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ANALYSIS OF DOUBLE BASE PROPELLANTS SERVICE LIFE RELATING TO MECHANICAL PROPERTIES IN EXTREME CLIMATIC CONDITIONS

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INTRODUCTION

Goals of this work were

- to investigate changes in double base (DB) propellants over ageing and
- to determine significance of nitrocellulose (NC) chain decomposition for evaluation of DB propellants service life.

Reasons for this research:

1. DB propellants are long term stored.
2. DB propellants are exposed to various temperature conditions when stored in field storages (e.g. in extreme climate zones).
3. Polymer NC is as a binder of DB is liable to relatively fast decomposition.
4. DB propellants markedly change its mechanical properties over operational temperature range.

USED METHODS

- Artificial ageing – simulation of time-temperature loading during storage.
- Size-exclusion chromatography (SEC) - determination of nitrocellulose polymer chain decomposition characteristics.
- Uniaxial compression and tensile tests - determination of changes of basic mechanical properties.
- Dynamic mechanical analyses – determination of transition temperatures and its shift.
- Reaction kinetics analyses – determination of predictive decomposition models.

TESTED DB PROPELLANTS

- Type 1 – standard DB made by Explosia a.s. (Pardubice, CZE).
- Type 2 – with alternative less toxic auxiliary plasticizer.
- NC properties – 12% nitrogen, wood cellulose.
- Extruded grains – 30 mm in diameter, 300 mm long.

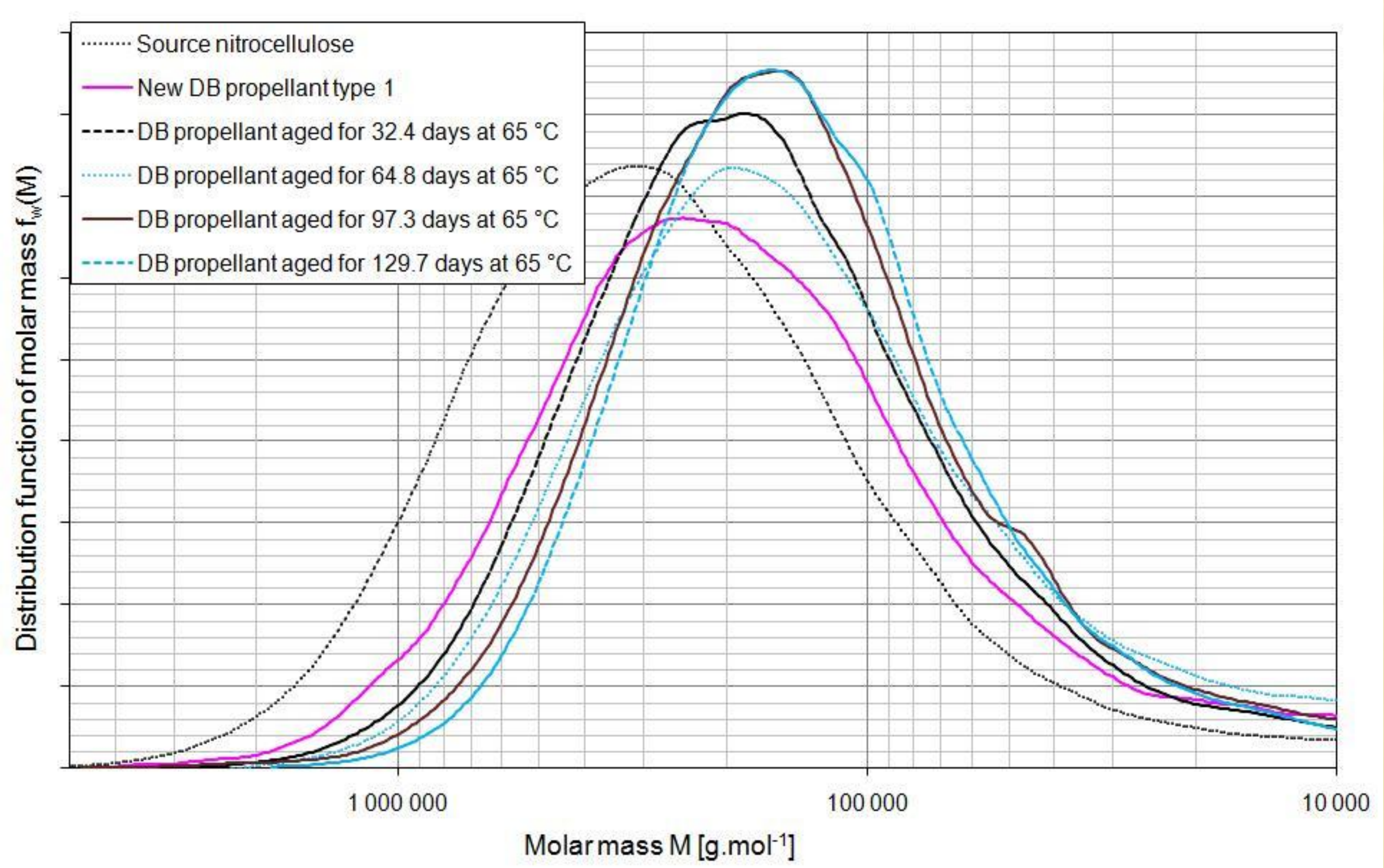
Propellant	Type 1	Type 2
Nitrocellulose	55.7 %	55.7 %
Nitroglycerine	28.3 %	26.0 %
Dinitrotoluene	8.5 %	
Alternative plasticizer		11.5 %
Ethyl centralite	2,9 %	2.9 %
Catalyzers	4,0 %	4.0 %

