

# Characterisation of aged Polymer Bonded eXplosives - Development of STANAG 4666

*IMEMTS – 2007 (Miami - Florida)*

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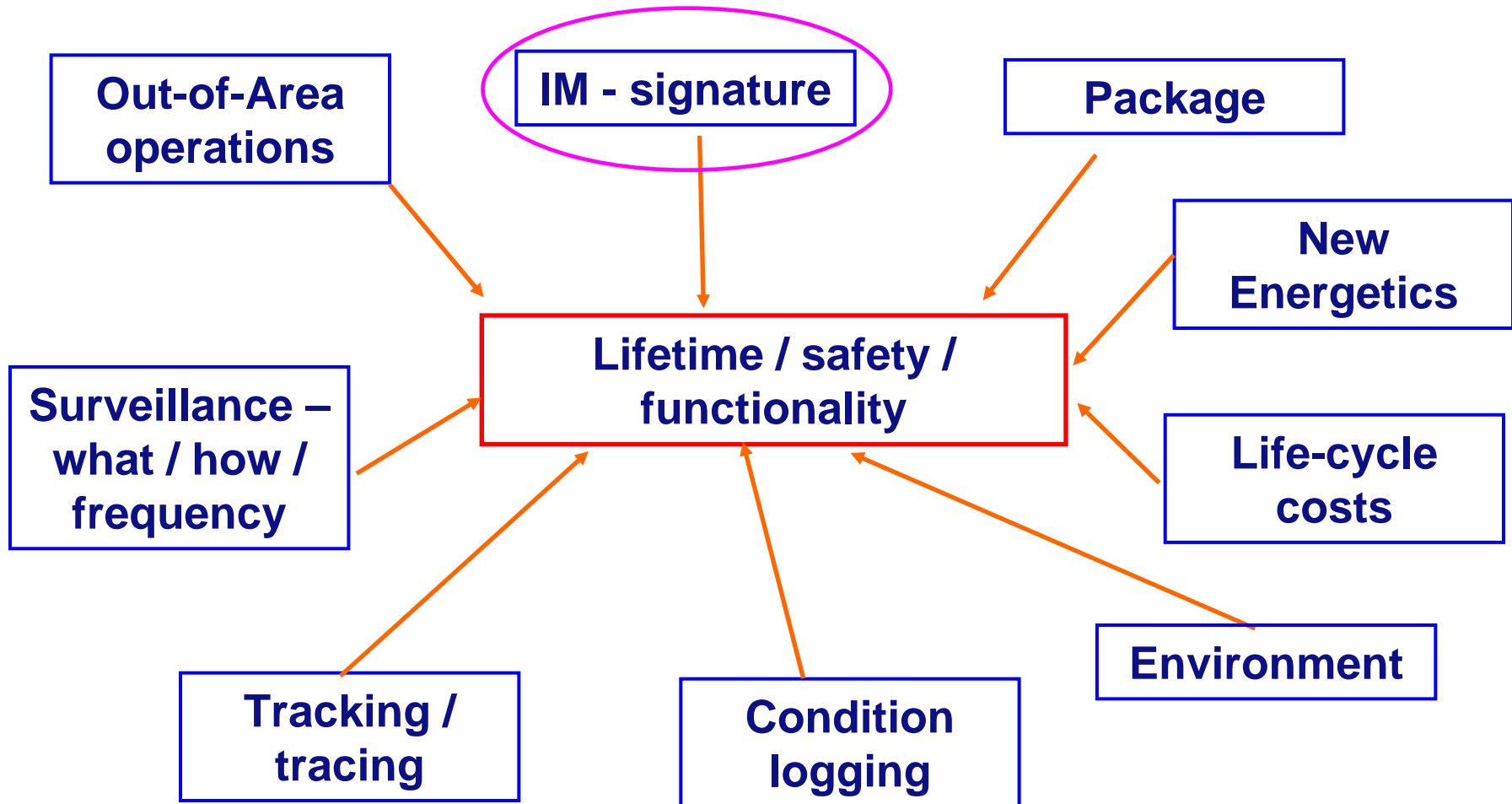
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# Overview

