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Exploring the HMX-based PBXs with the TATB Shock Sensitivity

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Characterization of the LS-PBXs conducted in terms of the WEAG Research Program ERG-114.009 "Particles Processing and Characterization"

Prof. Pedro Simoes & Eng. Vitor Redondo, Dept. Chem. Engineering: help in characterization of particles' density, PSD

Prof. Amilcar Romalho, Dept. Mech. Engineering of University of Coimbra: SEM particles' morphology.

Objective & Technical Concept

- **Major challenge:** ➔ to find a way for improving insensitivity characteristics of the HMX-based PBX ingredients --coarse-grained HMX particles, and “dirty binder”,
- ➔ and then to apply LS-ingredients for elaboration of the HMX-based PBXs with the shock sensitivity comparable to TATB [1], while keeping or even improving a detonation performance in comparison with the reference HMX-based PBXs

- ➔ Exploring novel, physically justified concept for designing the high performance LS-PBXs and RS-PBXs containing the HMX-filler in total amount 77 and 82 wt. %

➔Variety technological aspects on fabrication of the LS-HMX components are analyzed in a concept of novel morphological properties of β-HMX particles:

 ➔β-HMX seed has a maximum packed molecular structure: ρ_0 = 1.95 – 1.96 g/cm³ (ICT, TNO, Un. Coimbra: ρ_0 = 1.951 g/cm³; W.H. Rinkenbach (1951) ρ_0 = 1.96 g/cm³)

 ➔Outer layer represent a continuum the cluster-type substructures spaced by dislocation pits, cracks and fissures. The surface layer has the average density = 1.86 cm³.

➔ Eliminating the nano-porous (defective and sensitive) layer provides a way for decreasing shock reactivity & initiation sensitivity ➔ Idea for Chemical etching & Light-reflective coating of HMX grains

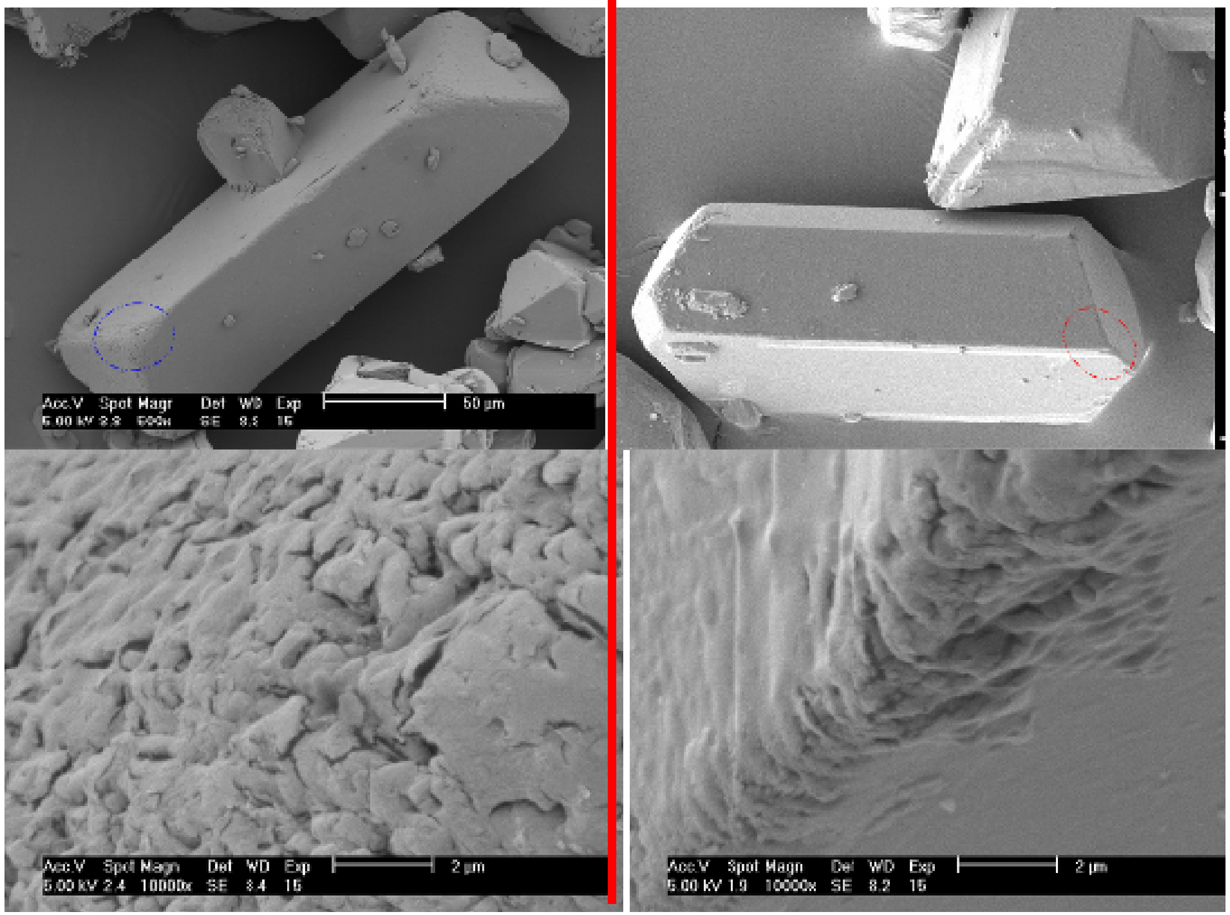
β-HMX Coarse Particles applied for PBX fabrication: Morphology & Density

Particles P01: "Ref. HMX(114µm)"
Ref. HMX Class-1 military grade (Dyno Nobel)
Mono-modal (PSD):
d_{50} =114,408 µm
ρ_0 = 1.881±0.006 g/cm³

Particles P03: "RC-HMX(130.9µm)"
fabricated (Fraunhofer ICT) through re-crystallization of the P01-material in the propylene-carbonate solution [5]
Mono-modal PSD:
d_{50} =130,925 µm
ρ_0 = 1.892±0.006 g/cm³

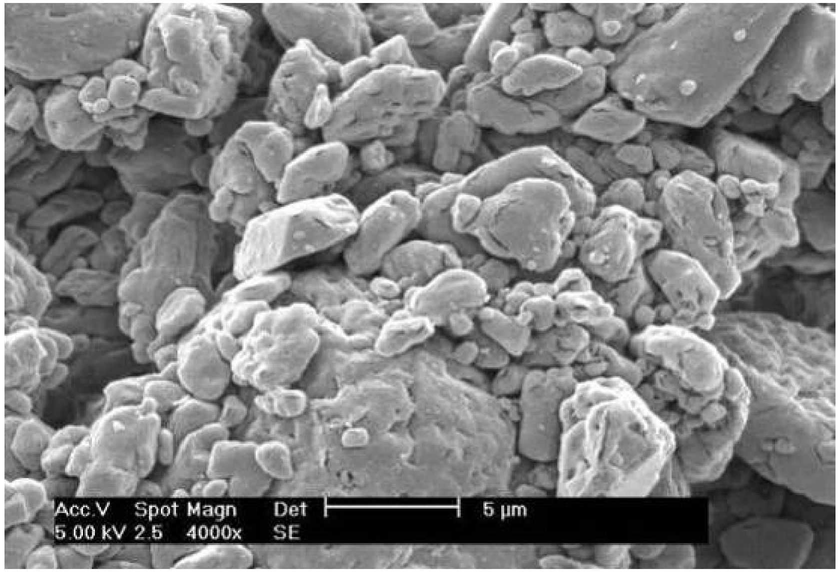
Density measured with application of standard helium and liquid pycnometry.