ARTIFICIAL AGEING

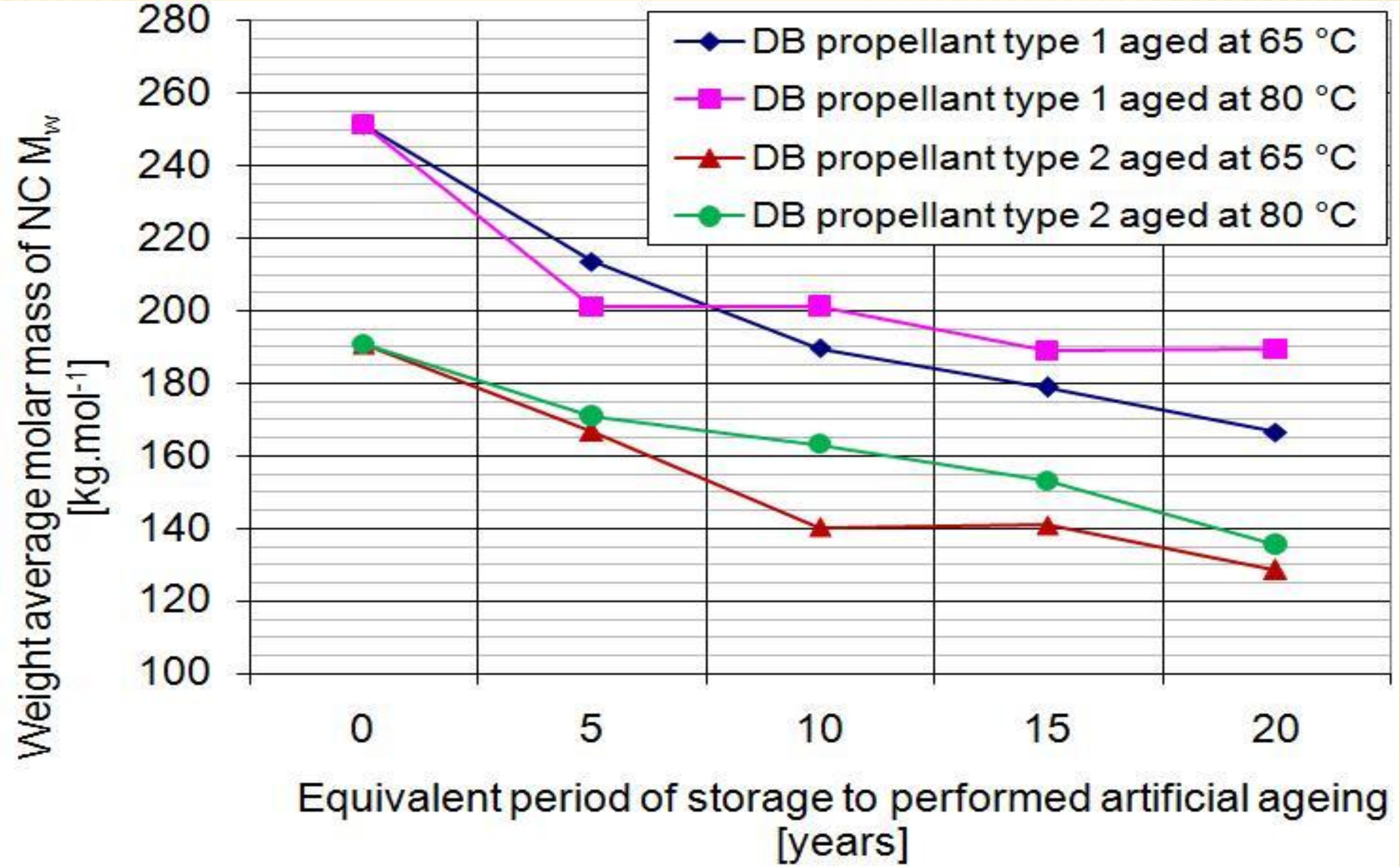
- Conditions set with respect to AOP-48.
- Ageing at two temperatures: 65 °C and 80 °C.
- Grains loaded in polymer coated aluminum bags.
- Ageing periods accordingly to Arrhenius equation (and known kinetic parameters of -NO_2 group decomposition):

