntas bevaras. Arbetet som presenteras här är resultaten från arbetspaket 2 och 3 (WP2 och 3), där åldringsegenskaperna för olika energetiska material har analyserats och analysmetoder för att kontinuerligt kontrollera effekten av åldring studerats.

FOI har valt att studera åldringsegenskaperna för två olika LOVA-krut NL007 och NL008 baserade på RDX och CAB. Den här rapporten innehåller resultat från en mängd olika analyser som gjorts på krutprover som utsatts för forcerad åldring motsvarande en lagringstid på mellan 0 till 20 år i 25°C. Resultaten från dessa analyser indikerar att krutkornen vid åldring kan bli spröda och spricka vid förbränning under högt tryck. Kvalitativ tillämpning av “the cracking pressure method” vid brinnkaraktärisering i ventilerad bomb har föreslagits som en möjlig analysmetod för att kontinuerligt kontrollera effekten av åldring hos kruten.

Nyckelord: LOVA-krut, åldringsegenskaper, NL007, NL008, brinnkaraktärisering i ventilerad bomb

Summary

EDA-IMA is an EDA-project where the impact of ageing on the low sensitivity properties of different energetic materials that are included in IM is studied. The aim of this project is to develop surveillance methods for these energetic materials if shown to be needed and suggest a methodology to predict for how long time the initial IM-properties of the munition is assessed to be maintained. The work reported on here is the results from work packages 2 and 3(WP 2 and 3) where the ageing properties of and surveillance methods for different energetic materials have been studied.

FOI has chosen to study the ageing behaviour of the two LOVA propellants NL007 and NL008 based on RDX and CAB. This report contains results from different analyses of propellant samples subjected to forced ageing at a simulated age between 0 and 20 years. The results from these analyses indicate that the propellant grains might become brittle at ageing and thereby crack at high pressure burning. A qualitative application of the cracking pressure method in vented bomb analyses is suggested as a possible surveillance method to be studied further.

Keywords: LOVA propellant, effect of ageing, NL007, NL008, burning characterization by vented bomb analyses, cracking pressure method

Contents

1 Introduction

Sweden is participating in the EDA-project (IMA , B-0219-GEM2-ERG) concerning ageing of insensitive munition (IM) together with France, Netherlands, Czech Republic, Germany, Finland and United Kingdom. This project started in January 2009 and will continue until 2013. The objective of the project is to

- study the impact of ageing on the low sensitivity properties of different energetic materials that are included in IM
- develop surveillance methods for these energetic materials if needed
- suggest a methodology to predict for how long time the initial IM-properties (according to MURAT, STANAG 4439 or MIL-STD 2105) of the munition is assessed to be maintained

The work planned for the project is divided into four work packages (WP) with the following titles and contents

WP 1: State-of-the art - a literature survey of current knowledge and methodologies to be used as a base for the other WP.

WP 2: Predictive methodologies - study the impact of ageing on the low sensitivity properties of different energetic materials included in IM.

WP 3: Surveillance – identify critical parameters and develop surveillance methods for the energetic materials studied. Suggest a methodology to predict for how long time the initial IM-properties of the munition is assessed to be maintained.

WP 4: Synthesis - summarize the results and conclusions from the work in WP2-3 in a collective report.

In this report the work progress at FOI of WP3 is described. Results from WP1 and WP2 have already been presented in reference [1] and [2] respectively.

FOI has chosen to study the ageing behaviour of two different LOVA-propellants (LOw Vulnerability Ammunition), NL007 and NL008 from Eurenco Bofors AB Karlskoga. These propellants are included in the low sensitivity ammunition to the anti-aircraft autocannon, 40 mm akan L/70, for the Swedish Army Combat Vehicle 90.

Both NL007 and NL008 are based on RDX and cellulose acetate butyrate (CAB) in different relations. It is well known that these types of propellants have good ballistic and low sensitivity properties [3-4], but will these properties be preserved after normal ageing of the propellants?

The aim of the work performed at FOI is to investigate the ageing behaviour of the propellants in general, with focus on changes in mechanical and thermal properties. Based on the results from WP2, the work in WP3 has been concentrated on vented bomb analyses to study the propensity as a method for propellant surveillance.

2 Energetic materials studied

As described in reference [2] the LOVA-propellants NL007 and NL008 studied, are based on RDX and CAB according to the compositions shown in Table 1.

Table 1. Compositions of the propellants studied.

Component	NL007	NL008
RDX	76.5 %	73 %
CAB (cellulose acetate butyrate)	9 %	12.7 %
NC (nitrocellulose)	7.2 %	5.3 %
TBC (Tributyl citrate, plasticizer)	7 %	8.6 %
Centralite I (NC-stabilizer)	0.4 %	0.4 %

Both of the propellants are 19-perforated and graphitized. For each propellant type, propellant grains from two different lots have been studied. One of the lots represents propellant grains that have been subjected to natural ageing while the production year of the other lot is chosen to be as late as possible. The production year and lot number of the propellants studied are given in Table 2.

Table 2. Production year and lot number of propellants studied.

	Lot number	Production year	Graphitization	Perforation
NL007g	17399003	1999	Yes	16
	20094701	2009	Yes	16
NL008g	17397001	1997	Yes	16
	20034702	2003	Yes	16
NL008ng	20044703	2004	No	7

A 7-perforated propellant originally produced for a study of electrothermal iginition, with the same composition as NL008g but without graphitization, has also been studied. This propellant was manufactured in 2004 at Eurenco Bofors and has been stored at FOI in a storage with a controlled relative humidity of 30 - 40 % and a temperature of 20 ± 5°C.

In this report, the graphitized NL008 propellant is denoted NL008g and the propellant with no graphitization NL008ng.

3 Test and ageing program

The thermal, mechanical and burning properties of the propellants studied have been analyzed by uniaxial compressive testing, density measurements, vented bomb, slow cook-off (SCO), differential scanning calorimetry (DSC) and high performance liquid chromatography (HPLC) (see Table 3).

Table 3. Different analyses performed together with property of the propellant studied.

Analysis method	Property studied
Uniaxial Compressive Testing	Mechanical properties
Density	
Vented bomb	Grain capacity to withstand high pressure. Burning properties in general.
Slow cook-off	Thermal properties
DSC	
HPLC	NC-stabilizer content

To simulate natural ageing, the propellants were subjected to forced ageing at three different elevated temperatures; 50, 65 and 80°C. Natural ageing is in this case defined as the effects of decomposition processes or reactions that occur spontaneously during storage of the propellants. The simulated age is achieved by multiplying a thermal acceleration factor (K_T) by the time at forced ageing according to the Swedish Defence Standard FSD 0223 [5] and STANAG 4527 [6]. The acceleration factor can be achieved from

$$K_T = e^{\frac{E_a}{R}\cdot\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \qquad (1)$$

where

K_T = Thermal acceleration factor
T_1 = Storage temperature (K)
T_2 = Ageing temperature (K)
E_a = Activation energy (J/mole)
R = The general gas constant (8.314 J/K mole)

Samples to be analyzed were collected at simulated storage times of 0, 1, 5, 10 and 20 years. The storage temperature is set to 25°C and the activation energy for degradation of the propellant to 90 kJ/mole [7]. Since CAB-based propellants are suspected to have bad low temperature properties some propellant grains have also been subjected to thermal cycling from +65°C down to -40°C. At the thermal cycling, the temperature was lowered down to -40°C for 24 hours at times corresponding to 1, 5, 10 and 20 years of ageing (see Figure 1).

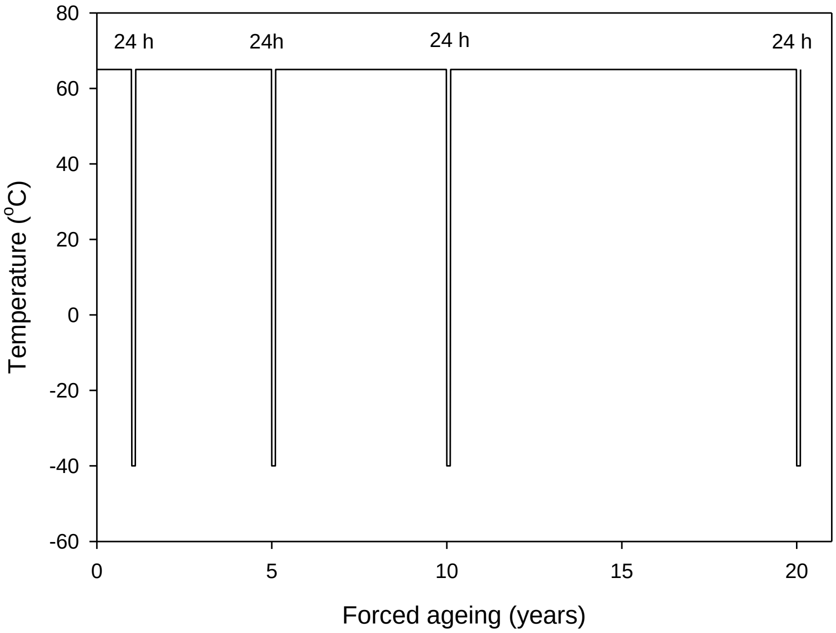


Figure 1. Schedule for thermal cycling.

The propellant samples were placed in sealed glass jars during forced ageing. Not more than 36 g of propellant was placed in each glass jar to ensure as homogenous ageing conditions as possible for the propellants to be analyzed. After the propellants were subjected to forced ageing, they have been stored at room temperature (≈ 20°C) until sample extraction for analysis.

4 Summary of results from WP2

Results from WP2 have previously been reported in reference [2]. Since then, more analyses have been performed and the results have also been evaluated in more detail. The evaluation of the results achieved from WP2 so far is summarized below. The testing of samples from propellant lots subjected to natural ageing is ongoing. The evaluation of the results from these tests will be reported on later.