1. Introduction Lifetime
2. History of STANAG
3. Workshop in Finland (2005)
4. Reference documents - Techniques
5. Aim of STANAG
6. What is changing, making material critical
7. Conclusion
8. Acknowledgement

# Lifetime



# Insensitive Munitions

- RNLA had not yet insensitive munitions
- TNO advised RNLA on adequate protection



Anti tank weapon at the back of jeep in  
Afghanistan: 1 bullet on AT-4 could be fatal

# Transport conditions - example



# Current-future activities for SG1

- In 2003 a survey of the member nations was conducted to determine which standards are needed
- Those high on the list include;
  - Standardization of surveillance activities
  - Update of ingredients specifications and methods
  - Standard to cover “Ageing of PBXs”

# History of STANAG 4666

- MSIAC workshop – May 2005
- Start for AC-326-SG 1 – CNG to set up a new document;

*The aim of this agreement is to standardize accelerated ageing and testing protocol by which aged samples of PBX's, cast-cured compositions using 'inert' or 'energetic' binders can be assessed and compared.*

- Title STANAG 4666 :  
Explosives: Explosives, assessment of ageing of Polymer Bonded Explosives (PBX's) cast cured compositions using inert or energetic binders
- Custodian nation : The Netherlands - TNO

# Areas to cover by the working group in Finland

- **What other specifications do people use to look at ageing of PBXs**
- **What is the aim/goal of this STANAG**
- **Can the STANAG help to fill gaps in STANAG 4170**
- **What is the scope of materials covered by this STANAG, e.g. for cast-cured inert binder PBXs only, pressed, etc**
- **Is only an update of STANAG 4581 required?**
- **Can/should sentencing criteria be suggested/included**
- **Is the STANAG to be designed to help find the critical ageing mechanisms of the PBX (e.g. a decision tree) or is this assumed prior to application?**



# NAVSEA 8020.C

- **Spells out mandatory requirements to qualify new energetic materials for USA usage**
- **Accelerated ageing is an essential part of the qualification process**
- **Conditions of ageing;**
  - **60°C, 1, 2, 4, 6, 8 months, sealed containers**
  - **70°C: 1, 2, 4, 6 months, sealed containers**
  - **25°C, 30% RH - until final (type qualification)**

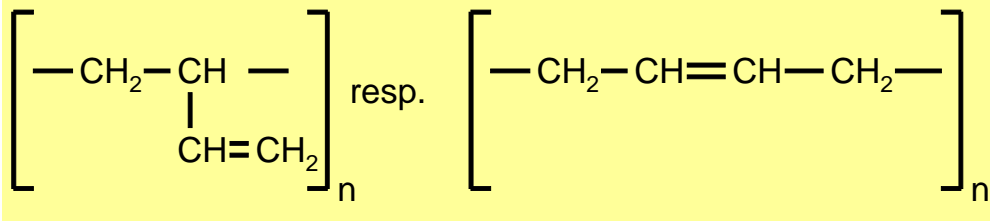
***Compositions based on polyester binders are aged under controlled 30% RH***

# NAVSEA 8020.C

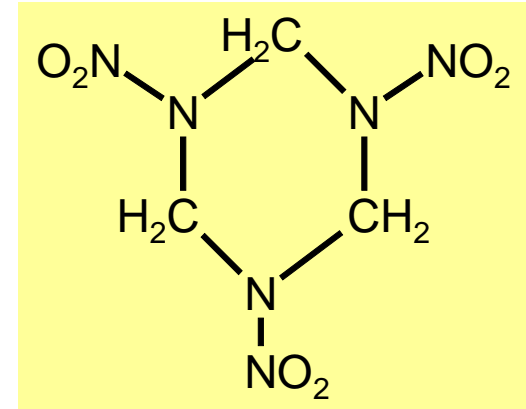
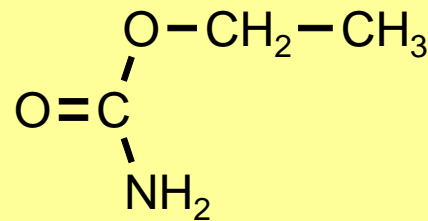
Requirements to meet qualification include:

- **No substantial change in:**
  - **Ignition temperature (DTA)**
  - **Impact sensitivity**
  - **Friction sensitivity**
  - **Shock sensitivity**
  - **Stabiliser/antioxidant level (% change)**
- **>20% change in mechanical properties may require further tests**
- **Safe(shelf) life at 25°C – minimum 20% stabiliser remaining at 20 years**
- **Safe use(service) life - <20% change in post-cure properties, no substantial change in shock sensitivity, no fissures after 30 days at 60°C in x-ray fissure test**

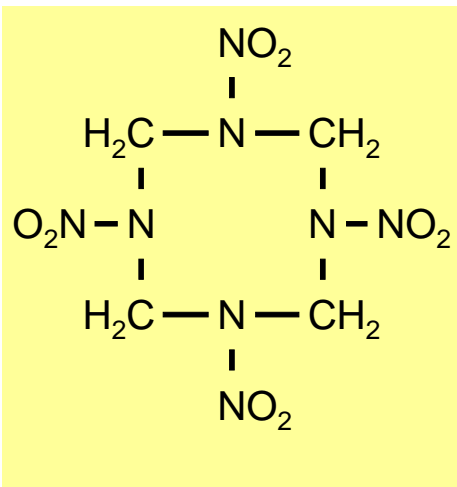
# PBX – energetic materials /// binders



HTPB

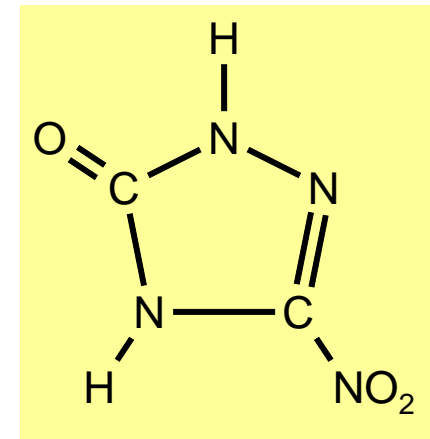


RDX



HMX

Poly-Urethane



NTO

# CAST PBX

- **80 – 90 % solid load**
- **10 – 20 % binder**
- **Binders : HTPB , GAP, PolyNimmo, PolyGlyn, HTPE (future ?)**
- **Energetic Material**
  - **RDX, HMX, RS-RDX, AP, Al, AN, TATB, NTO, DOA, DOS, IPD, TMETN, BDNPA/F, TEGDN**
  - **FOX-7, CL-20, AND, GAP-azide**

# What is leading to IM properties vs Ageing ?

- **Mechanical properties**
- **Friability**
- **Sensitivity**
- **Burning / detonation process**
- **One or two (or even more) IM compositions in a article**
- **Influence of humidity on one component or all**
- **Taking into account all stabilizers ?**

# First line of test methods

- **Molecular weight (diffusion processes / hardening) [GPC]**
- **Detonation velocity**
- **Porosity (ultrasound sufficient enough ?)**
- **Flyer impact**
- **Focusing on energetic part or binder ?**
- **What is maximum ageing temperature**
- **Ignitability – separate or ignition train**

# STANAG 4581 - Contents

- **Accelerated ageing conditions**
  - Bulk block sample
  - “Sealed” condition
  - Only one temperature – 60°C, 3/6 months
- **How to prepare test samples from aged ‘bulk’ material**
- **Chemical analysis methods**
  - Sol content
  - Cross link density
  - HPLC analysis of antioxidant content
  - GC analysis of plasticiser content
- **Mechanical tests**
  - Uniaxial tensile test (STANAG 4506)
  - Dynamic Mechanical analysis (DMA) (STANAG 4540)
  - Shore Hardness (ASTM D2240-00)
- **Refers to many other STANAGS for actual testing methods**

# Tests methods

## Possible new methods in STANAG 4666 edition 1

- **Tests for filler-binder interface**
- **Dilatometry (pressure)**
- **Microscopy (SEM, optical, FTIR imaging)**
- **TMA (expansion)**
- **Friability (critical dp/dt, critical velocity, number of repeats/velocities.....)**
- **Small scale sensitivity tests – one company uses ESD as key screening method**
- **Hardness techniques – shore hardness, DMA, others?**
- **Shock sensitivity**