Period of storage at 25 °C [years]	Corresponding period of artificial ageing at 65 °C [days]	Corresponding period of artificial ageing at 80 °C [days]
5	32.4	5.3
10	64.9	10.6
15	97.3	15.9
20	129.7	21.2

SEC CHROMATOGRAMS



AVERAGE MOLAR MASS OF NITROCELLULOSE



MODEL OF NITROCELLULOSE DECOMPOSITION

- Kinetic model of chain scission

(solve rate constant from molar masses)

$$\frac{m}{M_n(t_i,T)} = \frac{m}{M_n(0)} + k_M(T)t_i$$

- Arrhenius equation

(solve activation energy from rate constant)

$$\ln k_{Mi}(T_i) = \ln A - \frac{E_a}{RT_i}$$

Established kinetic parameters of decomposition in temperature range 65 °C to 80 °C:

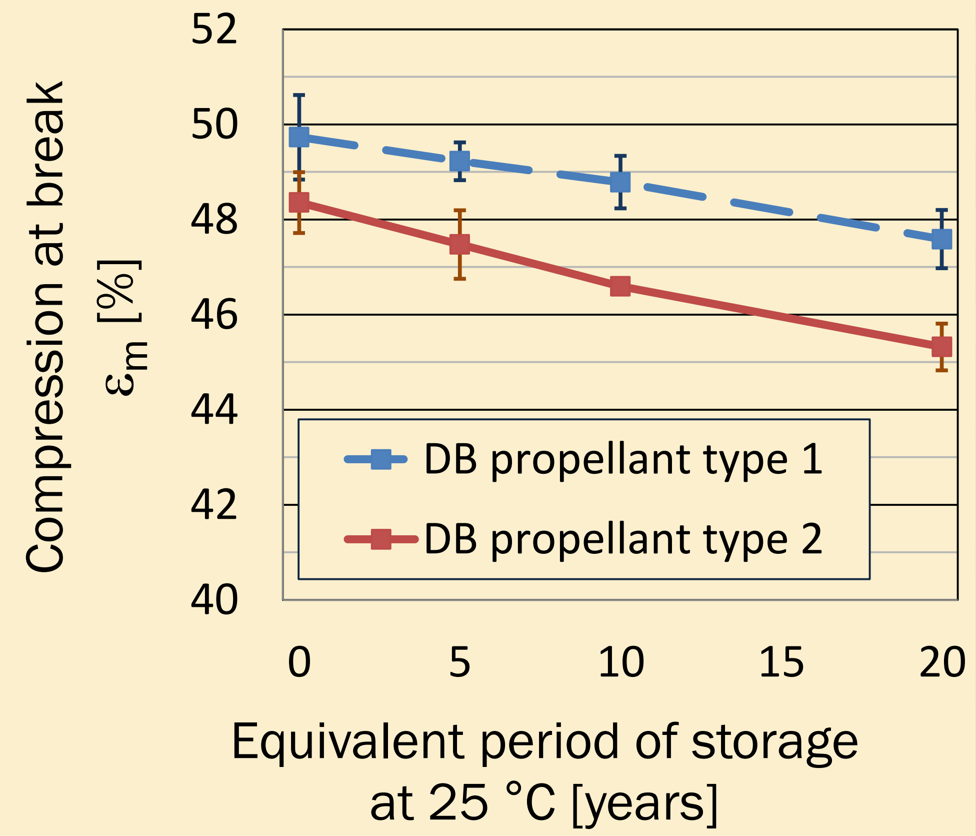
		DB propellant type 1	DB propellant type 2
Activation energy E_a	[kJ.mol^{-1}]	85	105
Frequency factor A	[-]	$1{,}84.10^3$	$3{,}28.10^6$

CHANGES IN MECHANICAL CHARACTERISTICS

Uniaxial tensile and compression tests:

change of ε_m measured at 21 °C (aged for 129.7 days at 65 °C)

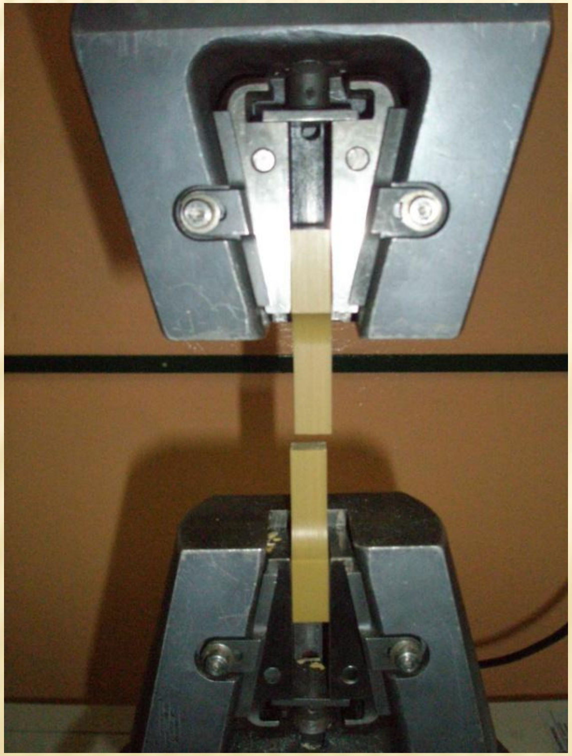
- in compression -4 % and -6 %,
- in tension -7 % and +13 %.

