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Decreasing a Shock Sensitivity of the HMX-based PBXs through the Morphology Modification of the HMX-Constituents

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2013 INSENSITIVE MUNITIONS AND ENERGETIC MATERIALS TECHNOLOGY SYMPOSIUM
Coronado Bay CA
October 7th-10th, 2013

ACKNOWLEDGEMENTS

Work was supported by Office of Naval Research and ONR Global under the ONR Grants N 00014-08-1-0096, 0014-12-1-0477 and ONR-G 62909-12-1-7131 with Drs. Clifford Bedford and Shawn Thorne as a Program Directors.

Research efforts were supported in part by the European Defense Agency & Portuguese MoD under the RSEM-Project Arrangement No B-0993-GEM2-GP (2012).

Experimental efforts on characterization of the RS-PBXs were conducted as a part of the WEAG Research Program ERG-114.009 "Particles Processing and Characterization".

Prof. Pedro Simoes (Dept. Chemical Engineering) and Prof. Amilcar Romalho (Dept. Mechanical Engineering of University of Coimbra) are cordially acknowledged for help in characterization of particles' density, PSD, and particles' morphology.

Objective & Technical Concept

- **Major challenge:**
- ➔ to find a way for improving the insensitivity characteristics of the HMX-based PBX ingredients --coarse-grained HMX particles, and "dirty binder", and then:
- ➔ to apply RS-ingredients for elaboration of the HMX-based PBXs with the shock sensitivity comparable to TATB, 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 RS-PBXs containing the HMX-filler in total amount up to 85 wt. %

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

Eliminating the nano-porous (defective and sensitive) layer of HMX-particles 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

"Ref. HMX(114µm)" particles

HMX Class-6 military grade (Dyno Nobel)

Mono-modal PSD:

d_{50} =114,408 µm

ρ_0 = 1.881±0.006 g/cm³

"RC-HMX(130.9µm)" particles

Fraunhofer ICT:

Re-crystallization of the "Ref. HMX(114µm)" in the propylene-carbonate solution

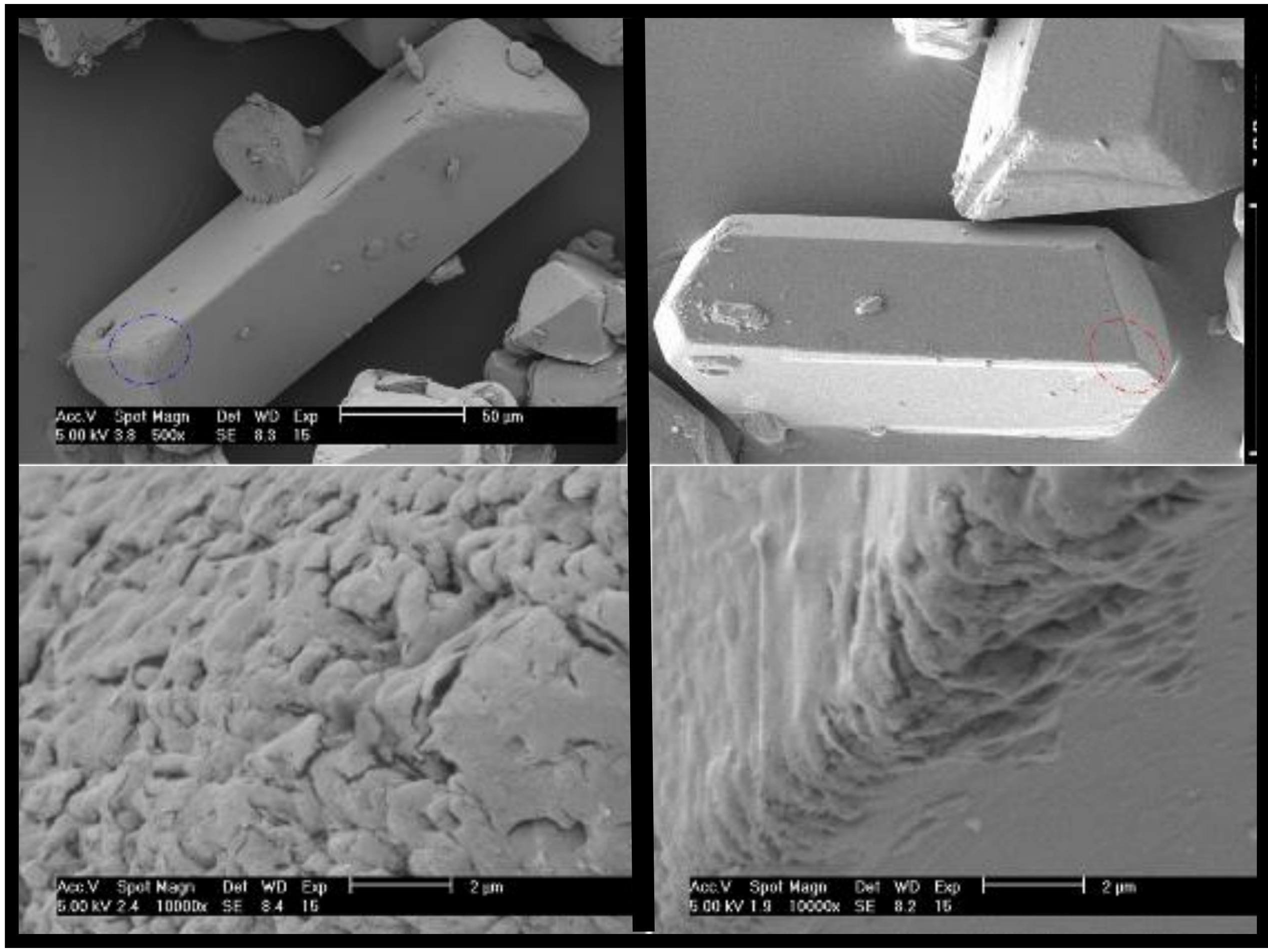
Mono-modal PSD:

d_{50} =130,925 µm

ρ_0 = 1.892±0.006 g/cm³

- **Density measurements:** **standard helium and liquid pycnometry**
- **PSD analyzers:**
- **Malvern Mastersizer 2000**