"Ref. HMX(114 µm)" | "RC-HMX(130.9 µm)"



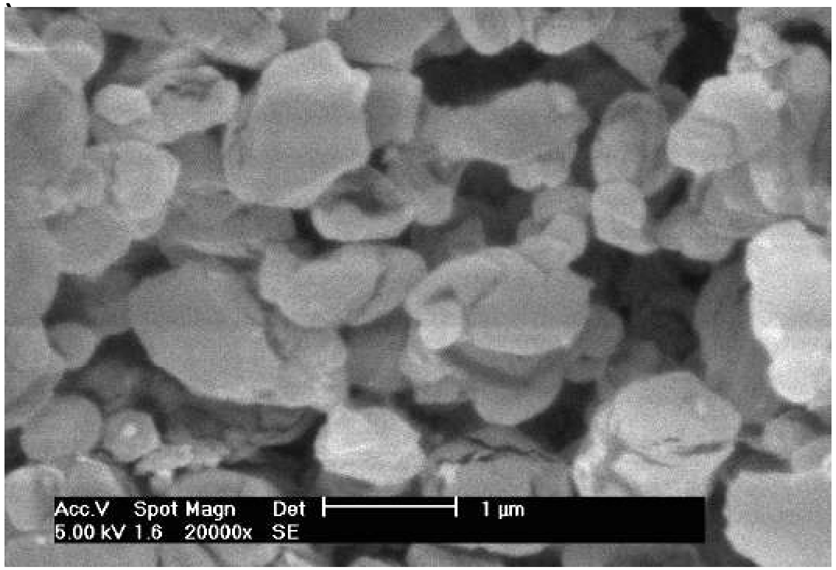
Outer layer represent a continuum the cluster-type substructures spaced by dislocation pits, cracks and fissures. Clusters are max. concentrated in vertexes & edges.
Surface layer: the average density = 1.86 cm³

β-HMX Fine & UF-Particles applied for PBX fabrication: Morphology and Density



Particles P04: "F-HMX (11.1 µm)"
obtained at Fraunhofer ICT with application of the "Rotor-Stator Milling" technology [6], particles P01 used as a row material
Mono-modal PSD: d_{50} = 11.06 µm
ρ_0 = 1.874±0.008 g/cm³

UF-particles P05: "UF-HMX (1.6)" obtained by comminuting the water slurry of P04-grains on "Annular Gap Ball-Mill" technology (Fraunhofer ICT [6])
Mono-modal PSD: d_{50} =1.64 µm
ρ_0 = 1.933±0.005 g/cm³
"UF-HMX (0.6)": ρ_0 = 1.951±0.005 g/cm³

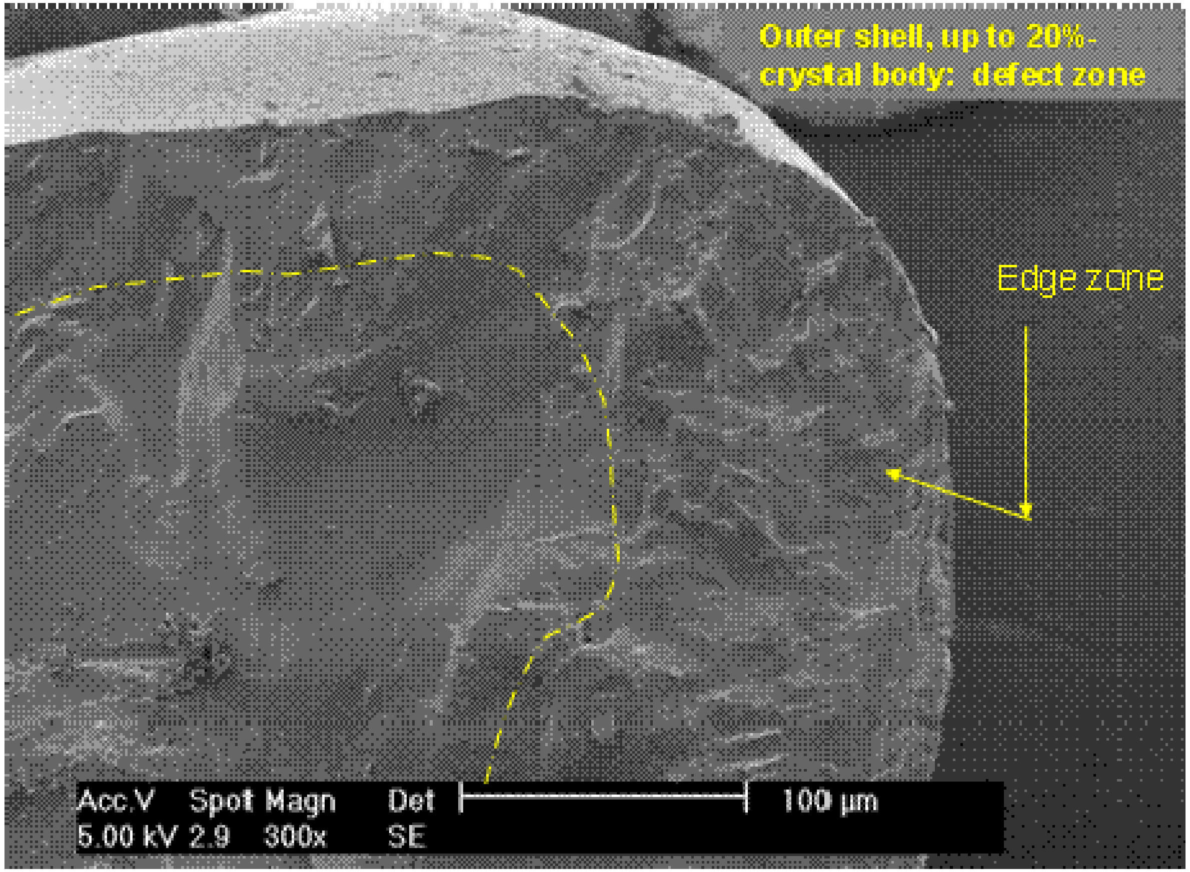


1) surface clusters ≈ P05 particles "UF-HMX (0.6 µm)"
2) P05-particles are almost free of substructures
3) P05-particles have a maximal density 1.951 g/cm³

➔ ➔ Particles P05 represent themselves clusters separated from the crystal's body at milling

β-HMX Coarse Particles applied for PBX fabrication: Morphology & Density

β-HMX (507.5 μm, ρ_0 =1.893±0.012 g/cm³) crystal was splitted in median zone of the *(0-1-0)*-facet



➔Thickness of the outer cluster-shell, in which the surface-defects are concentrated, attains ≈20% of crystal's cross-section, or occupies roughly ≈ 64% of its volume

➔The defects-less "seed" has 1.95 g/cm³-density and occupies ≈ 36% of crystal's volume

➔mean density of the surface defect zone can be roughly estimated by value ≈1.86 g/cm³

Relative volume of submicron-porosity $\upsilon_{\mu por}$ of particles determined with respect to the voids-free UF-HMX(0.6 μm)-particles: $\upsilon_{\mu por}$ = 100 %×(1-ρ_0/1.951).