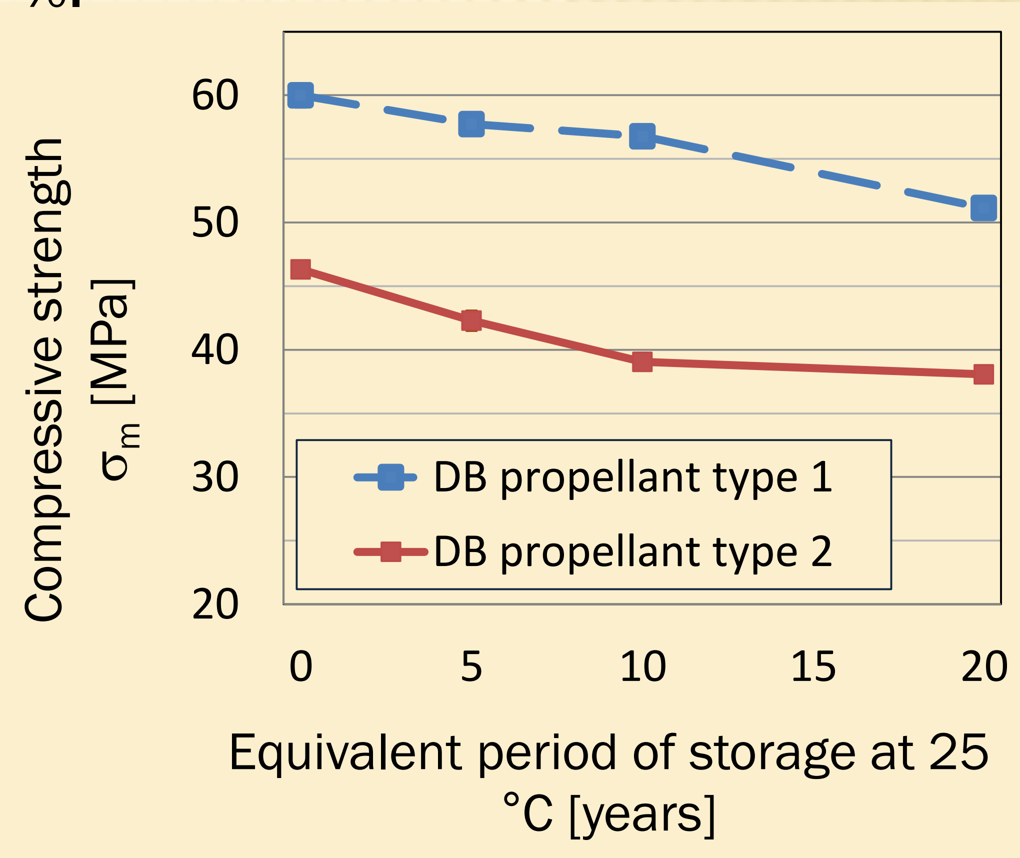


CHANGES IN MECHANICAL CHARACTERISTICS

Decrease of σ_m measured at 21 °C (aged for 129.7 days at 65 °C)