"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 g/cm³

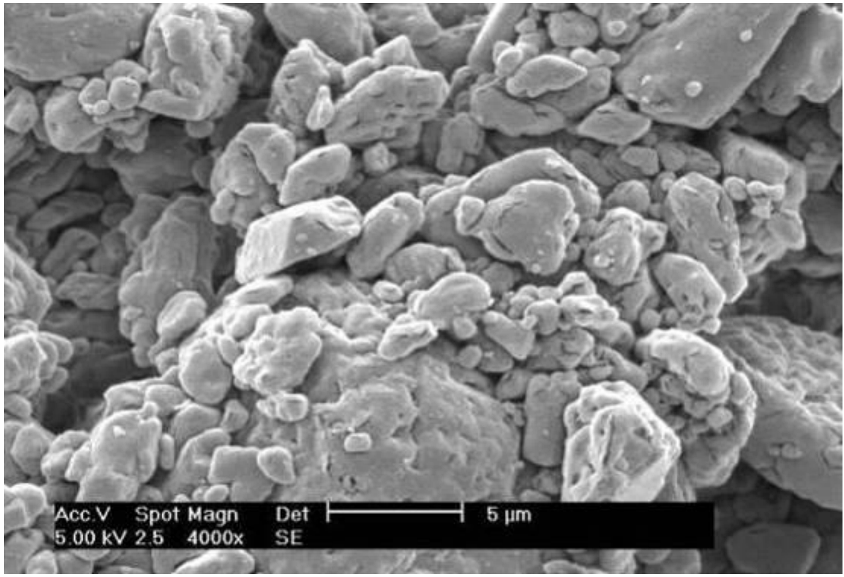
β-HMX Fine & UF-Particles applied for PBX fabrication: Morphology and Density

”F-HMX (11.1 µm)” particles

Fraunhofer ICT applied a “Rotor-Stator Milling” technology for comminuting particles “Ref. HMX (114µm)” as a row material.

Mono-modal PSD: d_{50} = 11.06 µm

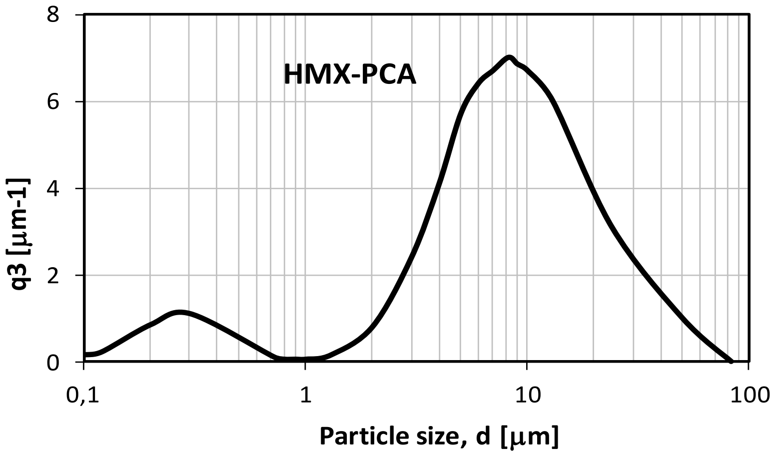
ρ_0 = 1.874±0.008 g/cm³

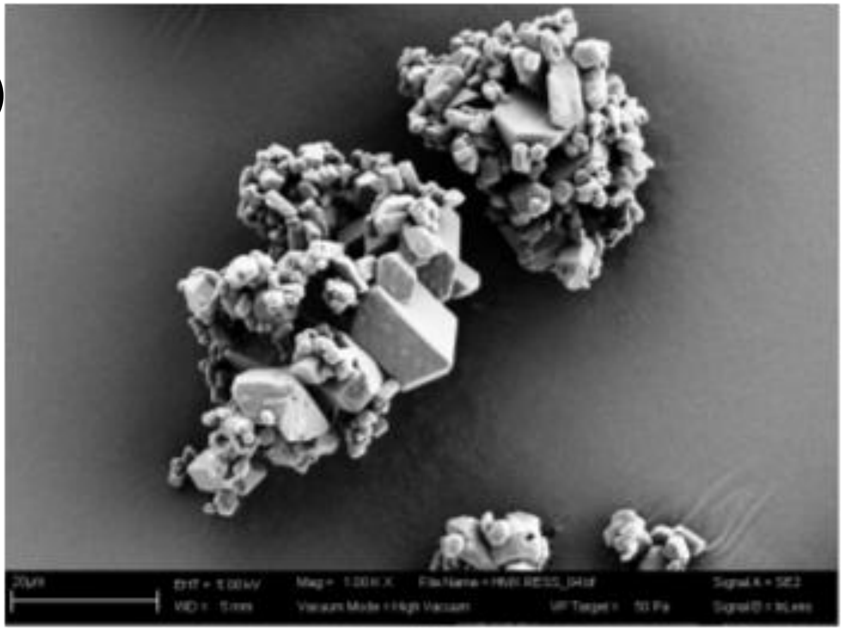


“F HMX-PCA (7.6 µm)” particles

Obtained at Fraunhofer ICT using the supercritical fluid technology for precipitation from γ-butyro-lactone solution (**Compressed Fluid Anti-solvent, PCA**)

Bi-modal PSD at median size d_{50} = 7.6 µm.