4.1 Uniaxial compressive testing

The mechanical properties of the propellant samples have been studied by uniaxial compressive testing according to STANAG 4443 (1st Ed) [9] with the exception of sample length to diameter requirement of 1:1. An INSTRON Universal Testing Machine, model 5565 fitted with a 5kN load cell was used for the analyses.

All samples were conditioned at room temperature for at least 1h prior to testing. The crosshead displacement speed was 50 mm/min at room temperature. Stress versus strain data was recorded using at least 10 points per %-strain. The results from the analyses are reported on as maximum stress (MPa), strain at maximum stress (%) and compressive modulus of elasticity (MPa).

Figure 2 shows the results from the uniaxial compression tests of the NL007g (production year 2009) subjected to forced ageing. Each interval in the error bars in Figure 2 is represented by at least 10 tests. As can be seen in Figure 2, the variation in results from one test to another is large and it is therefore difficult to draw any conclusions from the results. It is however obvious that the test method is not suitable for studying the mechanical properties of this type of propellant.

It should be noted however that it was not possible to conform to the sample to length requirement of 1:1 in STANAG 4443 at the uniaxial compressive testing of the NL007 and NL008 propellants. The large variation of the results might however only be an effect of the sample to length exception. It is possible that uniaxial compressive testing of propellant grains of the same composition as NL007 and NL008, but with grains of other dimensions, would be more successful.

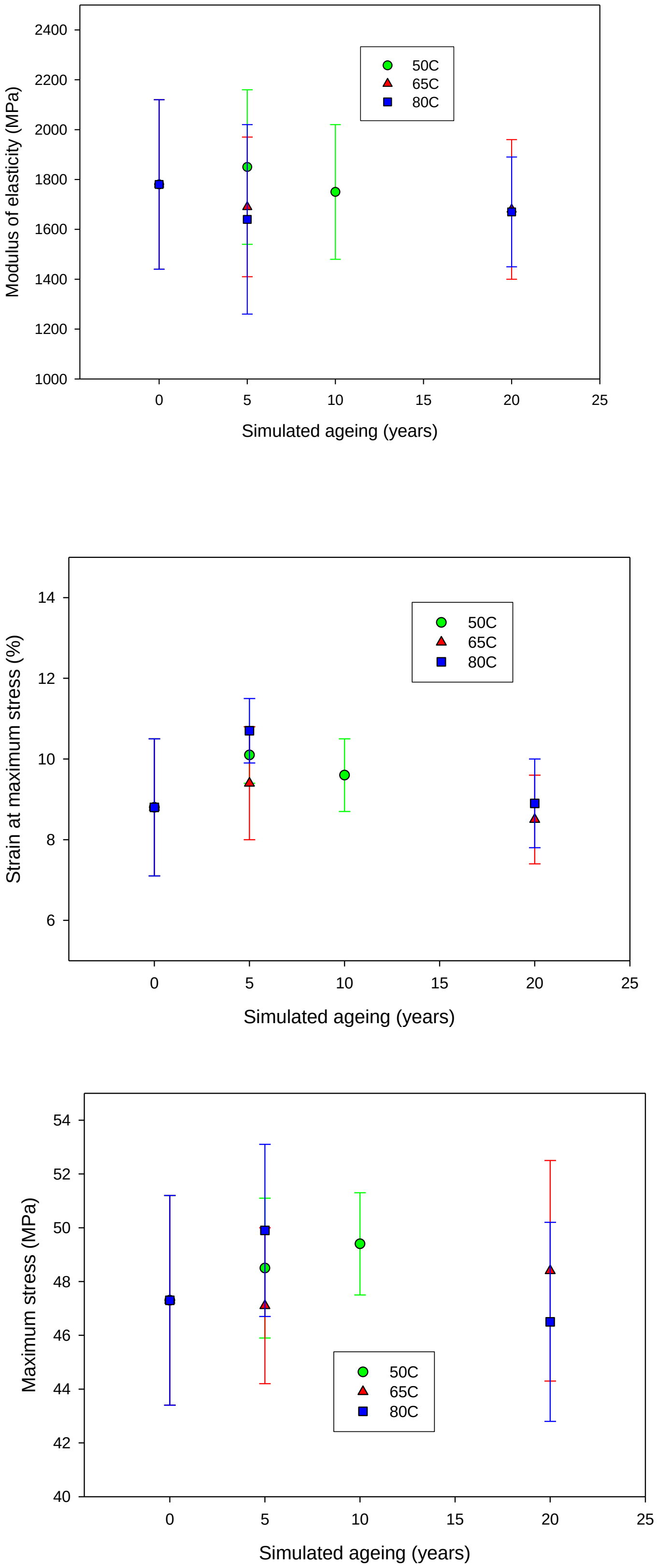


Figure 2. Results from uniaxial compression tests of NL007g (2009) subjected to forced ageing.

4.2 Slow cook-off

SCO have been performed to study the ability of the propellants to withstand premature ignition due to sustained heating of the surrounding environment. The results from this test cannot be compared with results from tests with the complete ammunition as in IM-tests. The results are only useful for studying the impact of forced ageing and thermal cycling of the propellants on the sensitivity to slow heating. This can be made by comparing the results from tests of aged samples with reference (unaged) samples.

The SCO-tests were performed according to STANAG 4491 [8]. The slow heating rate was 3.3°C/h. Only two trials are performed in every test instead of three as defined in the standard. As is reported on in Ref. [2], the results from SCO do not indicate that the forced ageing has an impact on the sensitivity to slow heating of the propellants studied.

4.3 Density measurements

A decreased density of the propellant grains is an indication of an increased porosity. This might lead to an increased surface area at burning and thereby an increased barrel pressure at launching. The density of propellant samples from NL007g, NL008g and NL008ng has therefore been calculated from helium pycnometer analyses results (see Figure 3).

In a helium pycnometer the sample is placed in a small container, the volume that is not accessible for the gas particles is measured and the density is calculated as the mass to volume ratio. Results from helium pycnometer analyses thus only reflect the interior density changes of propellant grains. Changes in grain surface structure causing an increased surface area cannot be studied.

Figure 3 shows the impact of ageing on the propellant density. A vague trend, indicating a decreased density at forced ageing of the propellant samples, can be seen. This trend is more pronounced at forced ageing at 50°C and at the start of the forced ageing. For NL008ng, the density is instead increasing at forced ageing.

In reference [10] it was observed that at evaporation of residual solvent present in the propellant grains, the plasticizer co-migrates to the grain surface. Forced ageing at elevated temperature might enhance residual solvent evaporation and plasticizer migration resulting in reduced mechanical strength. A deceased density can be a result of residual solvent evaporation or any other phenomena. DSC-analyses of aged and unaged propellant samples are therefore planned to study solvent evaporation in the temperature interval 20-150°C.

In Figure 4 helium pycnometer measurements of propellant samples subjected to thermal cycling down to -40°C are given. Also in this case, the density is initially decreasing for the graphitized and increasing for the non-graphitized propellants as an effect of forced ageing/thermal cycling.

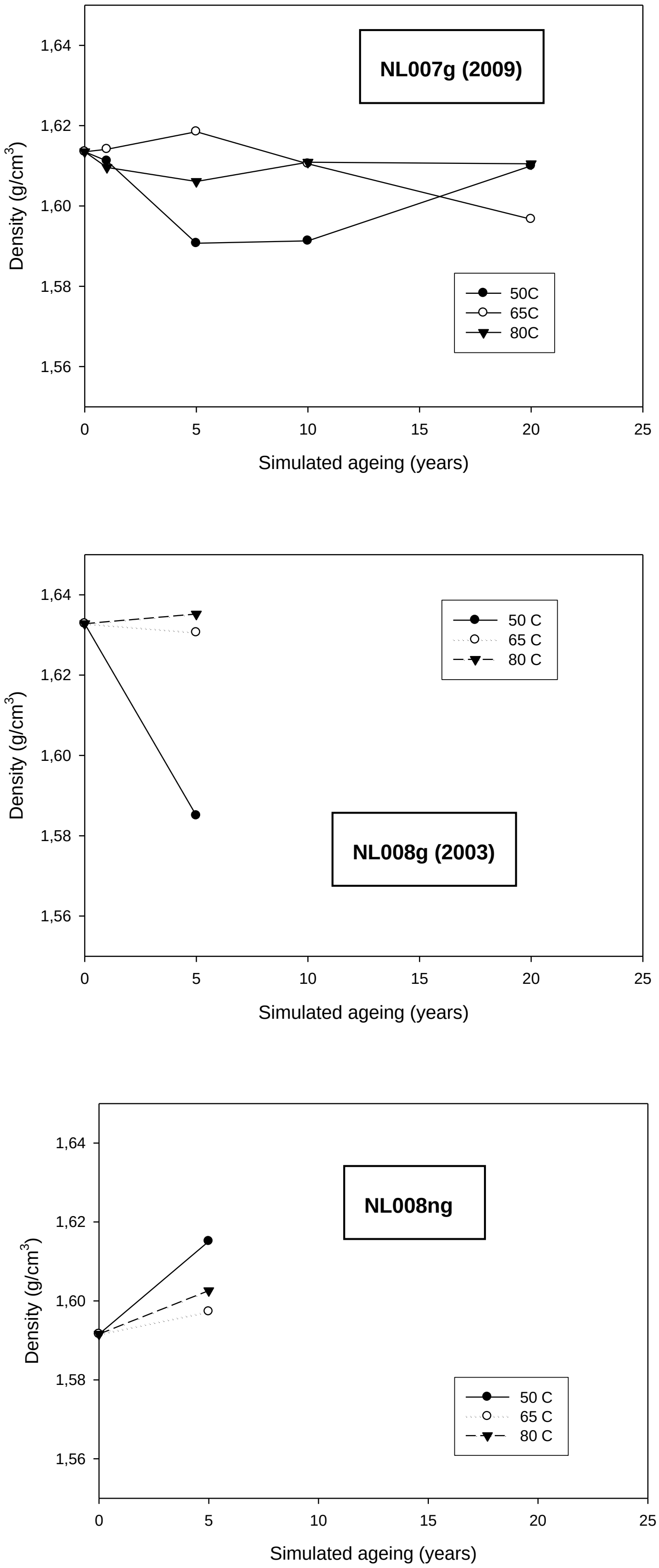
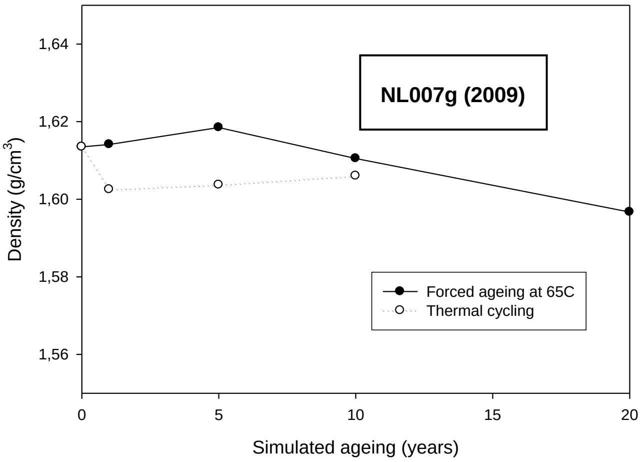
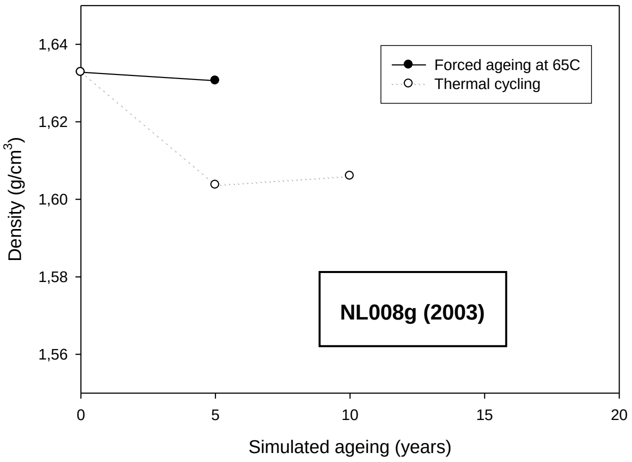