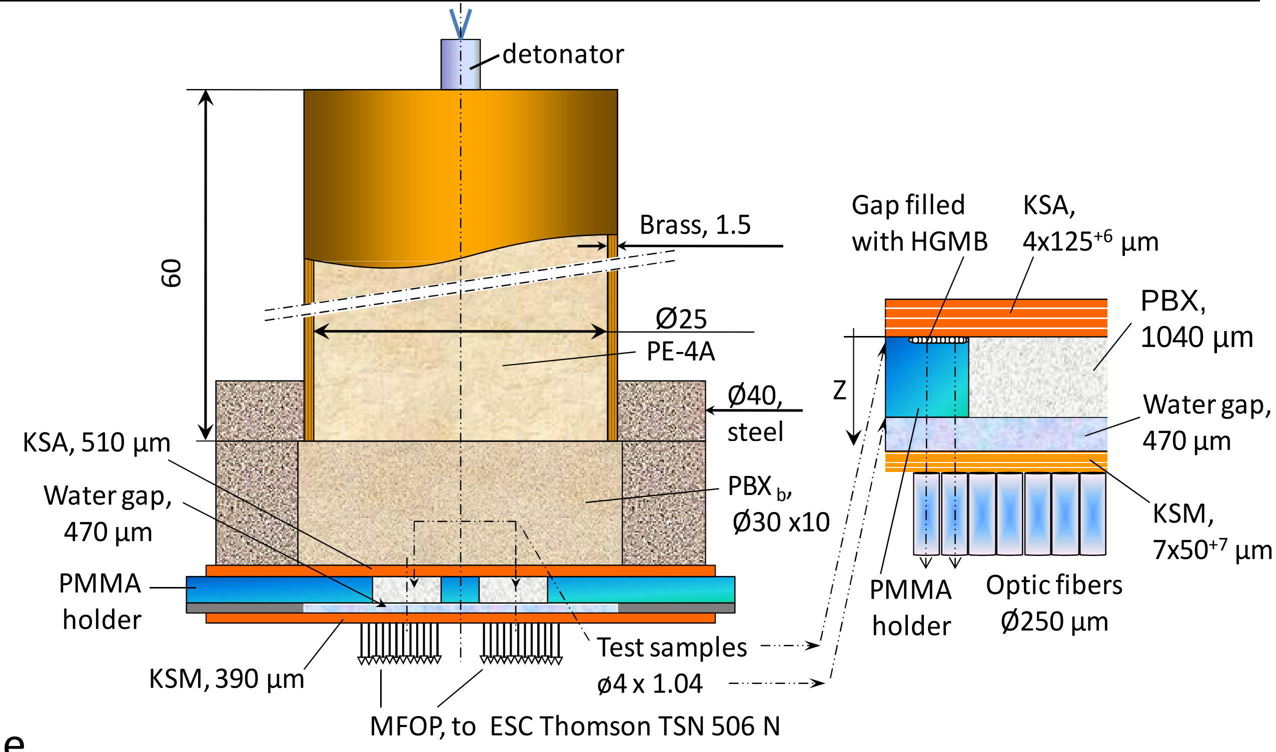
"Ref. HMX(114 μm)"	"RC-HMX(130.9 μm)"	" F-HMX (11.1 μm)"	"UF-HMX (1.6 μm)"
P01: $\upsilon_{\mu por}$ ≡ 1	P03: $\upsilon_{\mu por}$ =0.6	P04: $\upsilon_{\mu por}$ =1.7	P05: $\upsilon_{\mu por}$ =0.4

Shock Reactivity vs. Morphology and Density: *Kinetics Rate/Reaction Radiance Test*

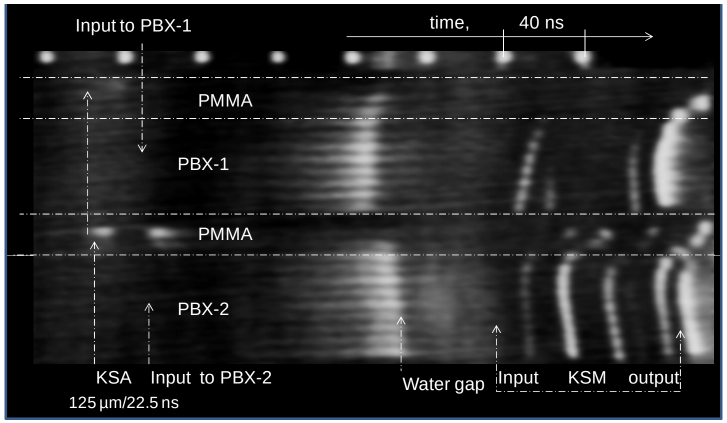
➔ HMX particles P01, P03, P04 and P05 bonded with epoxy binder in HMX/Epoxy 90/10 mass-ratio.

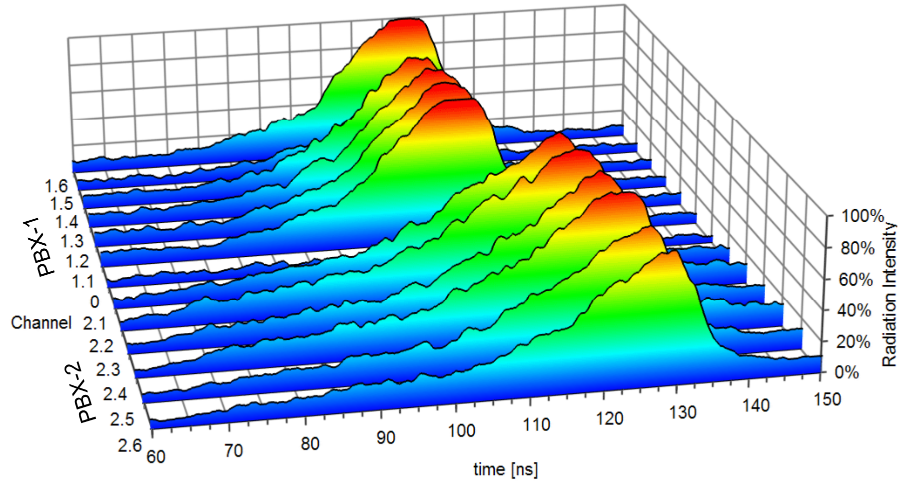
➔ Voids-free PBX-charges of 99%TMD & Ǿ4x1.04mm–size fabricated with use of slurry mixing, low pressure pressing, vacuum casting, & pressure curing in PMMA holder.

➔ Residual micro-voids were eliminated via filling interstitial space between particles with the gelatinized water under 10^{-3}mm Hg-vacuum.