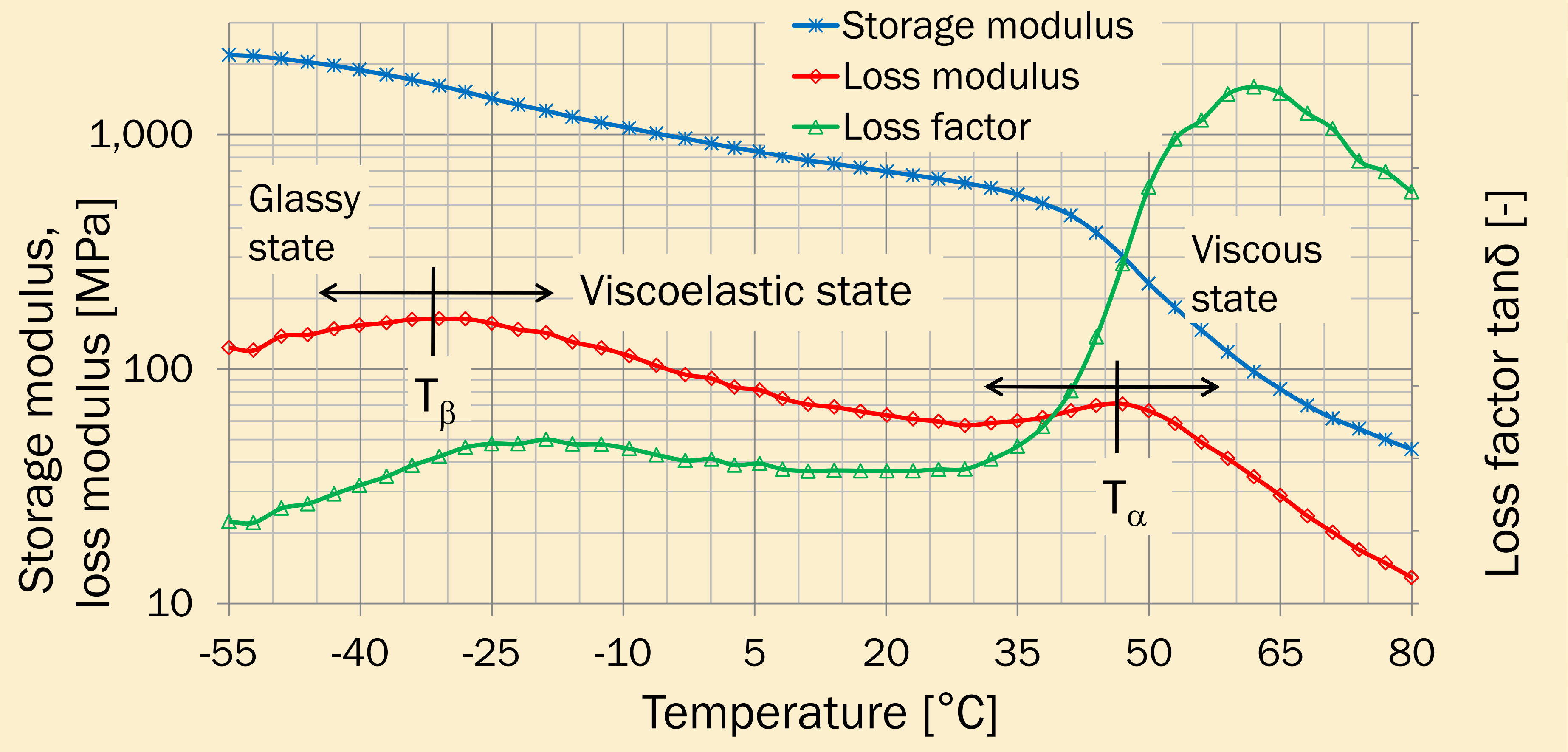
- in compression by 15 % and 18 %,
- in tension by 16 % and 9 %.