Figure 3. Results from helium pycnometer analyses of samples from NL007g, NL008g and NL008ng The propellant samples have been subjected to varying degrees of forced ageing.





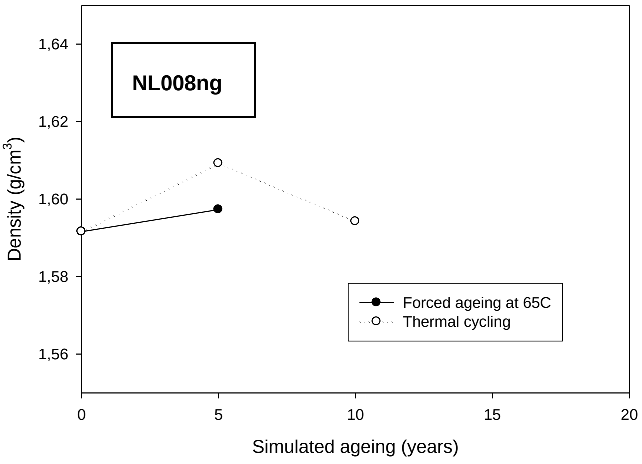


Figure 4. Results from helium pycnometer analyses of samples from NL007g, NL008g and NL008ng. All of the propellant samples have been subjected to forced ageing at 65°C and some of them also to thermal cycling down to -40°C.

4.4 Microscopy

A Nikon SMZ-10 optical stereomicroscope has been used for studying any visual anomalies resulting from forced ageing. No visual anomalies were found in propellant samples from either the NL007g, NL008g or NL008ng propellant lots [2].

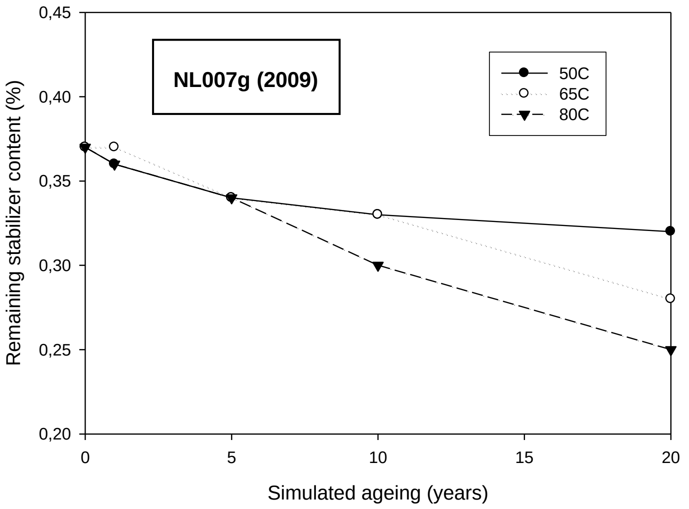
4.5 Stabilizer content

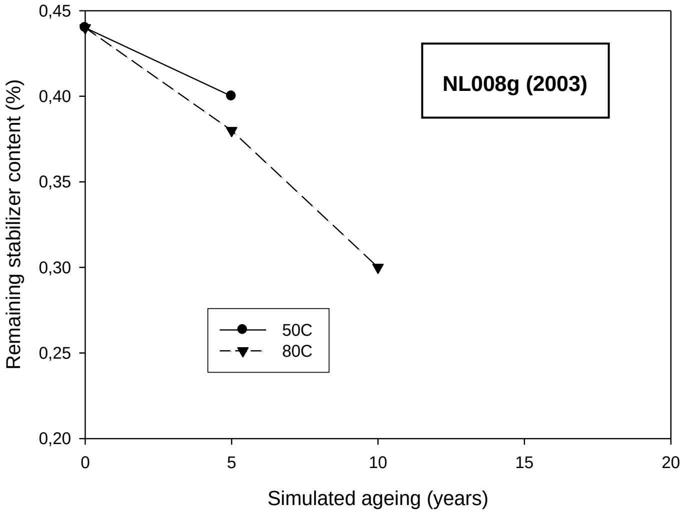
According to the specifications, NL007 and NL008 propellants initially have a stabilizer (Centralite I) content of 0.4 %. The stabilizer depletion as a result of forced ageing has been studied by HPLC.

As can be seen in Figure 5, a higher ageing temperature seems to result in a higher stabilizer depletion rate. The stabilizer depletion rate is however dependent on the NC-degradation rate. In the calculations of the thermal acceleration factor in Equation 1, the activation energy was set to 90 kJ/mole representing the CAB/RDX degradation process. The activation energy for the degradation processes in nitrocellulose based propellants is usually between 100 and 130 kJ/mole. In Figure 6 the activation energy is therefore varied between 100 and 120 kJ/mole in the calculations of the thermal acceleration factor. The correlation between stabilizer depletion at forced ageing for the different ageing temperatures seems initially to be best for an activation energy below 100 kJ/mole but for further forced ageing an activation energy around 120 kJ/mole gives the best fit.

According to Swedish recommendations for nitrocellulose propellant surveillance [11] the Centralite content should exceed 0.2 % for propellant lots to be approved for further storage/usage. As can be seen in Figure 5 and 6, the stabilizer content is exceeding 0.2 % in all of the propellant samples analyzed. Severe stabilizer depletion thus does not seem to be a problem at ageing of NL007g or NL008g. For NL008ng however, the stabilizer content has decreased from the original level of 0.4 % to 0.26 % by natural ageing of 6 years.

At FOI, samples from all propellant lots included in ammunition belonging to the Swedish Armed Forces are analyzed at least every fourth year. In this surveillance program for propellant stability testing, HPLC-analysis of stabilizer content is included. It is thereby possible to follow the stabilizer depletion at natural ageing of a certain propellant lot. Propellant samples from both NL007 and NL008 have been analyzed according to this surveillance program. For an NL007 propellant lot produced in 1999 (17399003) the stabilizer level declined to 0.38 % after 9-13 years of natural ageing. For a propellant lot from NL008g produced in 1997 (17397001) the stabilizer content has decreased to around 0.2 % already after 11-15 years of natural ageing. It would be interesting to further study the mechanism causing the enhanced stabilizer depletion rate in the NL008g (1997) and NL008ng propellant lots.