Calibrated booster ➔ P_0 = 18.7 GPa in HMX particles

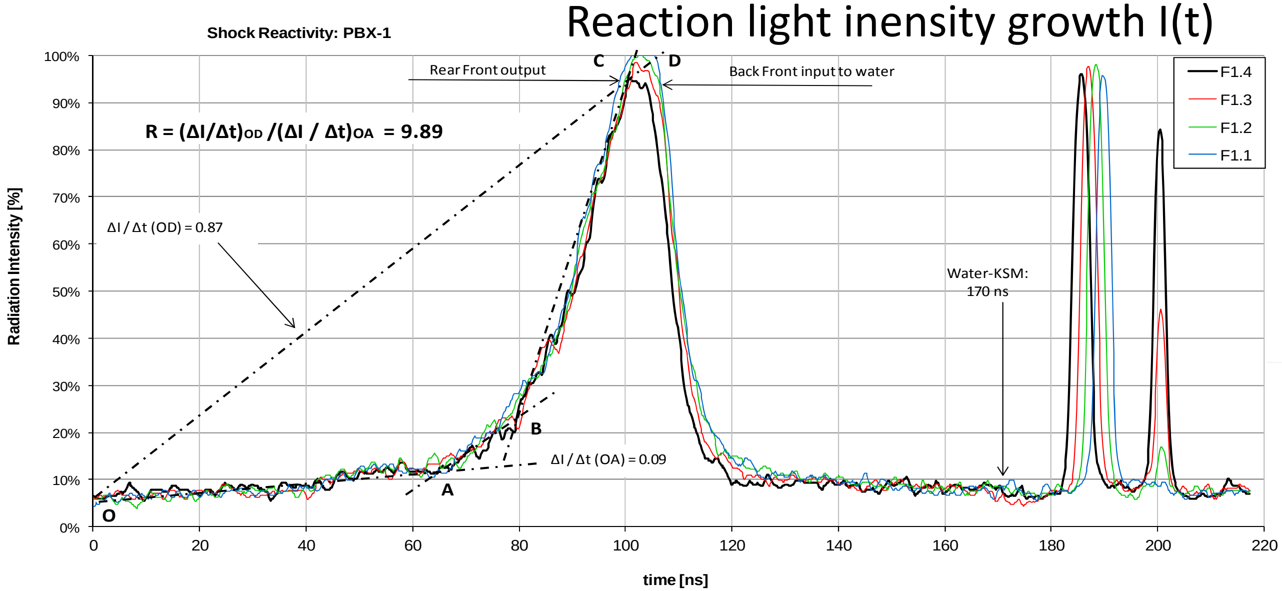




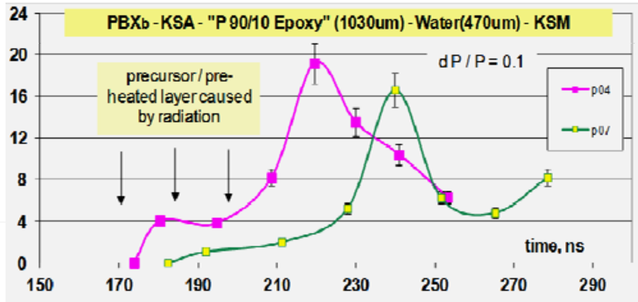
Kinetics Rate/Reaction Radiance Test

➔<u>Kinetics</u> and <u>dynamic</u> parameters of the reaction growth are recorded simultaneously:
1- reaction light transferred through the PBX-acceptor,
2 – spatially-resolved scenario of shock field formation in the optical monitor after the output from the reacted sample.

Reaction light inensity growth I(t)



Stress-field in optic monitor **P**(t)



<u>Absolute shock reactivity value **R** at **P**$_0$-initiation pressure</u>: determined for each i-acceptor as a ratio between mean rate of full radiation growth and the initial rate of the reaction light growth:
R = $[(I_{final} - I_{initial})/(t_{final} - t_{initial})]_{mean}/(\Delta I_0/\Delta t_0)_{mean}$.

<u>***Relative Shock Sensitivity***: **S = R(PBX$_i$)/R(PBX$_{ref}$)$_{Ref}$**</u> **vs.** <u>**nano-porosity of HMX particles**</u>

"Ref. HMX(114 μm)"	"RC-HMX(130.9 μm)"	" F-HMX (11.1 μm)"	"UF-HMX (1.6 μm)"
P01: $\upsilon_{\mu por}$ ≡ 3.6% S ≡ 1	P03: $\upsilon_{\mu por}$ = 3.0% S = 0.6	P04: $\upsilon_{\mu por}$ = 3.9% S = 1.7	P05: $\upsilon_{\mu por}$ = 0.9% S = 0.4

Low-Sensitive HMX-based PBXs: Shock Sensitivity determined in the Wedge Test

Wedge Test of four PBX comp. “HMX 82/18 wt.% HTPB”: F01, F02, F03 & F04; 0.97-0.99 TMD

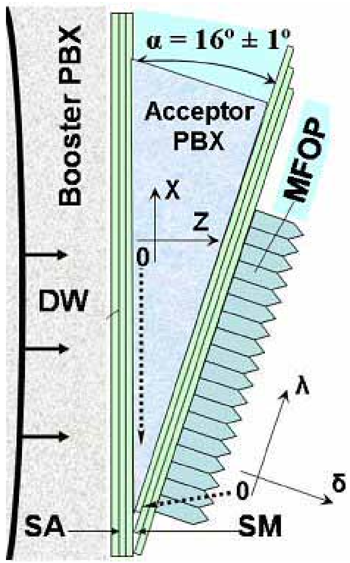
F01 = reference PBX, prototype of the PBXC-121
F01: 01/P04/HTPB 65.6/16.4/18 wt.%

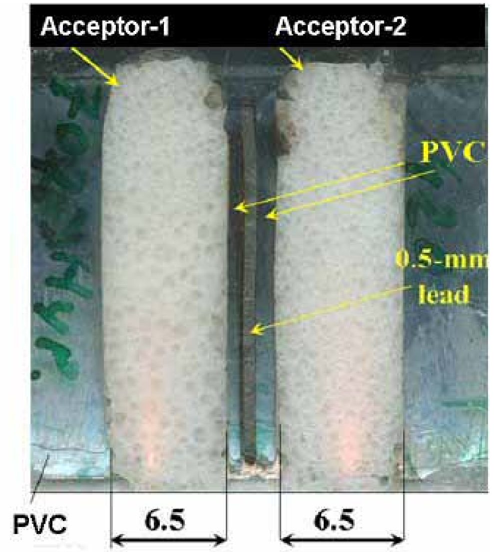
F02: P03/P04/HTPB 65.6/16.4/18 wt.%
“LS2--PBXC*-121”

F03: P01/P05/HTPB 65.6/16.4/18 wt.%
“LS1--PBXC*-121”

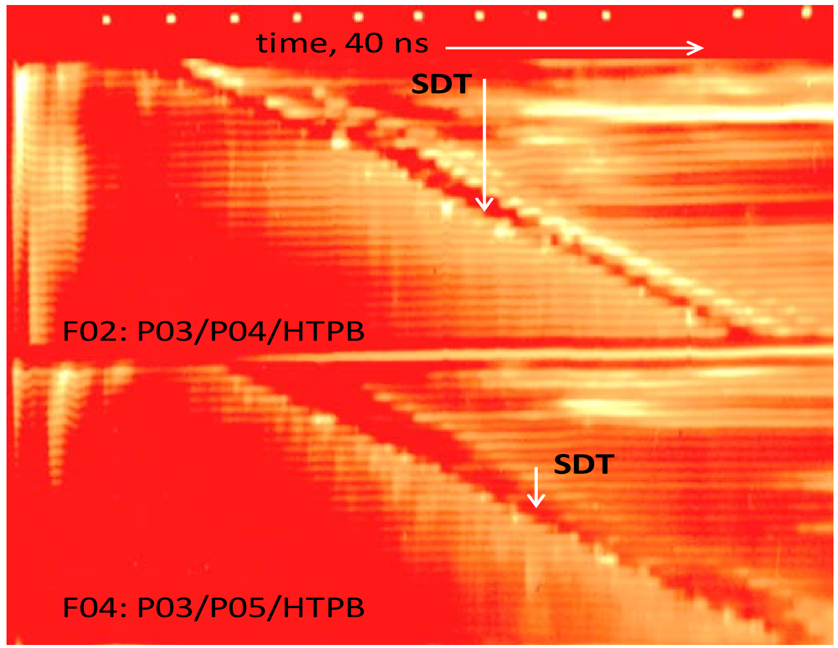
F04: P03/P05/HTPB 65.6/16.4/18 wt.%
“RS--PBXC*-121”

SDT-parameters t* and Z* were obtained with the accuracy better than 10 ns and 50 µm.