PCA-product represents agglomerations of UF-particles (d_{50} ≈ 0.3 µm) with ≈10 times larger particles

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

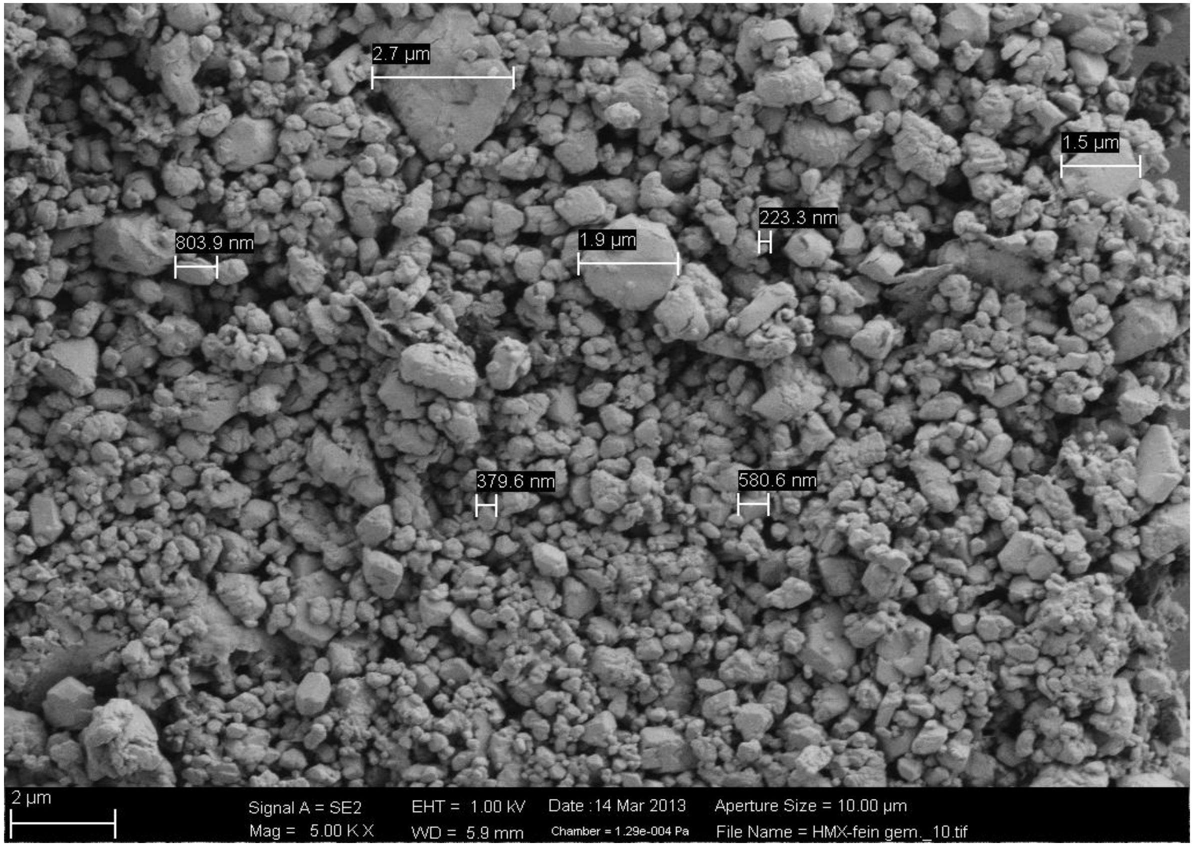
"UF-HMX (1.6 µm)"

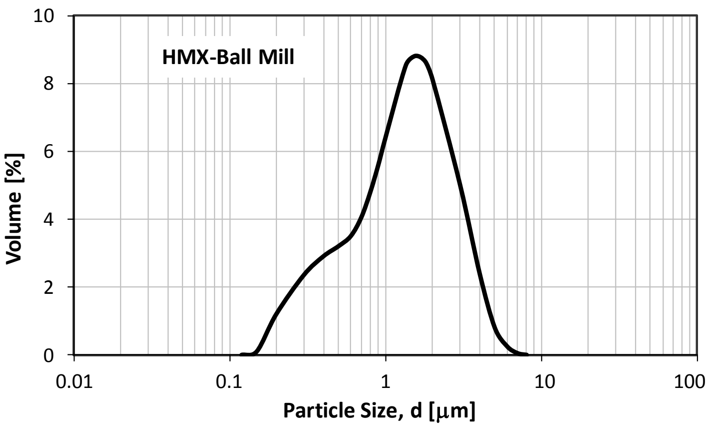
Fraunhofer ICT applied the "Annular Gap Ball-Mill" technology for further comminuting the water slurry of "F-HMX (11.1 µm)" particles.