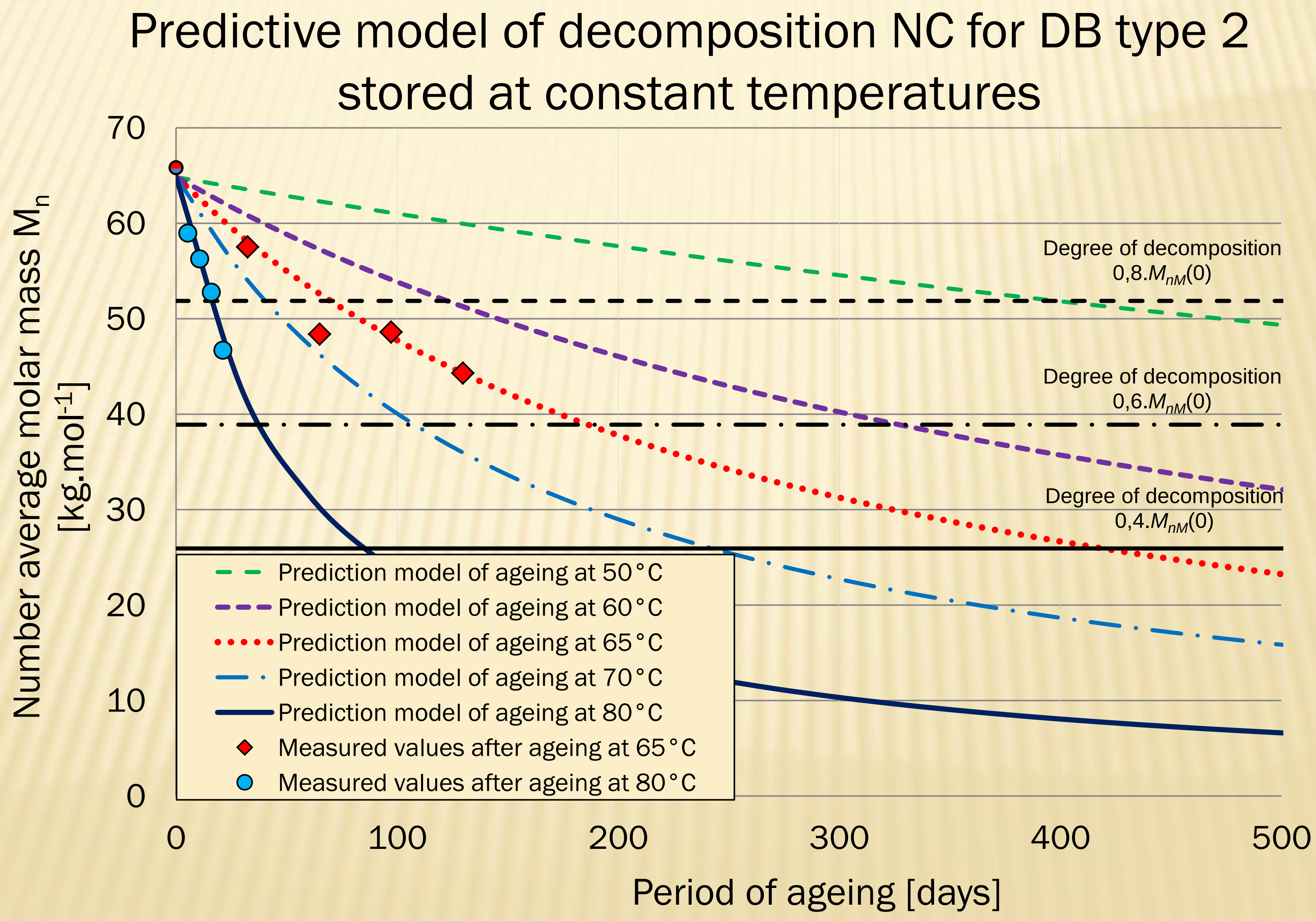


DYNAMIC MECHANICAL ANALYSES

- T_α lowers during ageing 46 °C ➡ 42 °C for both DB.
- T_β does not show any trend -32 °C, -37 °C for DB type 1, 2.



MODEL OF NITROCELLULOSE DECOMPOSITION



MODELING OF FIELD STORAGE CONDITIONS

- STANAG 2895 determines climatic categories and time-temperature loadings.

Temperature at storage	Period of temperature loading during one year
[°C]	[hours]
71	5,2
69	26,2
67	49,5
65	77,4
63	108,7