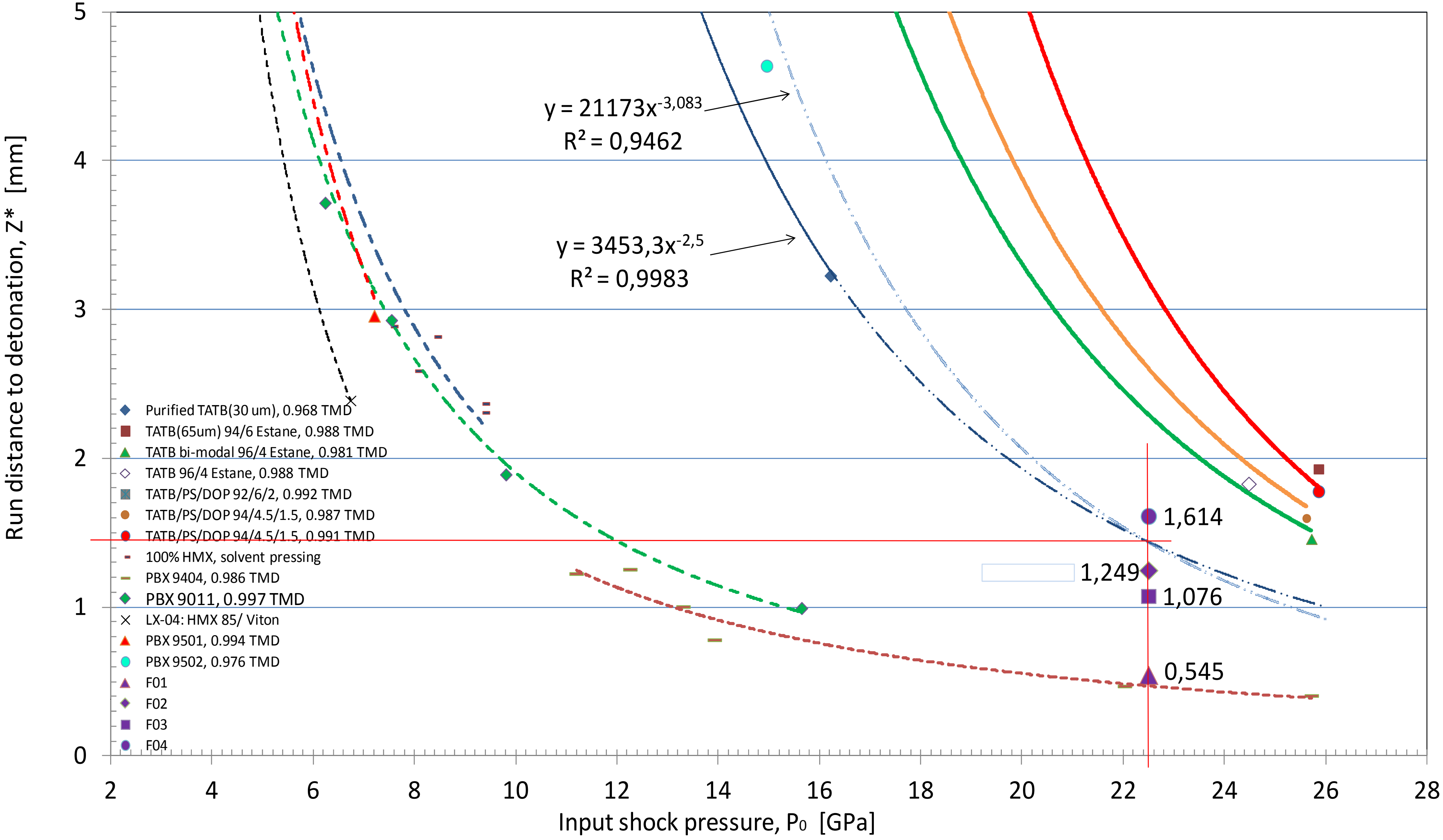




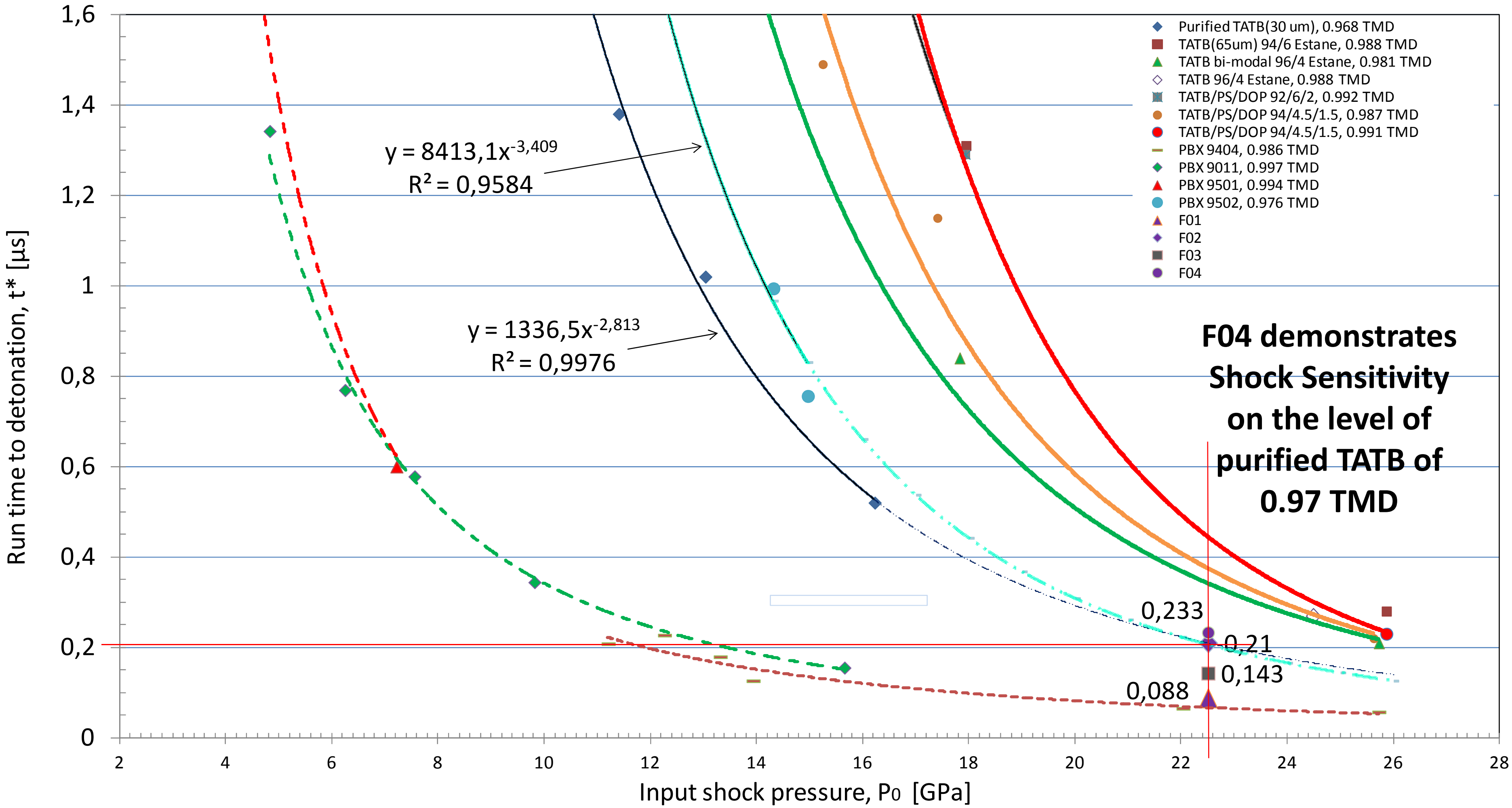
Calibrated booster ➔ P_0 = 18.7 GPa in HMX particles



Low-Sensitive HMX-based PBXs: Shock Sensitivity determined via the Wedge Test,   Z*



Low-Sensitive HMX-based PBXs: Shock Sensitivity determined via the Wedge Test, t*



1- ***F01 vs. F03***: substitution of “F-HMX(11.1 µm)” (P04) for the “UF-HMX(1.6 µm)” (P05) ➔ increase of t* and Z* in 1.6 and 2 times respectively;