Mono-modal PSD: d_{50} =1.64 µm

ρ_0 = 1.933±0.005 g/cm³

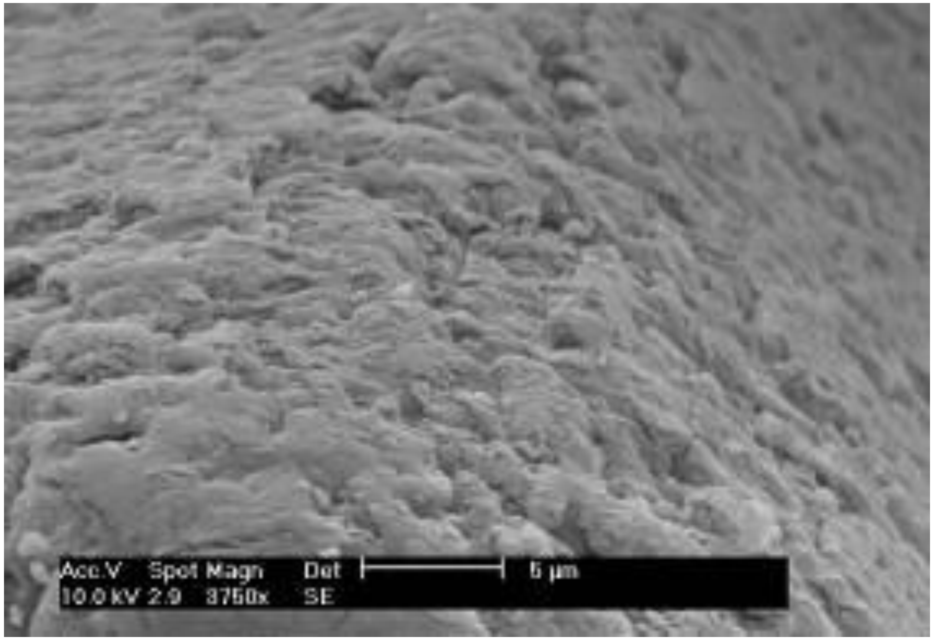
"UF-HMX (0.6 µm)": ρ_0 = 1.951±0.005 g/cm³





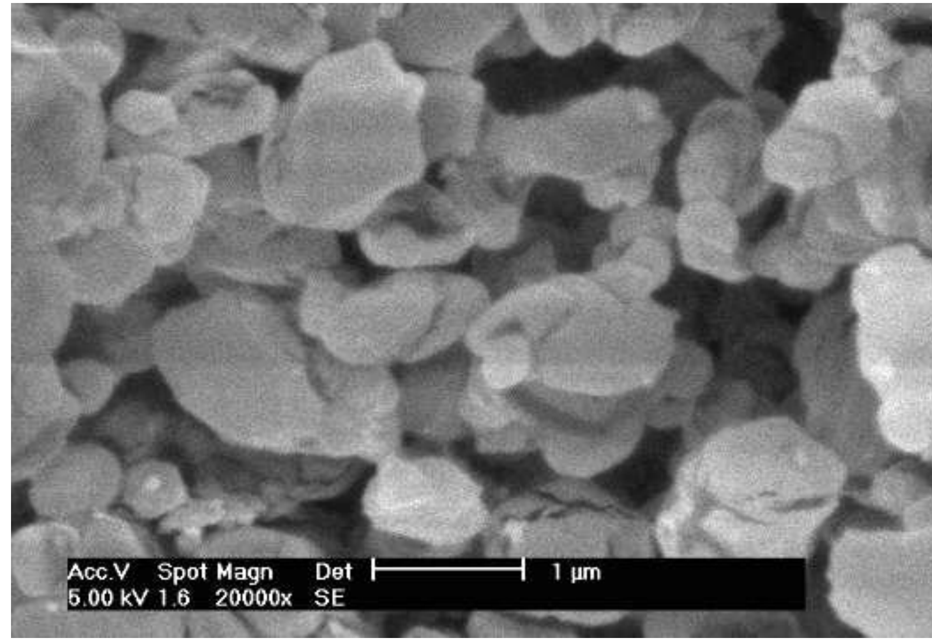
β-HMX Fine & UF-Particles applied for PBX fabrication: Morphology and Density

“β-HMX (137.5 μm)”: crystal’s surface structure



•Cluster structure of the surface layer
•0.5-1 μm-clusters are spaced by dislocation pits, cracks and fissures of 2-4 nm-size

“β-HMX UF-particle (1.6 μm)”



1) surface clusters ≈ “UF-HMX (0.6 μm)”
2) “UF-HMX (1.6 μm)” particles are almost free of substructures
3) “UF-HMX (0.6 μm)” particles have a maximal density 1.951 g/cm³

➔ “UF-HMX (0.6 μm)” particles represent themselves original clusters separated from the crystal’s body at commuting

What is a realistic max. density of β-HMX? – We've found: $\rho_0 = 1.951$ g/cm³

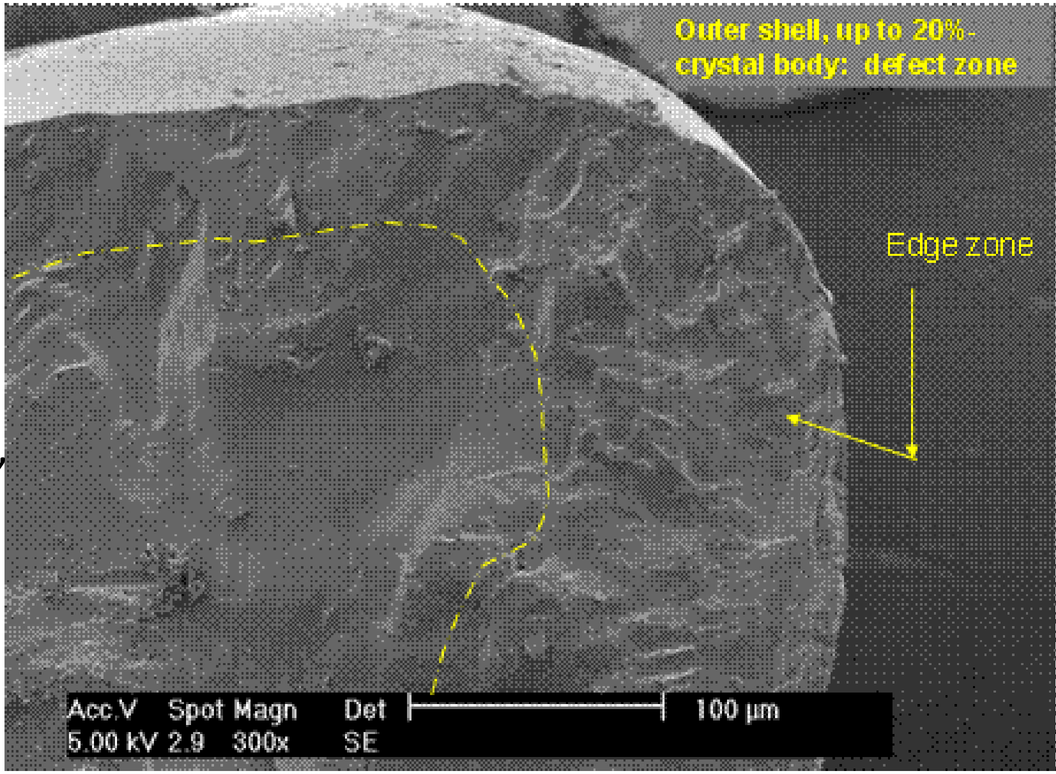
➔β-HMX seed has a maximum packed molecular structure: $\rho_0 = 1.95 – 1.96$ g/cm³ **(ICT, TNO, Un. Coimbra: $\rho_0 = 1.951$ g/cm³; W.H. Rinkenbach (1951) $\rho_0 = 1.96$ g/cm³)**