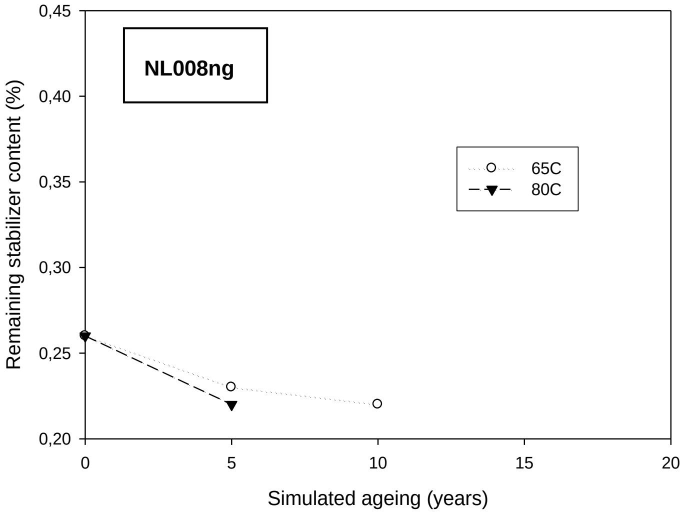
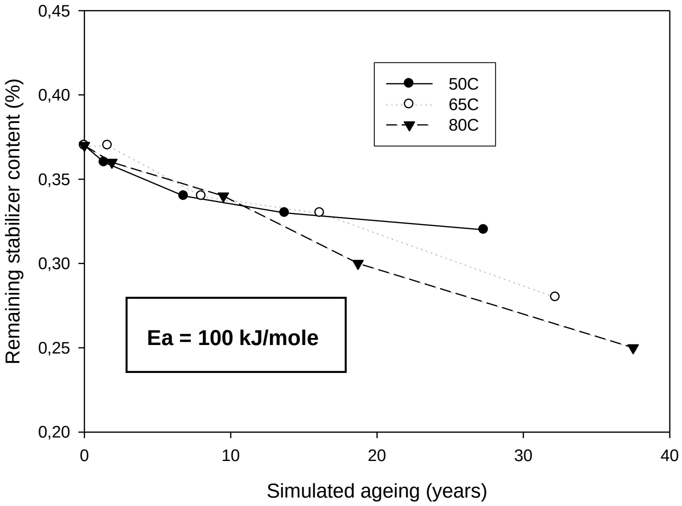
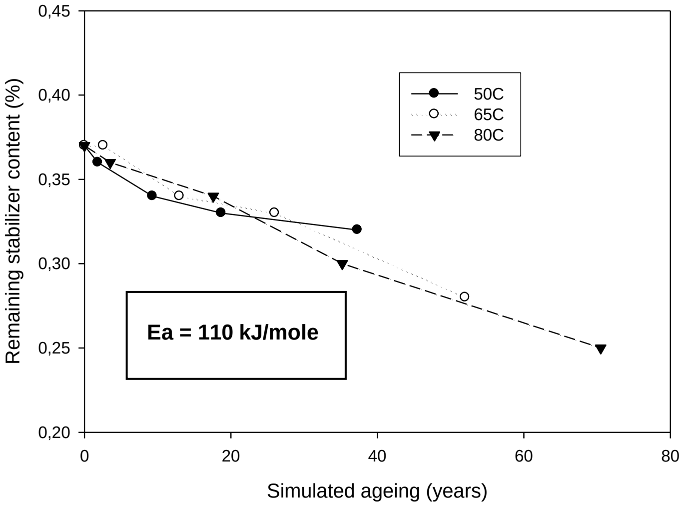


Figure 5. Stabilizer depletion as a result of forced ageing for propellant samples from NL007g, NL008g and NL008ng. An activation energy of 90 kJ/mole was used in the calculations of the thermal acceleration factor.





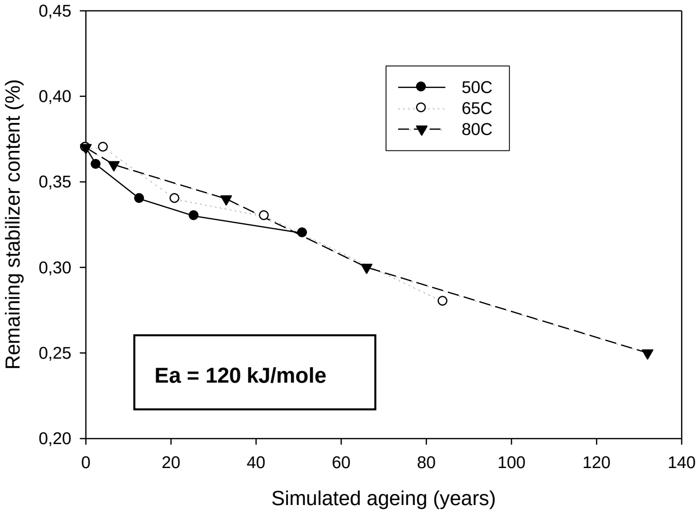


Figure 6. Stabilizer depletion as a result of forced ageing for propellant samples from NL007g(2009) for different choices of activation energy for the NC-degradation process.

4.6 Differential scanning calorimetry

DSC has been used for studying the impact of forced ageing on the thermal properties of propellant samples. The analyses were performed on a Mettler Toledo DSC 822. The samples were placed in sealed aluminum cups, heated with a rate of 10°C/min and purged with a flow of N_2-gas of 80 ml/min. The measurements were performed in the temperature range of -110°C to 300°C. No glass transitions were found. More details concerning the analyses conditions can be found in reference [2].

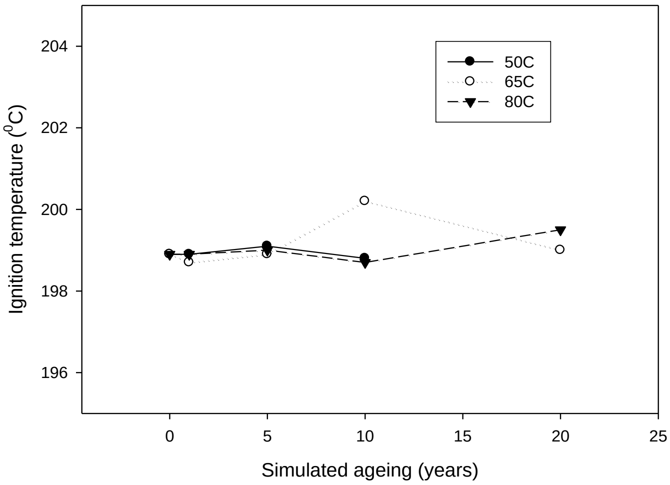


Figure 7. Ignition temperature of propellant samples from NL007g (2009) subjected to forced ageing.

As can be seen in Figures 7 and 8, the forced ageing has no substantial impact on either the ignition temperature or the melting point.

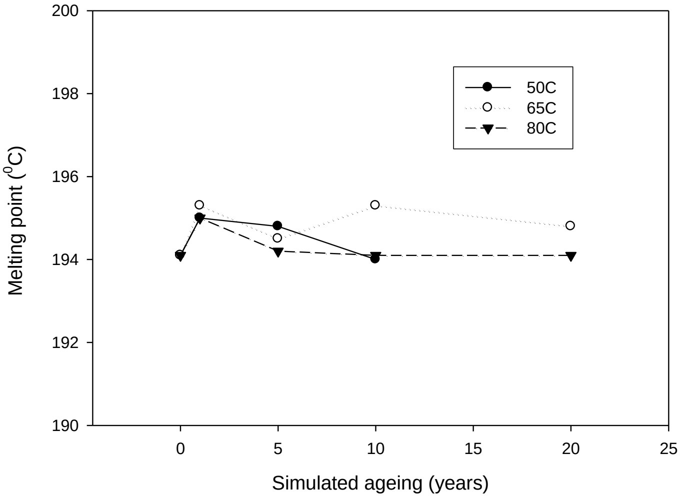


Figure 8. Melting point of propellant samples from NL007g (2009) subjected to forced ageing.

5 Possible LOVA-propellant surveillance methods – WP3

The impact of ageing on various properties of the propellant grains has been studied by several different analysis methods. In most of the analyses performed, no severe impact of ageing on the propellant properties has been found.

In the vented bomb analyses it was however revealed that forced ageing of the NL008ng samples probably has resulted in weakened mechanical properties. The burning rate calculated from the vented bomb analyses of NL008ng propellant samples increased significantly at forced ageing indicating cracking of grains at high pressure combustion as a result of reduced mechanical strength.

5.1 Vented bomb analysis method

The vented bomb analysis method has been chosen as a possible LOVA-propellant surveillance method to be studied further.

In the vented bomb used for the analyses of propellant burning properties at FOI, the propellant sample to be tested is placed in a small combustion chamber (see Figure 9).

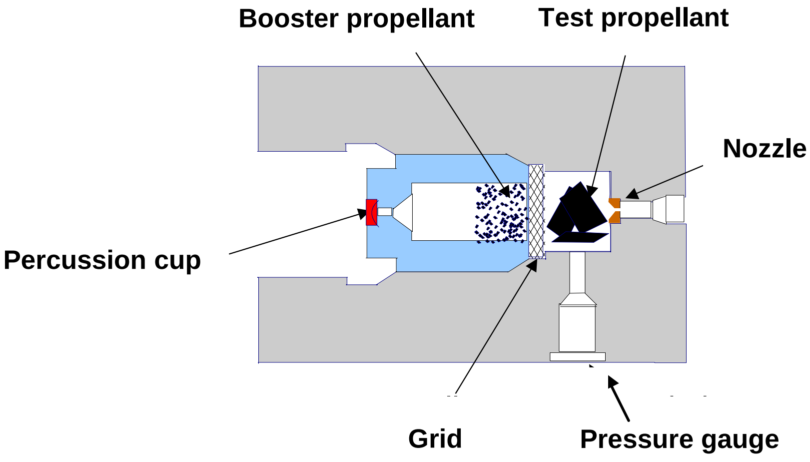


Figure 9. Vented bomb for analyses of propellant burning properties.

The combustion gases from the booster and test propellants are vented through a small nozzle. A suitable pressure in the chamber is achieved by varying the amount of booster propellant. The amount of sample analysed at each measurement varies between 0.3 and 0.5 g. The grains are never cut into pieces to avoid affecting the burning properties.

For characterization of the burning properties of a propellant sample, Vieille´s burning law [12-13]

$$r(p) = ap^{\mathrm{n}} \qquad (2)$$

where

r	burning rate
p	pressure
a	burning constant
n	burning exponent

has been used. In the calculation of the burning parameters, results from measurements performed at approximately 25, 50, 100, 140, 180 and 250 MPa have been used.

5.2 Cracking pressure method

The individual values of the burning rate at the different chamber pressures are calculated from the registered burning time of the propellant sample at the vented bomb analyses and the geometry as well as dimensions of the propellant grains. Thus, if the grains are cracking at a certain pressure due to low mechanical strength of the grains, the calculated value of the burning rate will increase due to changes of the grain dimensions. The actual value of the burning rate of the individual grains is unchanged but the gas generation rate is increased due to a sudden increase of the instantaneous burning area of the propellant sample.