# Proposed test methods in draft STANAG 4666

## CHEMICAL TESTS

- **1A** Measurement of the soluble fraction
- **1B** Measurement of crosslink density
- **1C** Measurement of antioxidant content (HPLC)
- **1D** Measurement of plasticizer content

## MECHANICAL TESTS

- **2A** Uniaxial tensile test
- **2B** Dynamic mechanical analysis
- **2C** Measurement of Shore A hardness
- **2D** Thermal Mechanical Analyses

# Cont'd

## THERMAL TESTS

- **3A**                      **Differential Scanning Calorimetry**
- **3B**                      **Thermogravimetry**
- **3C**                      **Pressure Vacuum Stability Test**
- **3D**                      **Heat Flow Calorimetry (HFC)**

## OTHER TESTS

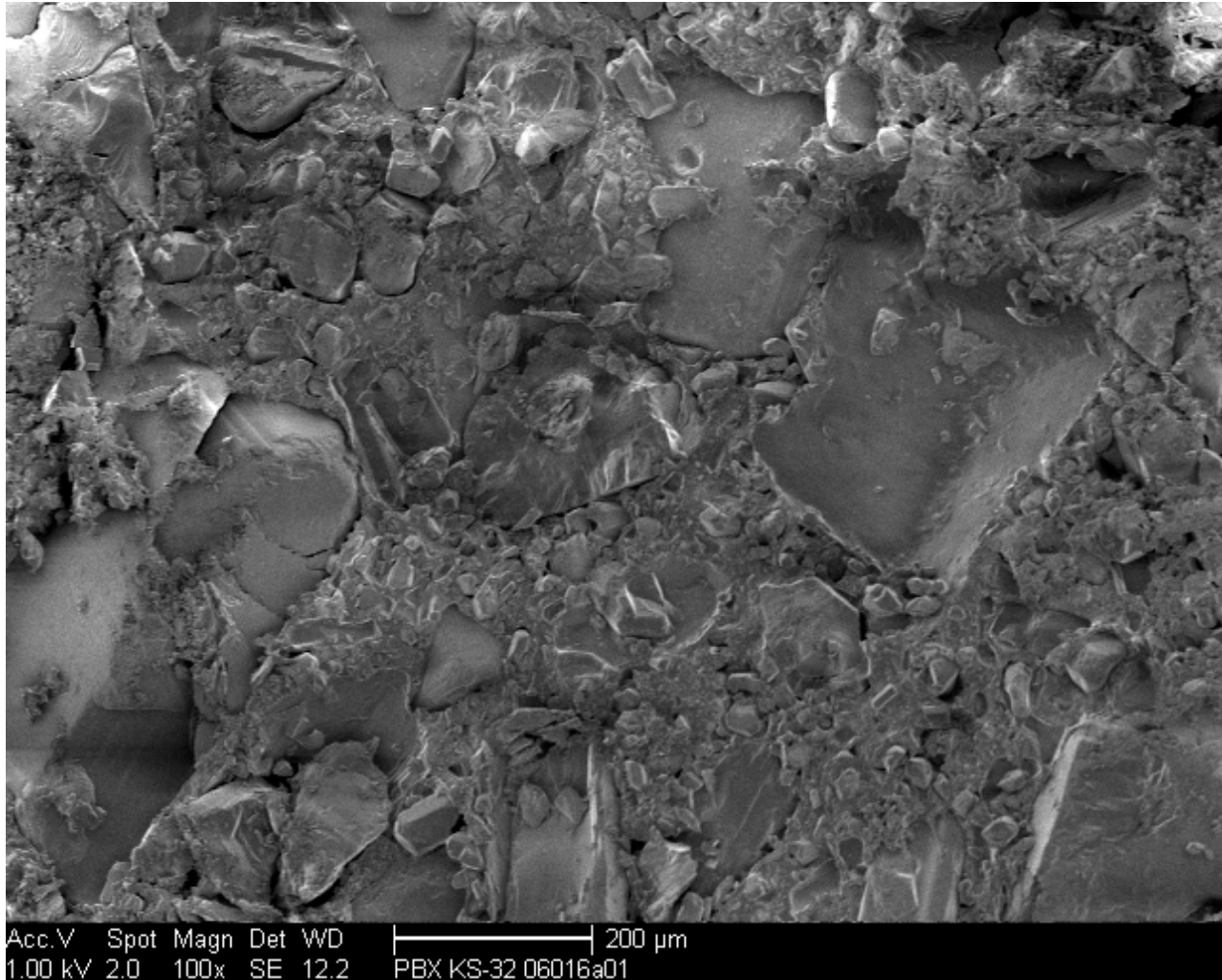
- **4A**                      **Scanning Electron Microscopy**
- **4B**                      **Shock Sensitivity**
- **4C**                      **Friability Test**
- **4D**                      **FTIR spectroscopy**