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

➔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

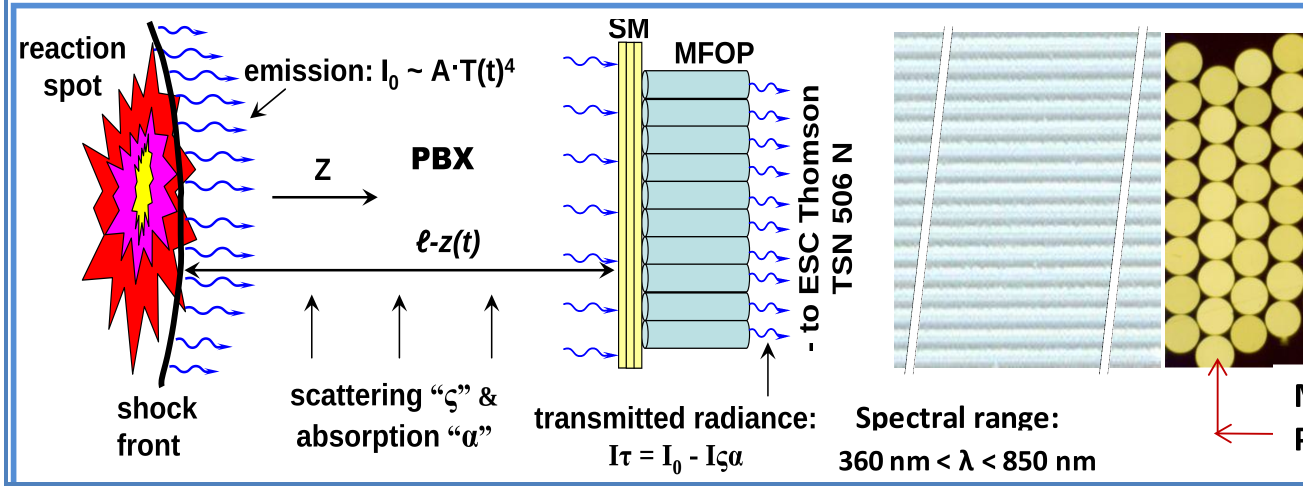
β-HMX crystal (507.5 µm, ρ0 =1.893±0.012 g/cm³) was splitted in median zone of the *(0-1-0)*-facet



Relative volume of nanoscale-porosity **υ** of particles determined with respect to the voids-free UF-HMX(0.6 µm)-particles: **$\upsilon = 100\,\% \times (1 - \rho_0/1.951)$.**

"Ref. HMX(114 µm)"	"RC-HMX(130.9 µm)"	" F-HMX (11.1 µm)"	F-HMX PCA (7.6 µm)	"UF-HMX (1.6 µm)"
υ ≡ 1	υ = 0.6	υ = 1.7	υ = 0.6	υ = 0.4

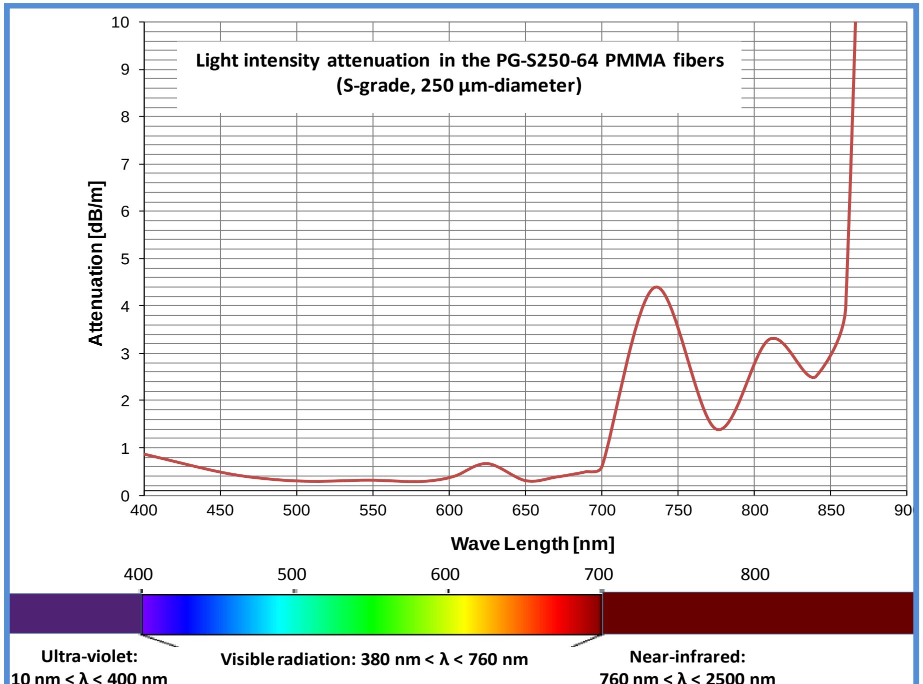
Multi-Channel Optical Analyzer MCOA-UC instrumented with optical fiber ribbon, stacked optical monitor (SM) and ESC Thomson TSN 506N