The cracking pressure method can be used as a quantitative method for finding the chamber pressure where the propellant grains crack or as a qualitative method for study if ageing (or any other parameter) has an impact on the propensity of the grains to crack at a certain chamber pressure. If the grains, when subjected to forced ageing, crack at a pressure where initially no cracking occurred, the forced ageing must also have resulted in an impact on the mechanical properties of the grains. An apparent substantial increase of the burning rate at 100 MPa due to forced ageing of the propellant sample is thus qualitatively interpreted as a reduced mechanical strength of the propellant grains.

5.3 Results from vented bomb analyses

In Figure 10 can be seen how the burning rate varies with the pressure for propellant samples from NL007g (2009) that have been subjected to forced ageing corresponding to 20 years of natural ageing and thermal cycling. The ageing temperature has been varied between 50 and 80°C in the different plots. In one of the plots the sample has been subjected to thermal cycling. It can be seen that the rate coefficient for the burning equation is not uniform within the whole pressure interval of 25 to 250 MPa. There are two different rate coefficients representing the burning equation for pressures below and above 50 MPa. This is a general trend in all measurements.

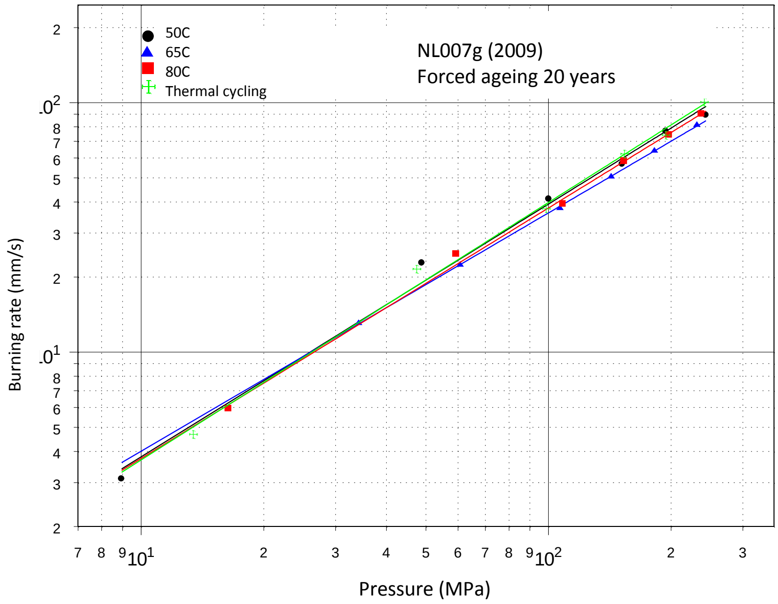


Figure 10. Burning properties of propellant samples from NL007g (2009) subjected to forced ageing corresponding to 20 years of natural ageing and thermal cycling. The ageing temperature has been varied between 50 and 80°C and the analysis temperature was 20°C.

In Figure 11, it can be seen how the burning rate varies with the pressure for propellant samples from NL008g (2003) that have been subjected to forced ageing corresponding to 5 years of natural ageing and thermal cycling. In this case the burning properties vary with ageing temperature. This phenomenon is even more pronounced for NL008ng as can be seen in Figure 12.

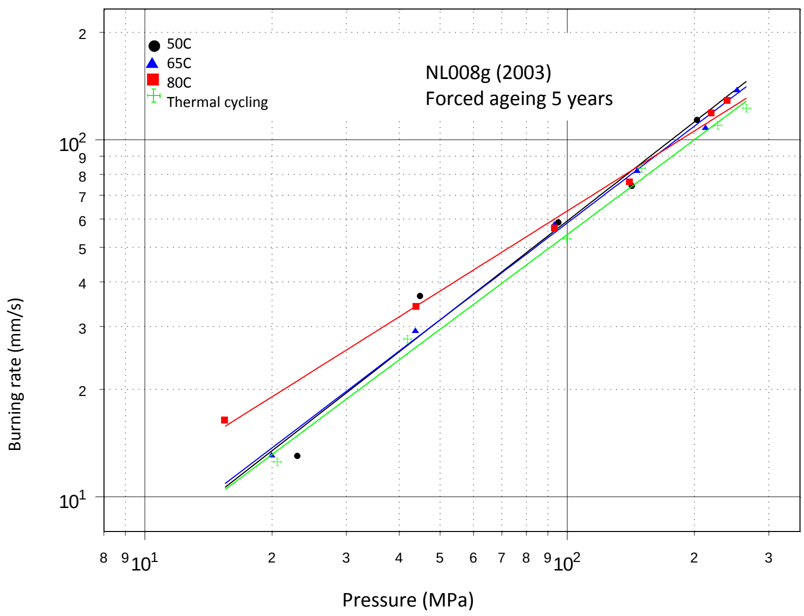


Figure 11. Burning properties of propellant samples from NL008g (2003) subjected to forced ageing corresponding to 5 years of natural ageing and thermal cycling. The ageing temperature has been varied between 50 and 80°C and the analysis temperature was 20°C.

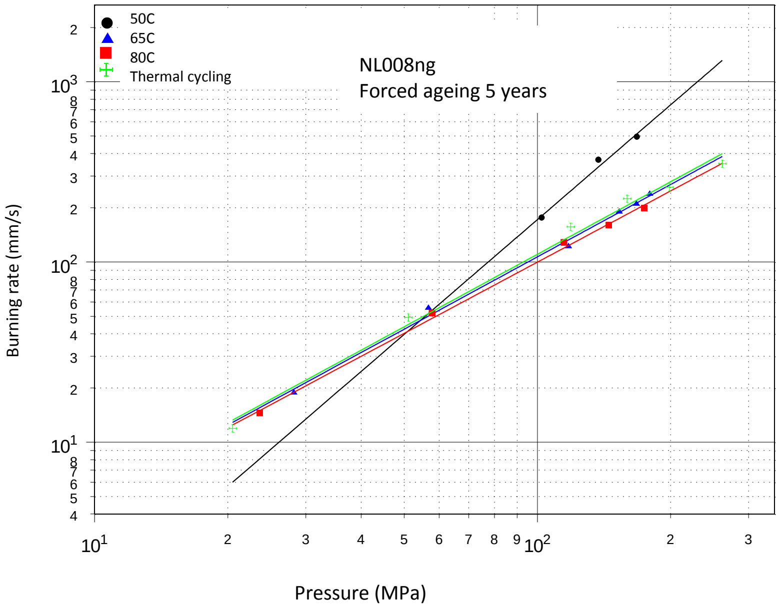


Figure 12. Burning properties of propellant samples from NL008ng subjected to forced ageing corresponding to 5 years of natural ageing and thermal cycling. The ageing temperature has been varied between 50 and 80°C and the analysis temperature was 20°C.

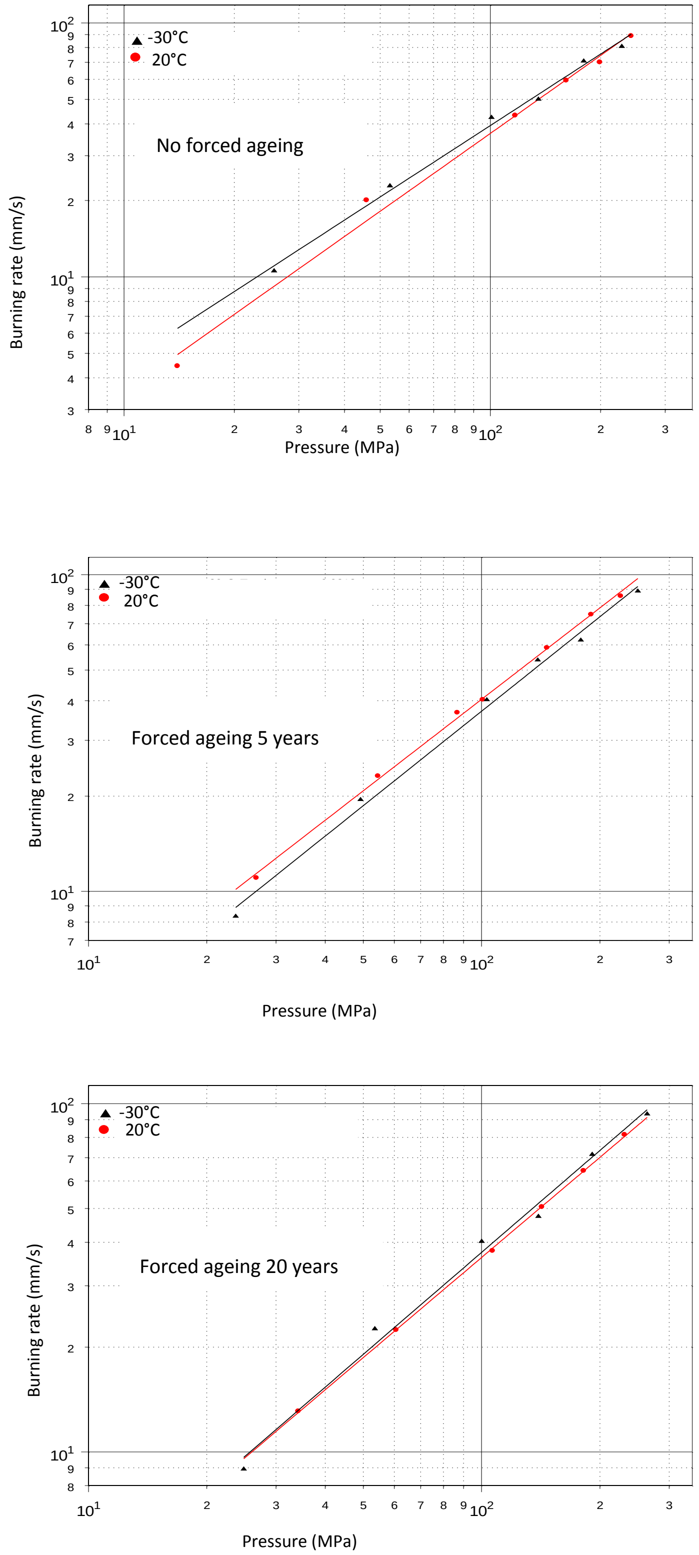


Figure 13. Impact of ageing on burning properties of NL007g (2009) at 20°C and -30°C.