# Examples for new techniques

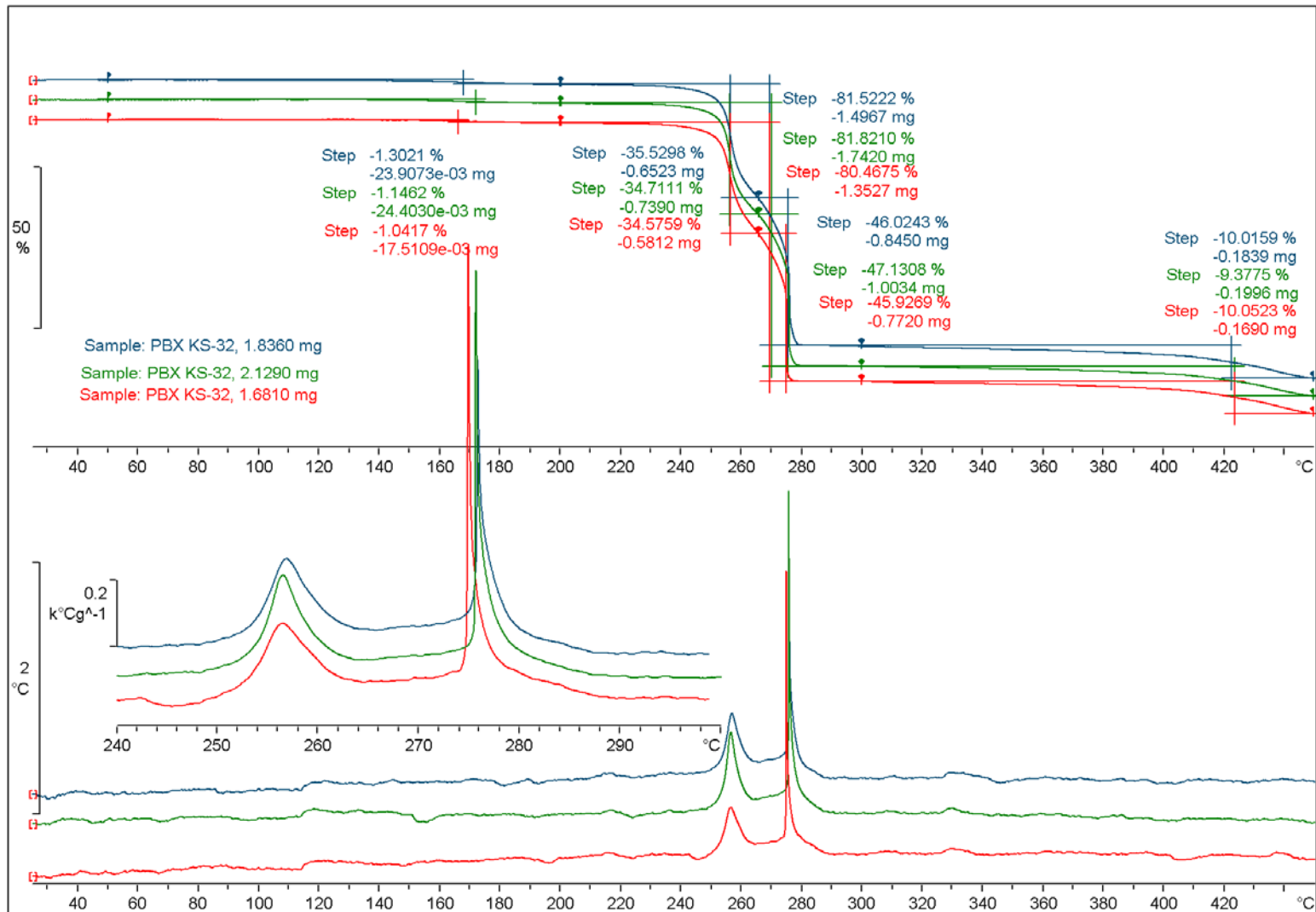
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# SEM