Panoramic Multi-Channel Optical Analyzer coupled with the ESC Thomson TSN 506 N:

Multi-fiber Optical Probe: PMMA-fibers, Ø250 µm

Light intensity attenuation in optical fibers



- **Meso-scale probing** of the 3D reaction zone structure;
- ***temporal and spatial resolution: 200 ps and 50-250 µm***
- **96 independent registration channels**;
- **<u>Kinetic parameters</u>:** time history of reaction radiance, 360nm < λ < 850nm spectrum
- Sensitive to radiation from near-UV up to near-IR
- **<u>Dynamic parameters</u>**: stress field (unlimited amplitude) in stacked optic monitor

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

➔HMX particles were bonded with HTPB and Epoxy binder in mass-ratios 82/18, 85/15 & 90/10

➔Six samples Ǿ4x1.04mm tested simultaneously

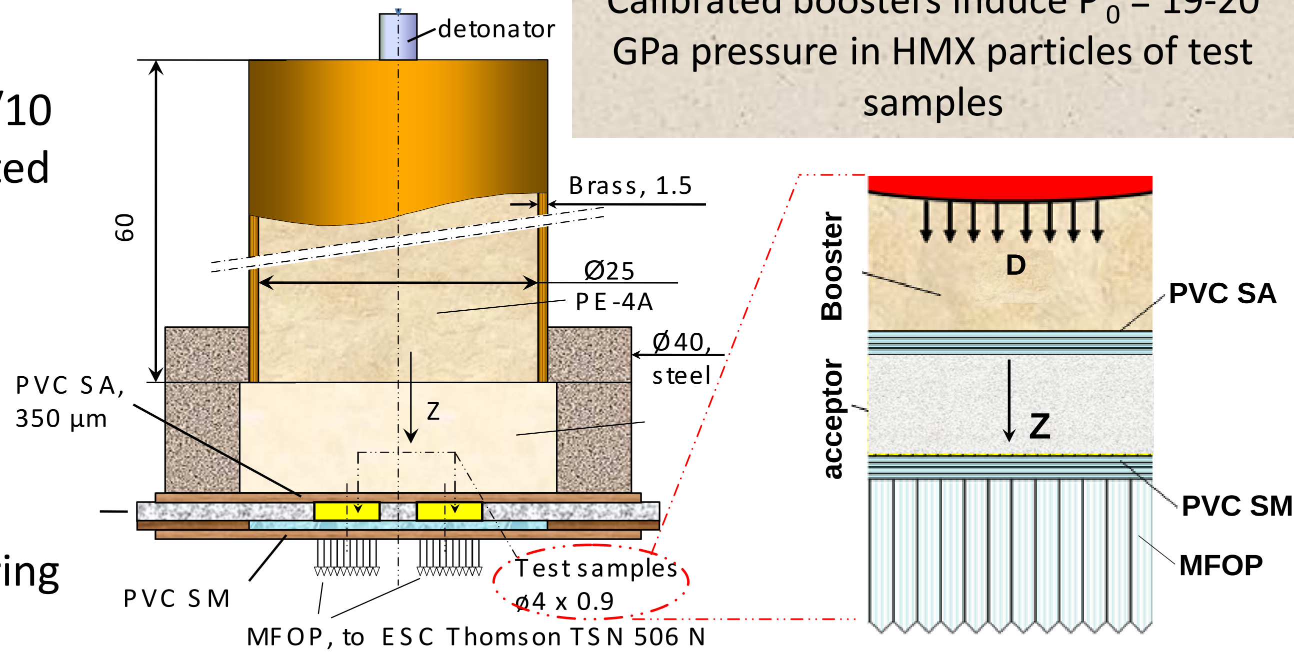
➔**HMX/Epoxy samples :**

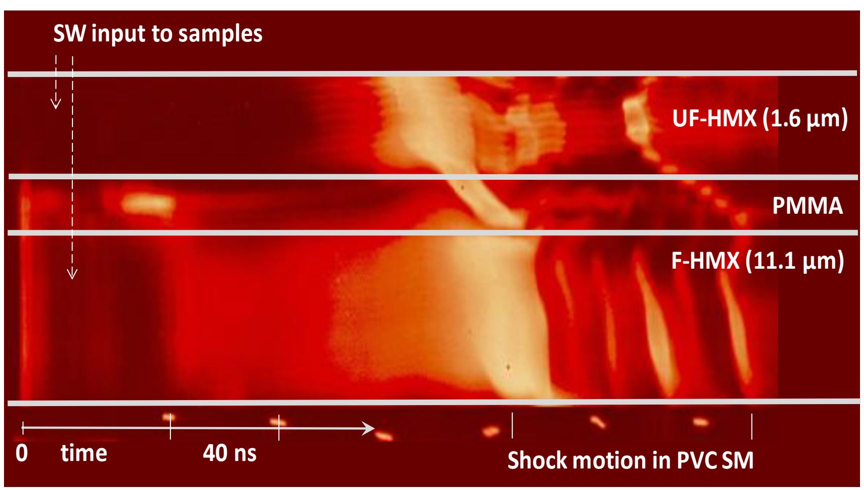
- voids-free PBX-charges of 99%TMD;