Since the NL007 and NL008 propellants are suspected to have bad low temperature properties the measurements have been performed both at 20°C and -30°C. In

Figure 13 the results from vented bomb analyses at both these analysis temperatures is shown. The samples analyzed have been extracted from the NL007g (2009) propellant lot and have been subjected to varying degrees of forced ageing. As can be seen in Figure 13, the analysis temperature does not influence the analysis results in a specific direction. The low temperature (-30°C) does not make the propellant grains brittle causing splitting of grains at burning.

5.4 Determination of burning parameters

From the plots of burning rate versus pressure it is possible to determine the burning parameters *a* and *n* in Vieille´s burning law (Equation (2)). To facilitate the evaluation of impact of ageing on burning properties, the burning rates at 100 MPa, burning constants (*a*) and burning exponents (*n)* for the burning of different propellant samples are compared.

In Figure 14 is given the impact of ageing on the burning exponent. For the NL007 propellants there is no dramatic change of the burning exponent with forced ageing. For the NL008 propellants however the burning exponent is increasing with forced ageing. This effect is especially pronounced for the NL008ng propellants with no graphitization where a high initial value of the burning exponent (~1.3) is increased further to around 1.95.

Figure 15 shows the impact of ageing on the burning constant. For the NL007 propellants there is no dramatic change of the burning constant with forced ageing. For the NL008 propellants however the burning constant is decreasing with forced ageing. This effect is especially pronounced for the graphitized NL008g propellants where a high initial value of the burning constant (~2.4) is decreased substantially to between 1 – 1.4 depending on the ageing temperature.

Figure 16 shows the impact of ageing on burning rate at 100 MPa. For the graphitized propellant samples there is no dramatic impact of ageing on the burning rate. For the NL008ng propellant samples however the high initial value of the burning rate at 100 MPa (~100 mm/s) is increased further to around 180 mm/s.

Thermal cycling does not seem to have had a severe impact on the mechanical strength since there are no considerable changes in either burning exponent, burning constant or burning rate at 100 MPa.

In Figure 17 it can be seen how the burning properties vary with the initial temperature of the propellant sample. There is a difference between the initial values resulting from analyses at the two different temperatures for all of the burning parameters. The values for the burning exponent and burning constant after 5 years of forced ageing are almost identical for the different analysis temperatures while the burning rate at 100 MPa is somewhat higher for an analysis temperature of 20°C than at -30°C.

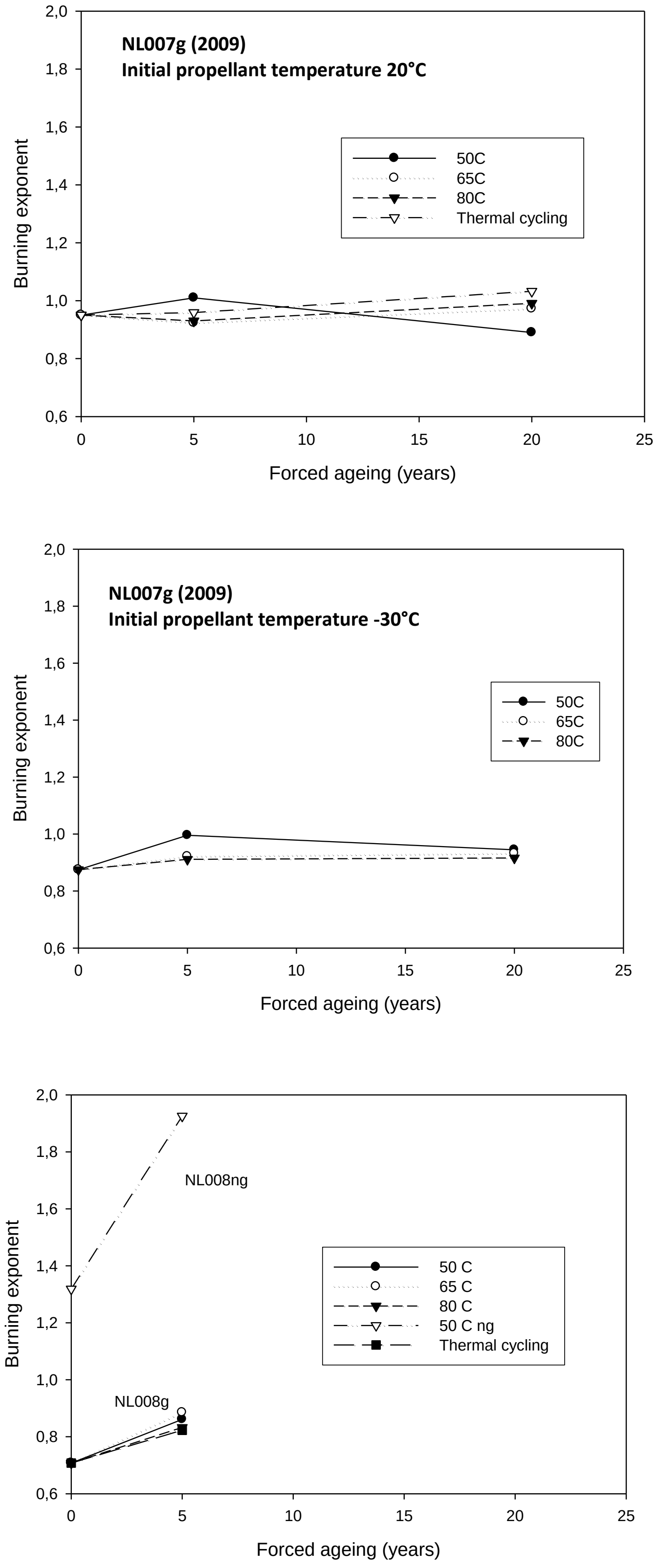
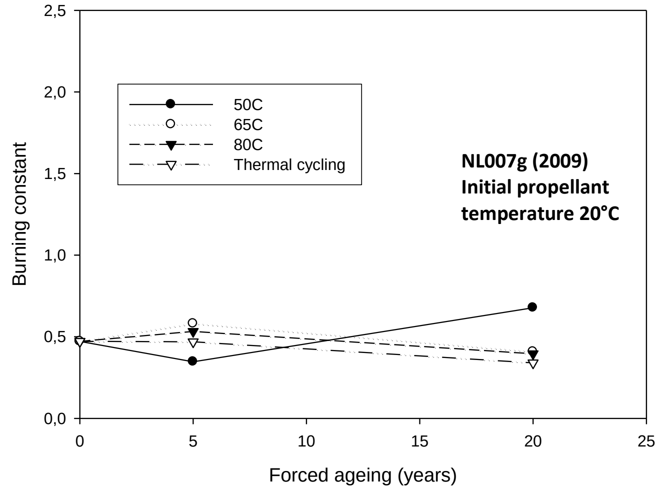
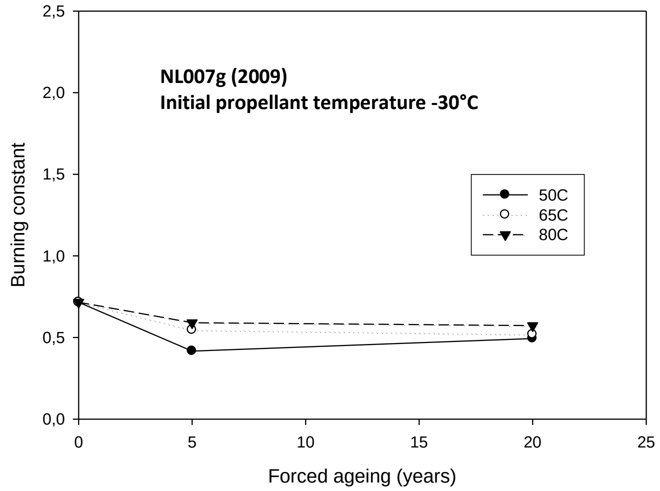


Figure 14. Impact of forced ageing on burning exponent.





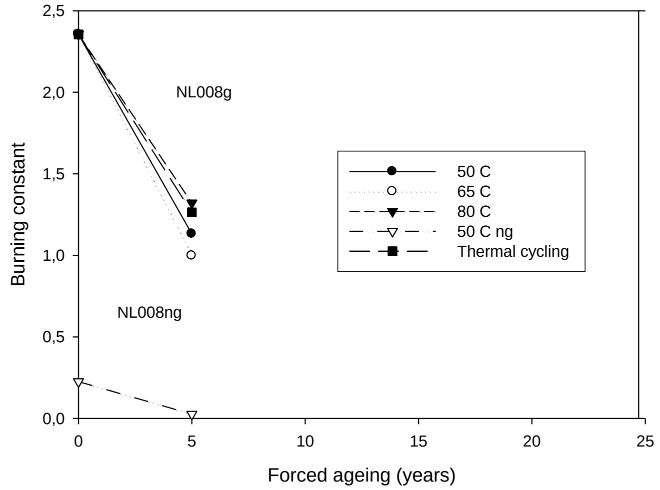
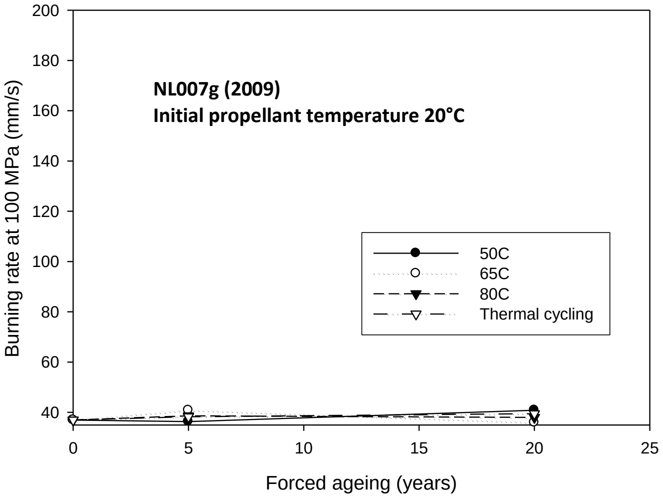
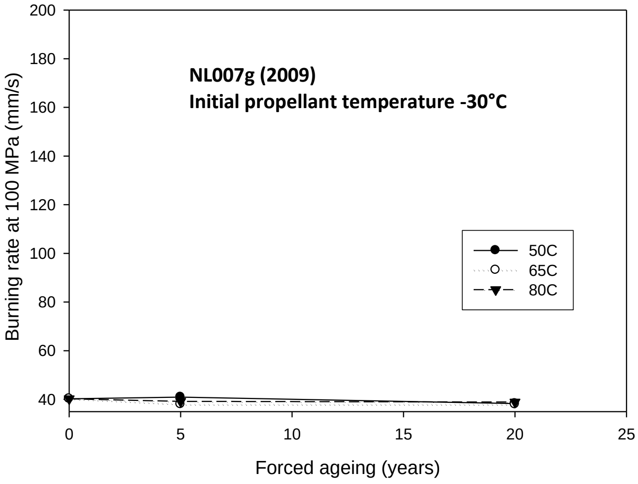