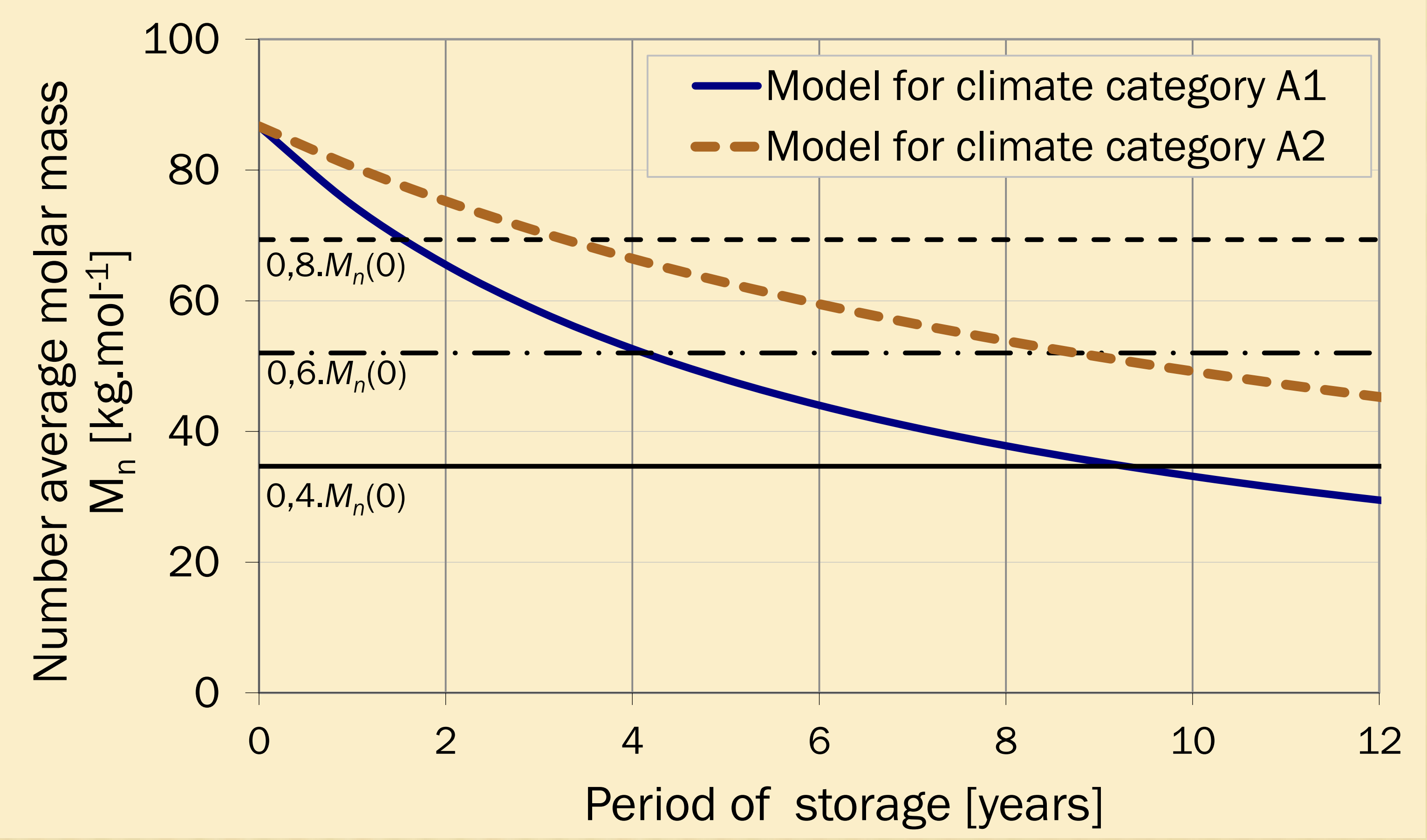
- Data were used to establish predictive model based on Arrhenius equation in form:

$$M_n(t_n,T_n) = M_n(0) - \sum_i^n \left(M_n(t_{i-1},T_{i-1}) - \frac{m}{\frac{m}{M_n(t_{i-1},T_{i-1})} + A_i \exp\left(-\frac{E_{ai}}{RT_i}\right) t_i} \right)$$

NC CHAIN DECOMPOSITION IN FIELD STORAGE

Service life related to NC chain decomposition:

- 9,5 years and 11,5 years for DB type 1 and type 2 in climate category A1 (limiting condition 0,4 $M_n(0)$)



CONCLUSION

Performed artificial ageing of two types of DB propellant at 65 °C during 129.7 days leads to decrease of values of chemical and mechanical properties:

- M_n by 34 % and 33 %
- σ_m at 21 °C in compression by 15 % and 18 %
- ε_m at 21 °C in compression by 4 % and 6 %
- T_α by 4 °C (46 °C -> 42 °C)
- E_a of NC chain scission at temperature range 65 °C to 80 °C were established to be 85 $kJ.mol^{-1}$ and 105 $kJ.mol^{-1}$.

CONCLUSION

Described processes and changes lead to:

DB propellants tend to get markedly softer at temperatures near upper operational limit (~ 50 °C) after ageing.

Service life of DB propellants related to NC decomposition and mechanical characteristics changes could determine overall service life.

Service life of DB related to M_n, when stored in field conditions in extreme climates, could be limited to ~10 years (accepted condition of limiting decomposition 0,4.M_n(0)).

Thank you for your attention

Questions?