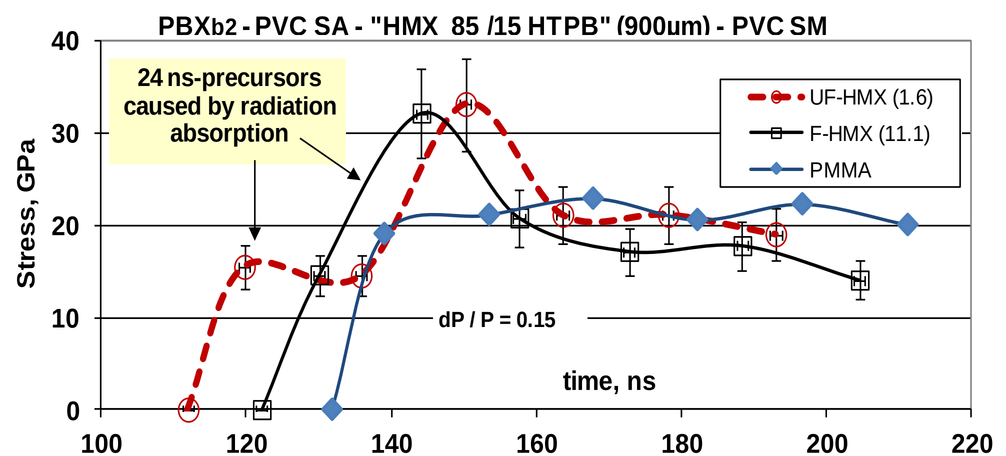
-fabricated with use of slurry mixing, low pressure pressing, vacuum casting, & pressure curing in PMMA holder.

-HMX/HTPB samples: 96-98 TMD

Calibrated boosters induce P_0 = 19-20 GPa pressure in HMX particles of test samples



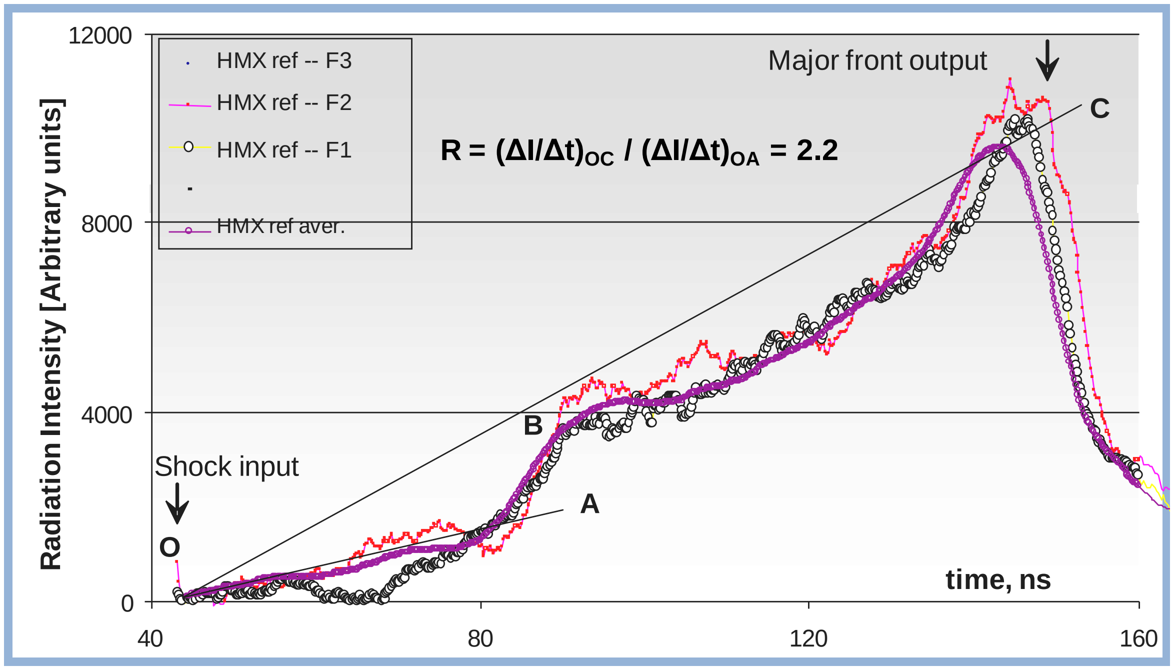




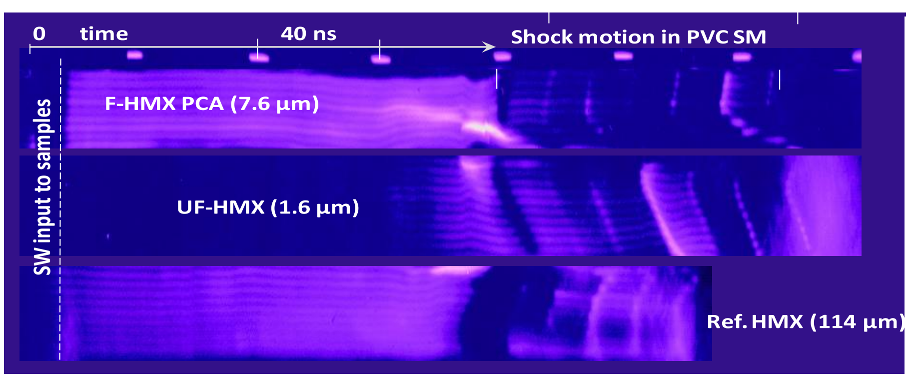
Kinetics Rate/Reaction Radiance Test: Basic Concept