Figure 15. Impact of ageing on burning parameters for propellant samples from NL007g (2009).





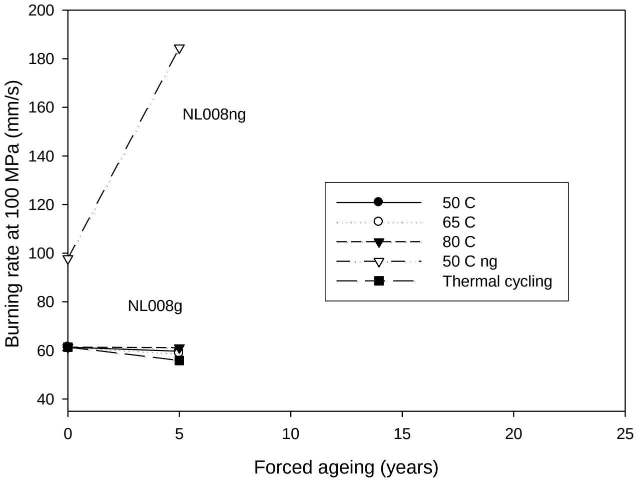


Figure 16. Impact of ageing on burning parameters for propellant samples from NL008g (2003) and NL008ng. The initial propellant temperature was 20°C.

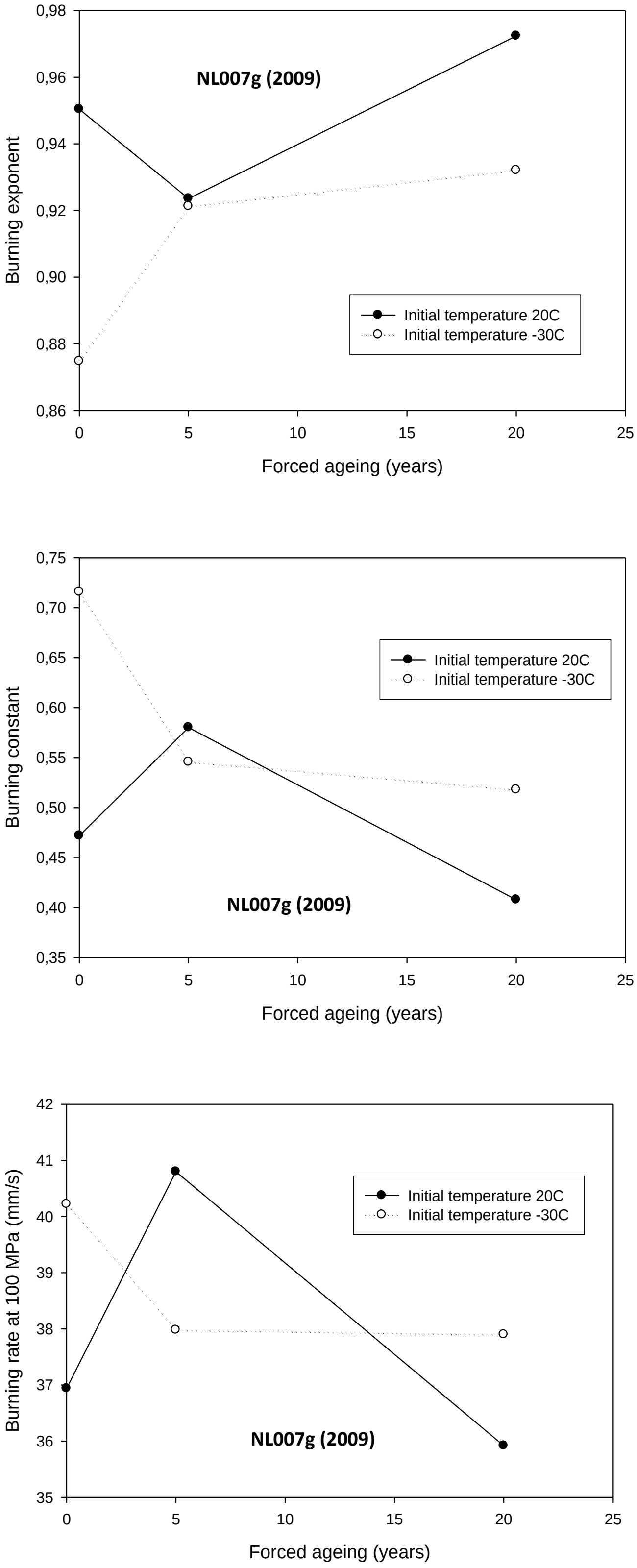


Figure 17. Impact of ageing on burning parameters for propellant samples from NL007g (2009). The ageing temperature was 65°C and the initial propellant temperature was 20°C and -30°C.

In Figures 18-20 the scaling of the plots in Figures 13 and 14 for NL007g (2009) has been expanded. In Figure 17, it can be seen that ageing at 50°C results in a complete different trend in how the burning parameters vary with the degree of forced ageing.

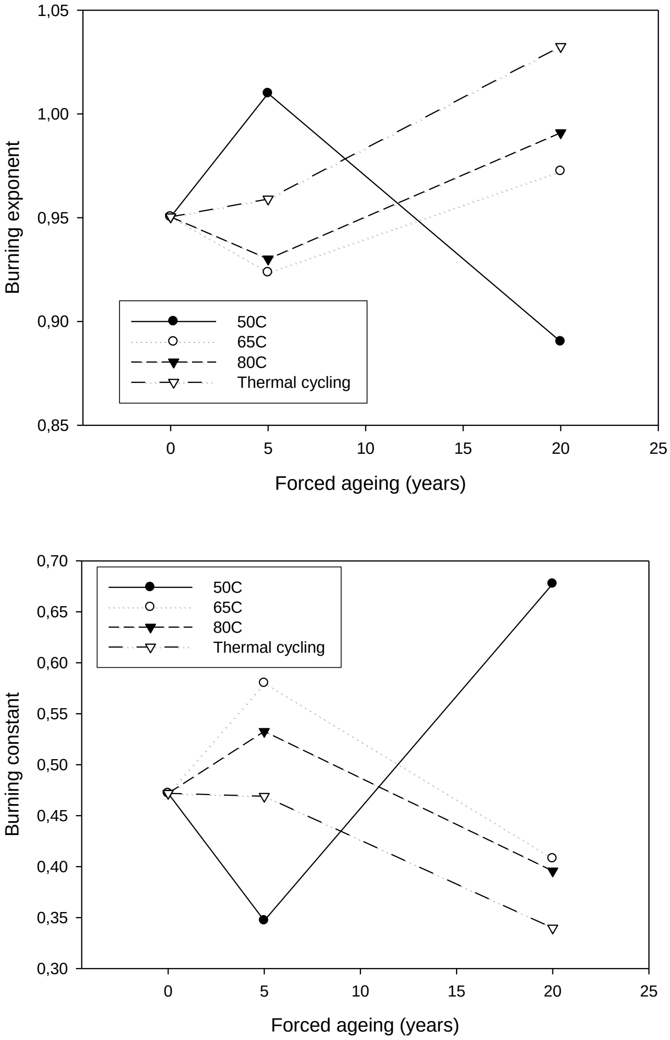


Figure 18. Impact of ageing on burning parameters for propellant samples from NL007g (2009). The initial propellant temperature was 20°C.

At an initial propellant temperature of -30°C on the contrary, the changes of burning exponent and burning constant at forced ageing follow the same trend at all of the ageing temperatures (see Figure 19).