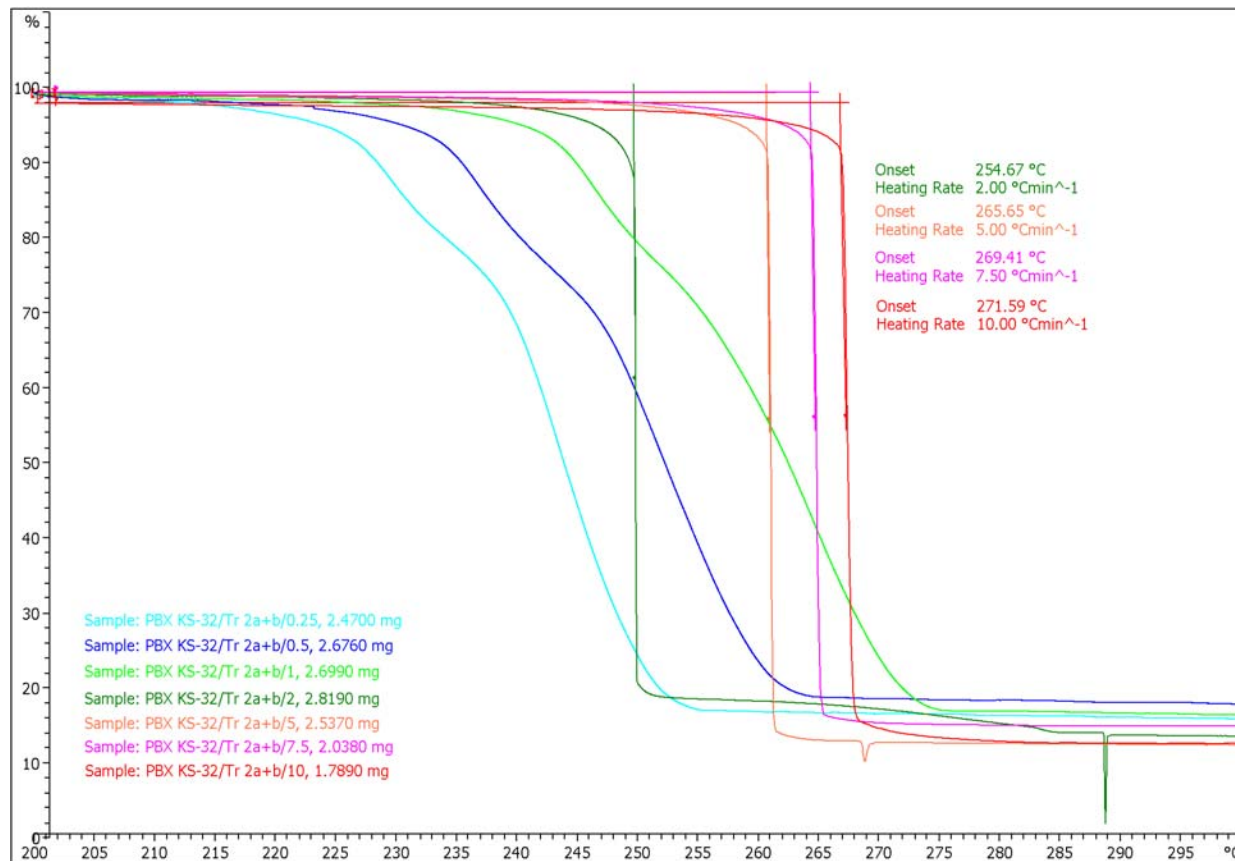


# Thermal analysis (TG-SDTA)

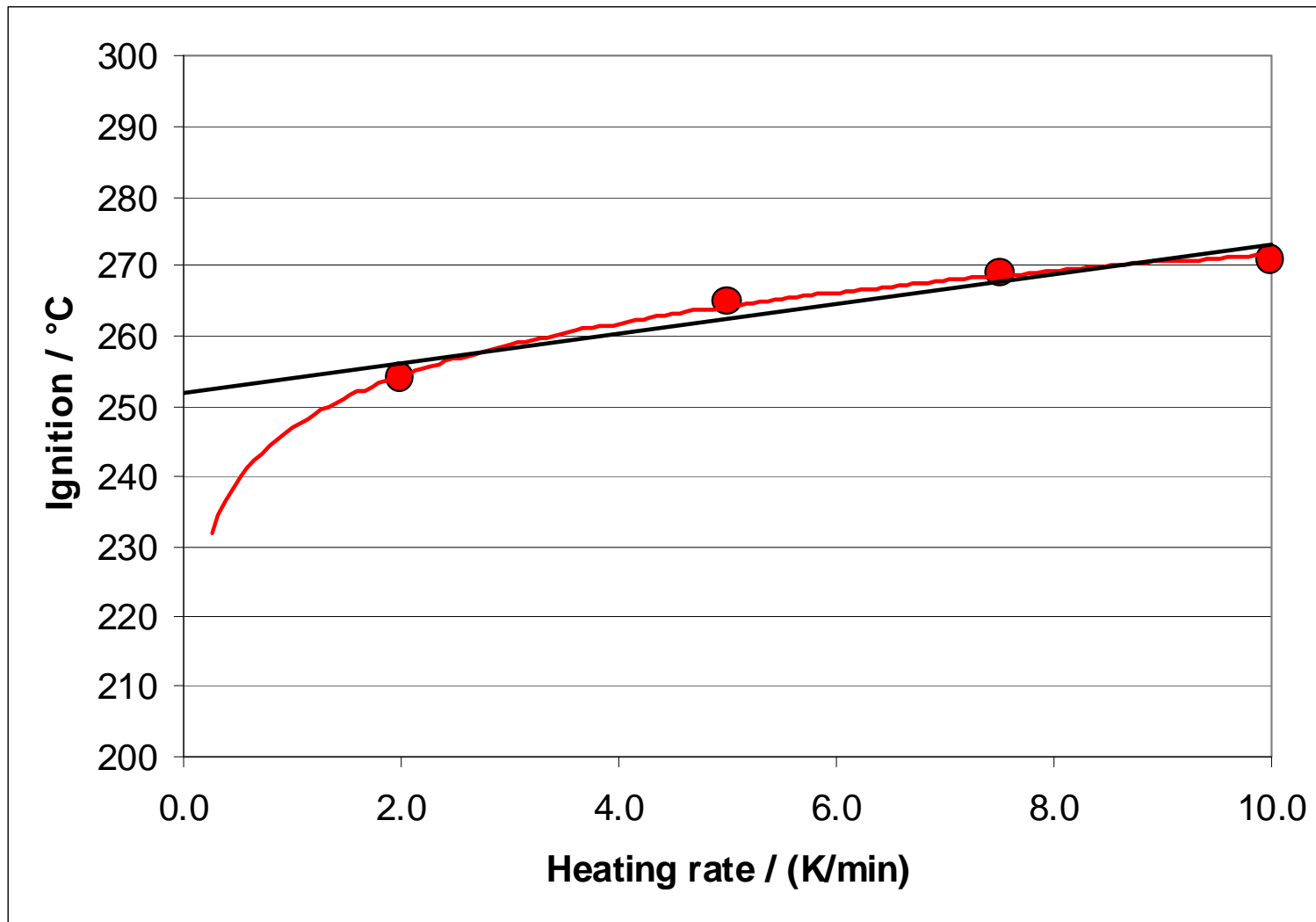


# Kinetics

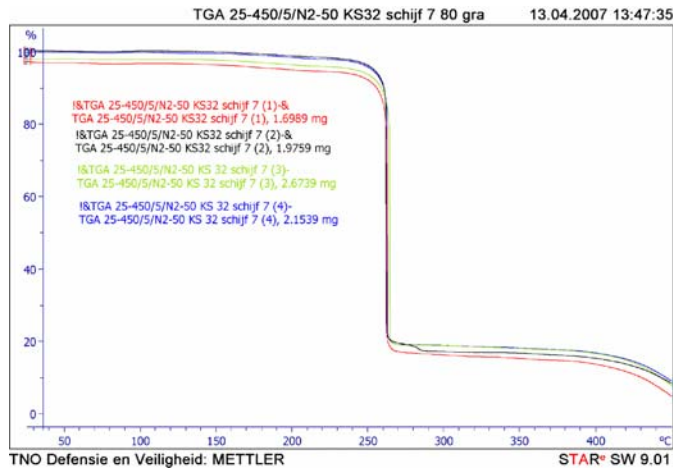
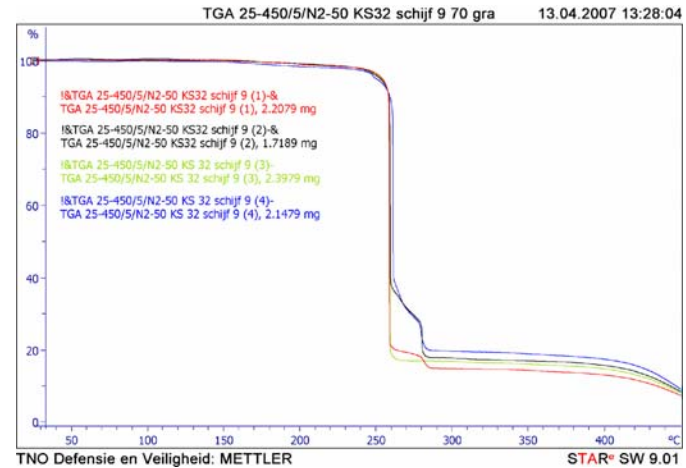
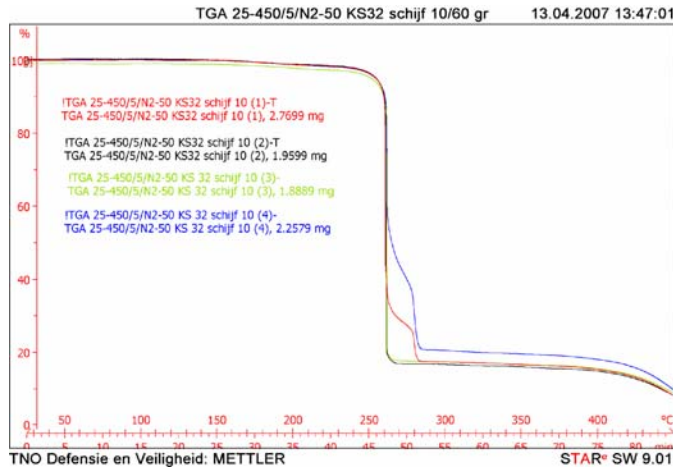
- The applied heating rates are: 0.25 K/min; 0.5 K/min; 1 K/min; 2 K/min; 5 K/min; 7.5 K/min; en 10 K/min



# Ignition temperature



# Aged at 60 / 70 / 80 C



**Decomposition profile is changing as function of ageing temperature**



# Discussion / Conclusion

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# Discussion / conclusion

- **Proposed test methods has to be evaluated**
- **Additional tests are advisable to be performed on different compositions by participating countries**
- **First edition of STANAG will be set-up and forwarded to the SG-1 members**

# Acknowledgement

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- Co-authors:
  - TNO Richard Bouma (member of AC-326-SG-1)
- Custodiangroup, AC326-SG-1 on life assessment
- Audience for listening

# Center of Expertise for Lifetime Studies

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