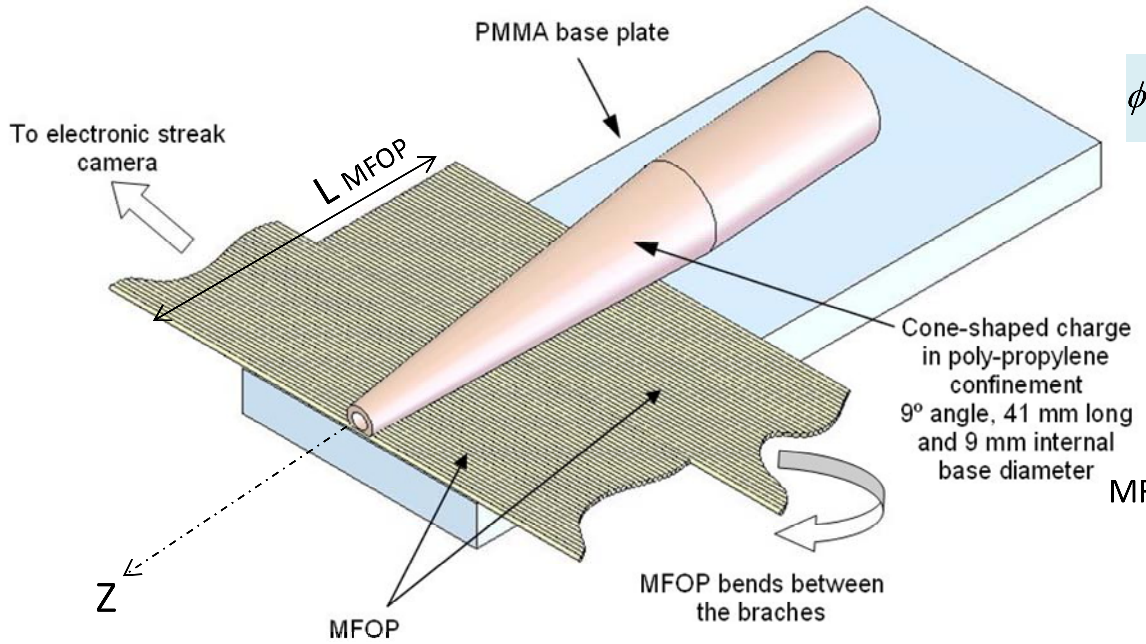
2 – ***F01 vs. F02***: changing the ingredient “Ref. HMX (114 µm)” (P01) to “RC-HMX (130.9 µm)” (P03) ➔ increase of both t* and Z* in 2.3 times;

3 – ***F01 vs. F04***: replacing both constituents “Ref. HMX (114 µm)” and “F-HMX (11.1 µm)” by “RC-HMX (130.9 µm)” and “UF-HMX(1.6 µm)” offers increasing t* and Z* in 2.6 and 2.9 times respectively.

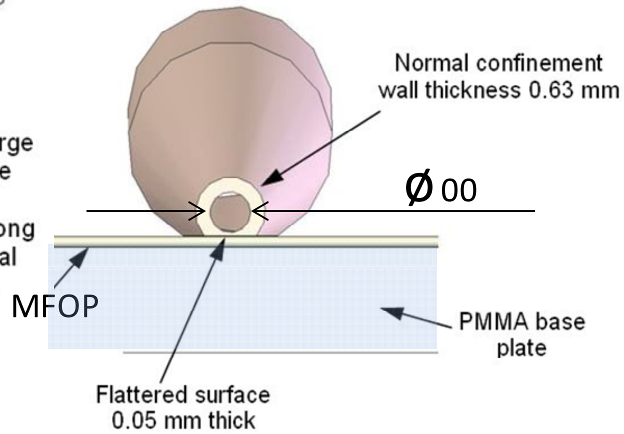
Shock Sensitivity of PBXs F01-F04 determined via the Detonation Failure Cone Test

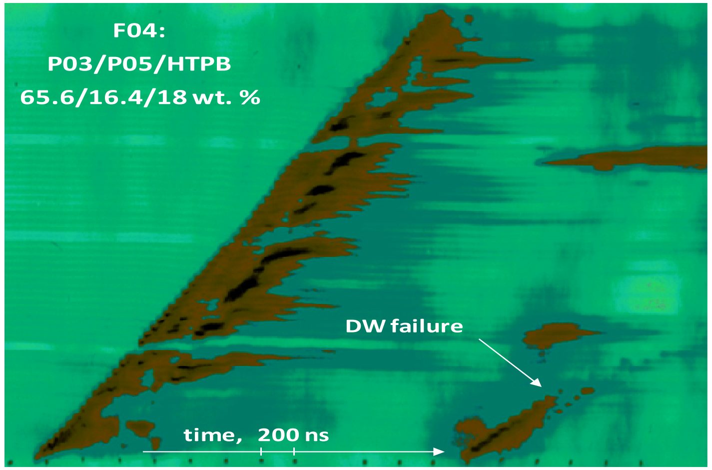
Detonation Failure Diameter is a measure of Shock Sensitivity of crystalline HE [Dremin, 1997]

Detonation Failure Cone Test instrumented with multi-fiber probe *MFOP* and electronic streak camera Thomson TSN 506 N



$$\phi(z) \approx \phi_{00} + 2.(L_{MFOP} - z).tg\left(\frac{\alpha}{2}\right) \quad (1)$$

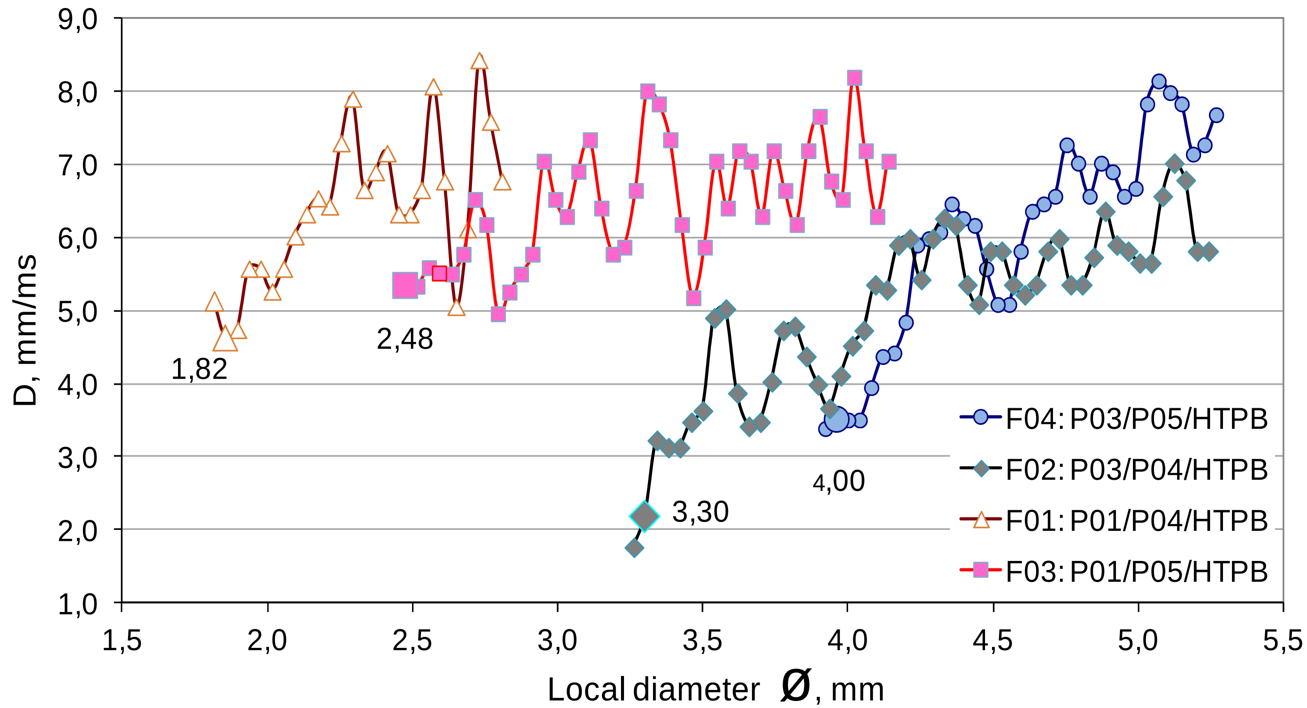




➔ Local speed of detonation front is obtained from the run time through the space between two adjacent fibers: $D_i = 250\ \mu m / \Delta t_i$. Measurements of D_i-values were conducted with the 6% accuracy.