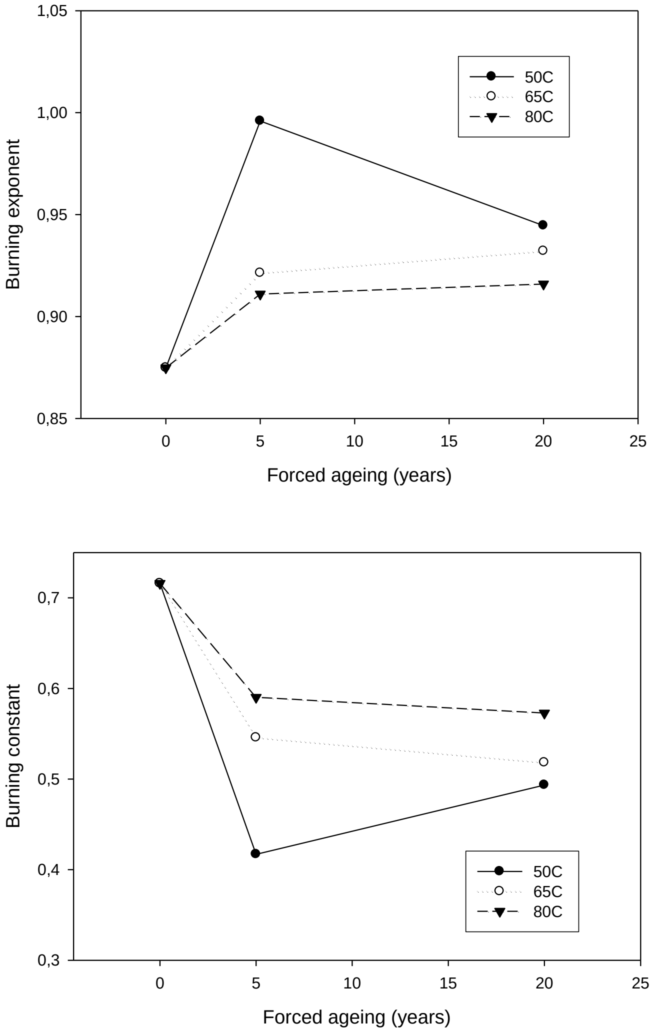
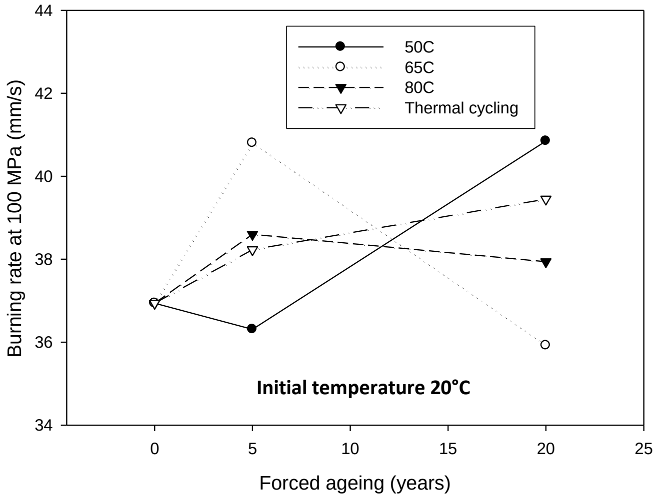


Figure 19. Impact of ageing on burning exponent and burning constant for propellant samples from NL007g (2009). The initial propellant temperature was -30°C.

For the burning rate at 100 MPa, ageing at 50°C results in a complete different trend in how the burning rate vary with the degree of forced ageing for both an analysis temperature of 20°C and -30°C (see Figure 20).



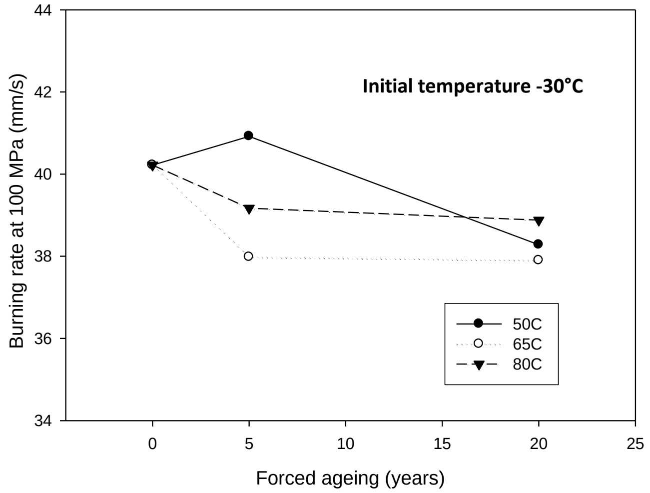


Figure 20. Impact of ageing on burning rate at 100 MPa for propellant samples from NL007g (2009).

5.5 Evaluation of burning properties

The values of the burning parameters are design properties that vary with the designated application for a specific propellant.

A burning exponent close to 1 means that the burning rate increases almost linearly with the pressure in the gun barrel. An increase of the burning exponent of the propellant at ageing might result in higher barrel pressure at launching than originally designed for. A burning exponent above 1 is often achieved for porous propellants.

For almost all propellant samples analysed, the burning exponent is increasing somewhat with forced ageing. How this increase in burning exponent would affect the barrel pressure at launching has however not been evaluated.

Since a burning exponent above 1 is often associated with porous propellants there might have been a decrease in density of the propellant grains as an effect of forced ageing. As stated earlier in this report, the density is initially decreasing somewhat for the graphitized propellants as an effect of forced ageing. The decreased density is however not followed by a dramatic increase in burning rate for these propellants. There is thus no indication of a reduced mechanical strength due to formation of interior pores at forced ageing of the graphitized propellants.

The value of the burning constant is affected by the initial temperature of the propellant. A low value of the burning constant is an indication of a burn rate with low dependency of the initial temperature of the propellant and is thereby a favourable property. For almost all propellant samples analysed, the burning constant is decreasing with forced ageing.

A dramatic increase of the burning rate calculated from vented bomb analyses means that the propellant grains most probably have been cracked during the combustion. The burning rate varies with pressure according to Vieille´s burning law. The burning rate at 100 MPa has been chosen as a reference value for comparison when studying the impact of ageing on the burning rate.

For propellant samples from NL007g (2009) and NL008g, the burning rate at 100 MPa is not increasing dramatically as an effect of forced ageing. For propellant samples from NL008ng however, the burning rate at 100 MPa is increasing from 117 mm/s to 185 mm/s when subjected to forced ageing corresponding to 5 years of natural ageing. This should be compared to a burning rate of around 60 mm/s at 100 MPa for propellant samples from NL008g. The burning rate is thus unusually high even for NL008ng that has not been subjected to forced ageing (though subjected to natural ageing for around 6 years).

The stabilizer content is 0.4 % for pristine propellant from NL008g and NL008ng. Both for NL008ng and NL008g (1997) the stabilizer content has decreased to levels around 0.2 % already after 6 and 11 years of natural ageing respectively. For NL008g (2003) however, the stabilizer level has not decreased at all after 7 years of natural ageing. The burning properties of NL008g (1997) has not yet been analyzed but it will be studied if there is a connection between high stabilizer consumption and reduced mechanical strength of the propellant grains.

6 Discussion and conclusions

The analyses and tests performed so far of propellant samples from NL007g and NL008g do not indicate that forced ageing of the propellants have a severe negative impact on important propellant properties. The results from characterization of the burning properties of NL008ng indicate however that the mechanical strength of the grains has been reduced by natural and forced ageing since cracking of the propellant grains occur at high pressure combustion. The only difference between NL008ng and NL008g is that NL008ng has not been graphitized this effect of ageing might therefore also occur for propellant samples from NL008g and NL007g. A high stabilizer consumption at natural ageing was found for propellant samples from NL008ng and NL008g (1997) but not for NL008g (2003). The burning properties of propellant samples from NL008g (1997) will be compared with those from NL008g (2003) to study if there is a connection between high stabilizer consumption and high cracking probability (reduced mechanical strength) of the propellant grains at combustion. It would also be interesting to further study the mechanism(s) causing the enhanced stabilizer depletion rate in the NL008g (1997) and NL008ng propellant lots.

Some of the propellant samples have been subjected to thermal cycling from +65°C down to -30°C to study the impact of temperature changes on the mechanical strength of the grains. The results from the vented bomb analyses did however not show that the cracking probability/mechanical strength of the grains was enhanced/reduced severely at thermal cycling.

There is a vague trend indicating a decreased density at forced ageing of the propellant grains. This trend is more pronounced at forced ageing at 50°C and at the start of the forced ageing. For NL008ng, the density is instead increasing at forced ageing. This can be an effect of that different kinds of surface phenomena occur depending on if graphite is present on the surface or not. In Reference [10] it was observed that at evaporation of residual solvent present in the propellant grains, the plasticizer co-migrates to the grain surface. Forced ageing at elevated temperature might enhance residual solvent evaporation and plasticizer migration resulting in reduced mechanical strength. A deceased density or any other phenomena can be a result of residual solvent evaporation. Thermal analyses as DSC and thermogravimetric analysis (TGA) of aged and unaged propellant samples are therefore planned to study solvent evaporation in the temperature interval 20-150°C.

Forced ageing at an elevated temperature is a well-tested and often used method for simulating natural ageing at a short time. From the results in Figures 3, 11, 12, 18 and 20 it can however be seen that the impact of ageing on different propellant properties differs depending on the ageing temperature. For an ageing temperature of 50°C, the size of the properties or the trend of how the properties vary with ageing time, are quite different than for ageing at 65°C or 80°C. It is not clear why this difference is achieved. Possible explanations can be that the activation energy is not representative for the decomposition mechanism studied (affecting the acceleration factor) or that a certain decomposition mechanism that affects the propellants properties takes place at 65°C and 80°C but not at 50°C. A non-representative activation energy is not plausible since that would not lead to different directions of how the trend of the properties vary with ageing time as in Figure 14. The results is however an indication of that it can be risky to rely on that the variations of propellant properties that has been demonstrated to take place at forced ageing also will occur at natural ageing and that it is important to be careful at selection of ageing temperature.

Since reduced mechanical strength of the grains (increased cracking probability at high pressure combustion) from NL008ng has been revealed at characterization of the burning properties in a vented bomb, this type of analysis has been chosen as a possible LOVA-propellant surveillance method to be studied further. Results from vented bomb analyses of propellant samples from NL008g (1997) that has only been subjected to natural ageing for 15 years will be compared with corresponding results from analyses of samples from NL008g (2003) subjected to forced ageing. The impact of the humidity of the propellants samples on the results from vented bomb analyses will be studied as well as possible variation of the burning properties between different propellant grains.

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