➔ Detonation Failure Diameter df was determined with the accuracy better than ±0.04 mm.

Shock Sensitivity of PBXs F01-F04 determined via the Detonation Failure Cone Test



Detonation failure diameters, d_f (measured with the accuracy better than ±0.04 mm)

PBX	F01	F02	F03	F04	PBX-9404 [1]	Purified TATB [1], 100 wt. %	PBX-9502 [1]
d_f, mm	1.82	3.30	2.48	4.00	1.18 ±0.2	4.0mm (ρ_0= 1,860 g/cm³)	< (8 – 10) (0.97 TMD)

The RS-PBX F04 "P03/P05/HTPB 65.6/16.4/18 wt.%" is possessing the Detonation Failure diameter on the level of the purified TATB explosive material of 0.97 TMD

Detonation Reaction Zone (DRZ) Test of long PBX charges

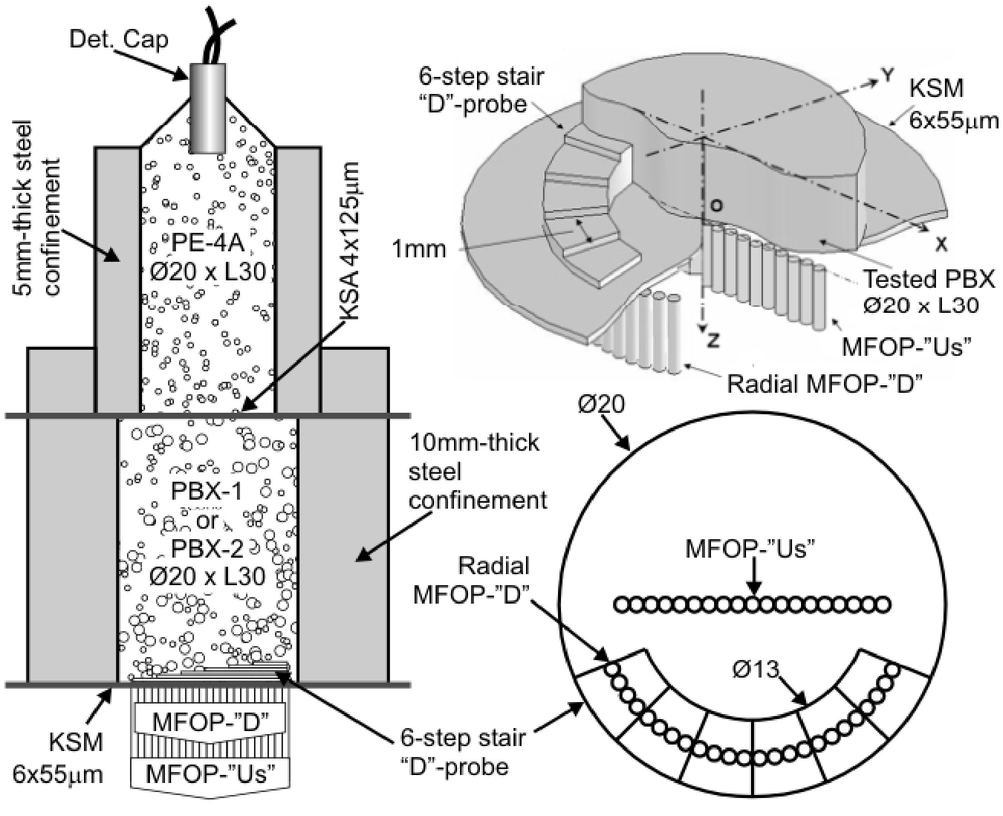
The DRZ-Test is instrumented with the MFOP-probes (connected to the electronic streak camera Thomson TSN 506 N), Kapton stacked optic monitor (KSM), and calibrated booster PE-4A.

➔ The test PBX-materials were soft (non-cured) formulations:

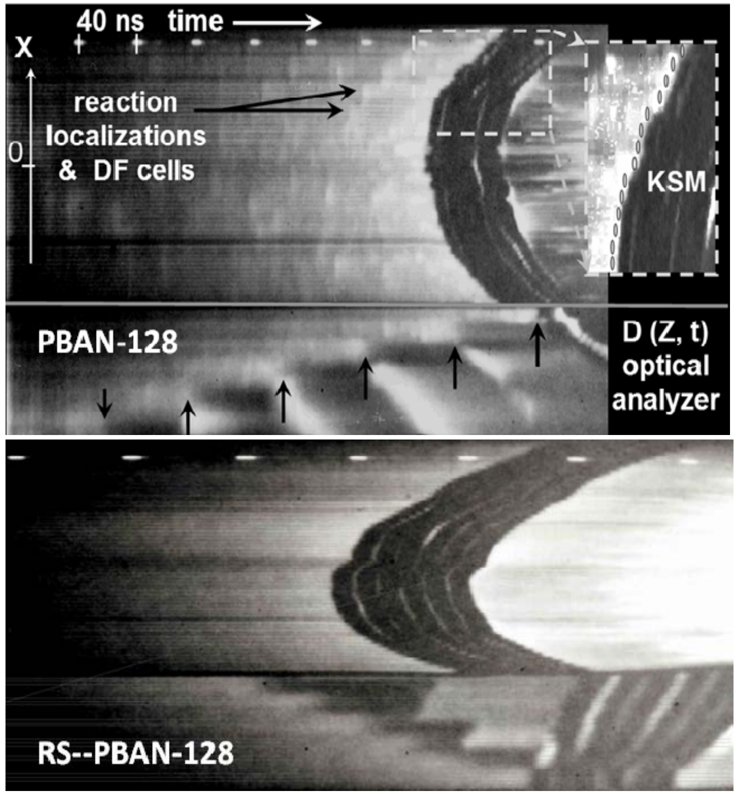
1 - PBAN-128 “$HMX_{Class\text{-}2}$77/23 HTPB”, 1.452 g/cm^3 (0.954 TMD) &

2 - RS—PBAN-128 “P03/P05/HTPB 60.8/15.2/24” 1.459 g/cm^3 (0.971 TMD).

The $HMX_{Class\text{-}2}$ particles have a density 1.917 g/cm^3 and a bi-modal PSD, with the mass-median size of coarse fraction $d_{50\ “C”}$ = 56.0 µm.



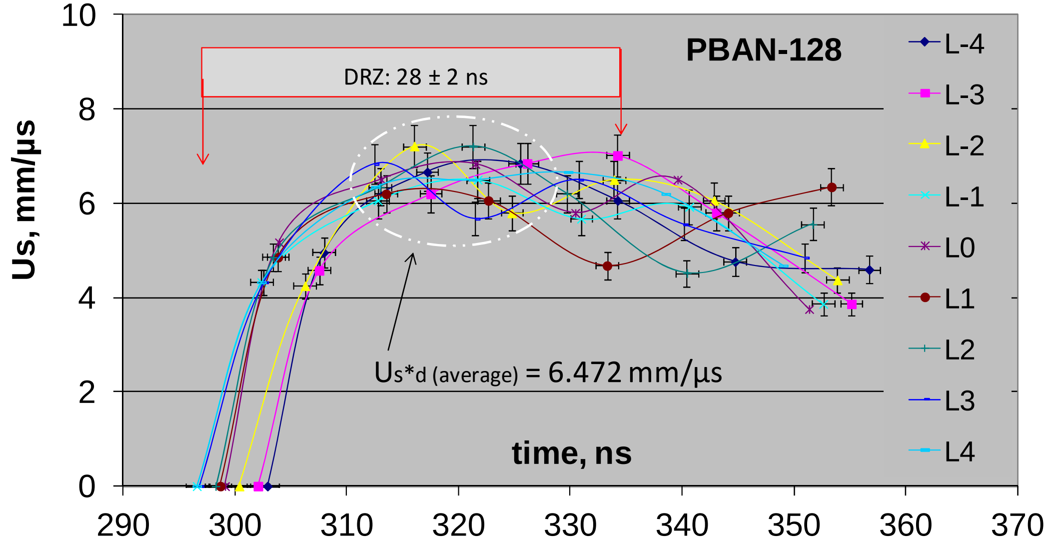
Local values Us_i in optic monitor were measured with the 6%-accuracy

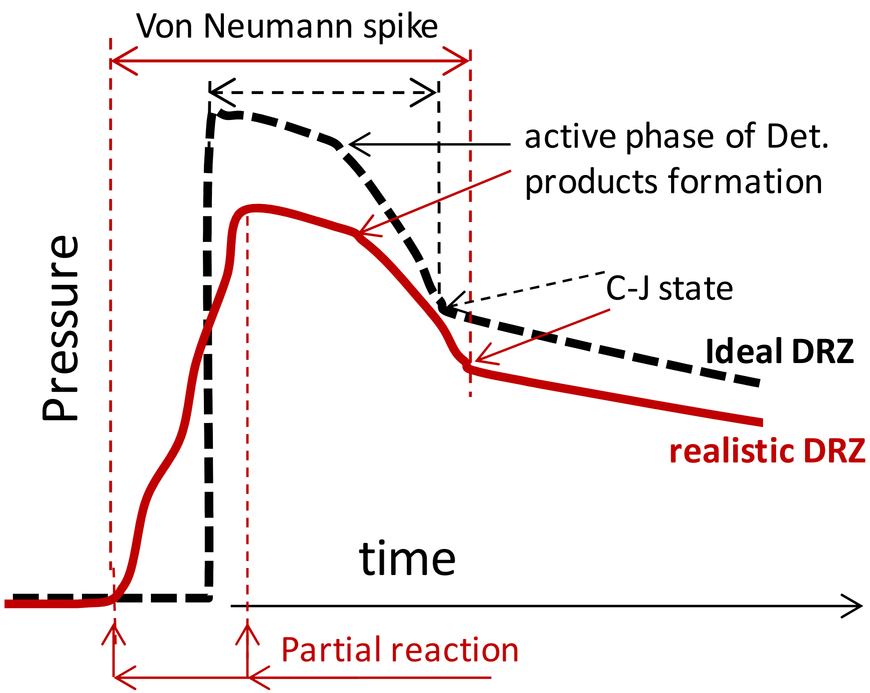


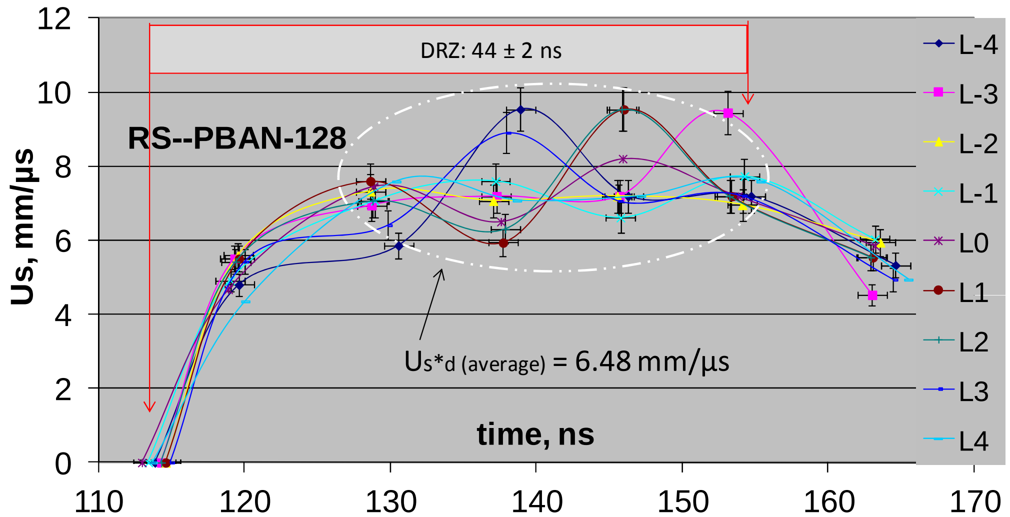
Spatially-resolved histories Us (t) of the DRZ-driven shock field in the KSM-optical monitor: 9-channel Probing in central area 0.25x2.25 mm of shock front surface in the KSM.

➔Us(t)-profiles describe a meso-scale structure of the DRZ, namely the initial region of the Von Neumann (VN) spike and beginning of its fall.

➔Steady drop in the Us(t)-histories indicates the onset of the active phase of detonation products formation, and this instant is applied as a measure of the DRZ-duration, t_{DRZ} & DRZ-width $Z_{DRZ} \approx D \bullet t_{DRZ}$







DRZ Performance : PBAN-128 vs. RS—PBAN-128

➔Detonation pressure: $\mathbf{P_d = ½ P_d{}^*{}_{KSM} \bullet ((\rho_0 \bullet D)_{PBX} + (\rho_0 \bullet Us^*{}_d)_{KSM})/(\rho_0 \bullet Us^*{}_d)_{KSM}}$ (Goranson formula [1 & 10])

Us^*_d is the maximum speed in the VN-region of the Us(t)-history (averaged value),

$P_d{}^*{}_{KSM}(Us^*_d)$ is a corresponding pressure of the shock front in the KSM

Parameters of the DRZ-structure in the PBAN-128 and RS—PBAN-128

PBX	TMD	ρ_0, g/cm^3	$\rho_{0/TMD}$	D, mm/µs	Us*d KSM mm/µs	Pd* KSM, GPa	Pd, GPa	t DRZ, µs	Z DRZ, µm	Z DRZ/d 50 C
PBAN-128 HMX 77/23 HTPB	1.522	1.452	0.954	8.177	6.472	28.23	32.81	28	228	4.1
RS-PBAN-128 P03/P05/HTPB 60.8/15.2/24	1.503	1.459	0.971	8.200	6,480	28.34	32.67	44	361	3.4

➔RS—PBAN-128 is identical in detonation performance (D & Pd) to Ref. PBAN-128.

➔Basic difference implies that the width of the DRZ is in 1.6 times greater than in PBAN-128.

➔ Nevertheless, for both PBXs, a width of the VN spike-zone is estimated by 3-4 rows of d_{50}-size-particles of coarse constituent.

Conclusive Remarks

➔ We've presented a new physically-justified approach to link between the morphology of particles' surface structure and shock reactivity

➔PBX-formulations composed with the re-crystallized particles P03 and a micron-size particles P05 (such as RS--PBXC-121 "P03/P05/HTPB 65.6/16.4/18" and RS—PBAN-128 "P03/P05/HTPB 60.8/15.2/24") are possessing the insensitivity on the level of the TATB and simultaneously demonstrate improved detonation performance characteristics.

➔When β-HMX crystal is subjected to strong shock (~20 GPa), the intense reactions are dominated in the surface zones--vertexes and edges--with max. concentration of cluster-structures

➔In this context, results on shock reactivity of the defects-less HMX particles (KR/RR Test and Wedge Test of P03 and P05 particles-in-binder) strongly support the idea to minimize the amount of the surface micro-defects via the re-crystallization / or comminuting particles up to the 0.5-1 μm-size.

➔We also suggest that chemical etching of coarse particles up to full dissolving of the surface layer in which the crystal's defects are concentrated, will provide a further decreasing the initiation sensitivity.

➔Chemically etched particles become close to a "seed" of the original HMX crystals in size and in density (1.95 g/cm^3) and consequently will be more insensitive and more powerful in energetic density.

➔Depositing the micro- and nano-layers of the LS-energetic lubrificants will sufficiently decrease a role of shear-driven plastic deformation in reaction initiation scenario of HMX grains, improving shock insensitivity