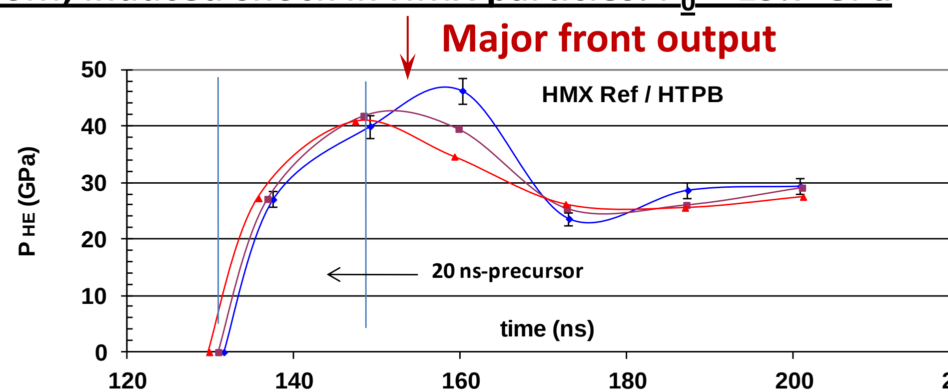
Absolute shock reactivity value R at P_0-initiation pressure is determined for each i-acceptor as a ratio between mean rate of full radiation growth and the initial rate of the reaction light growth:

$$R = [(I_{final} - I_{initial})/(t_{final} - t_{initial})]_{mean} / (\Delta I_0/\Delta t_0)_{mean}$$

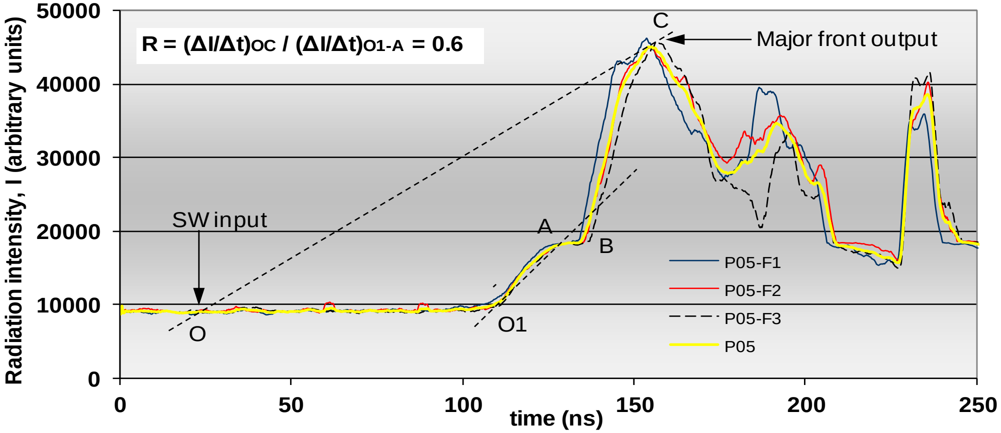


PBX $_{b2}$ – PVC SA – P 85/15 HTPB (1010 μm) – PVC SM; induced shock in HMX particles: P_0 = 19.7 GPa

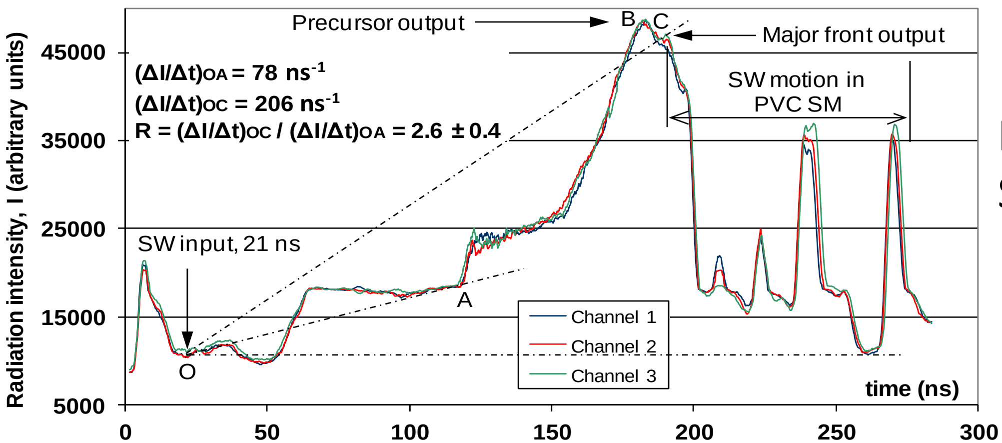




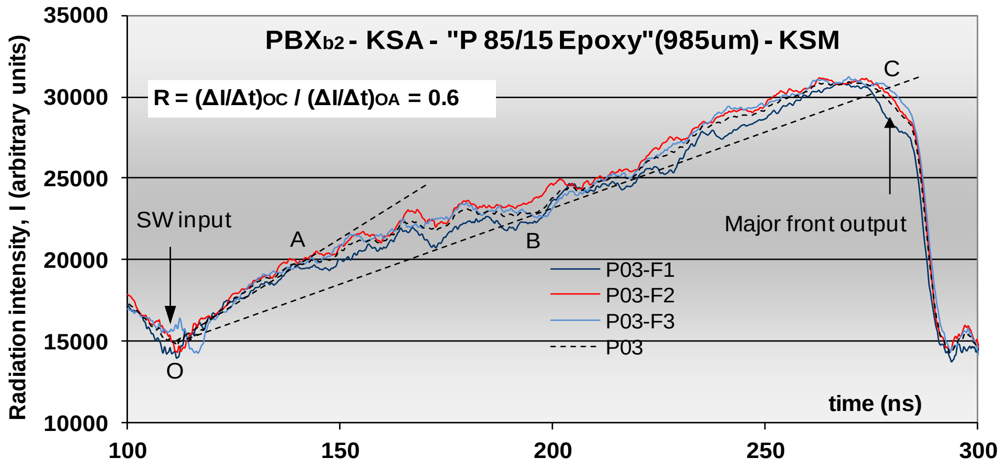
KR/RR Test data



PBX b2 - “UF-HMX (1.6 µm) 85/18 HTPB”-PVC SM; 985 µm-sample

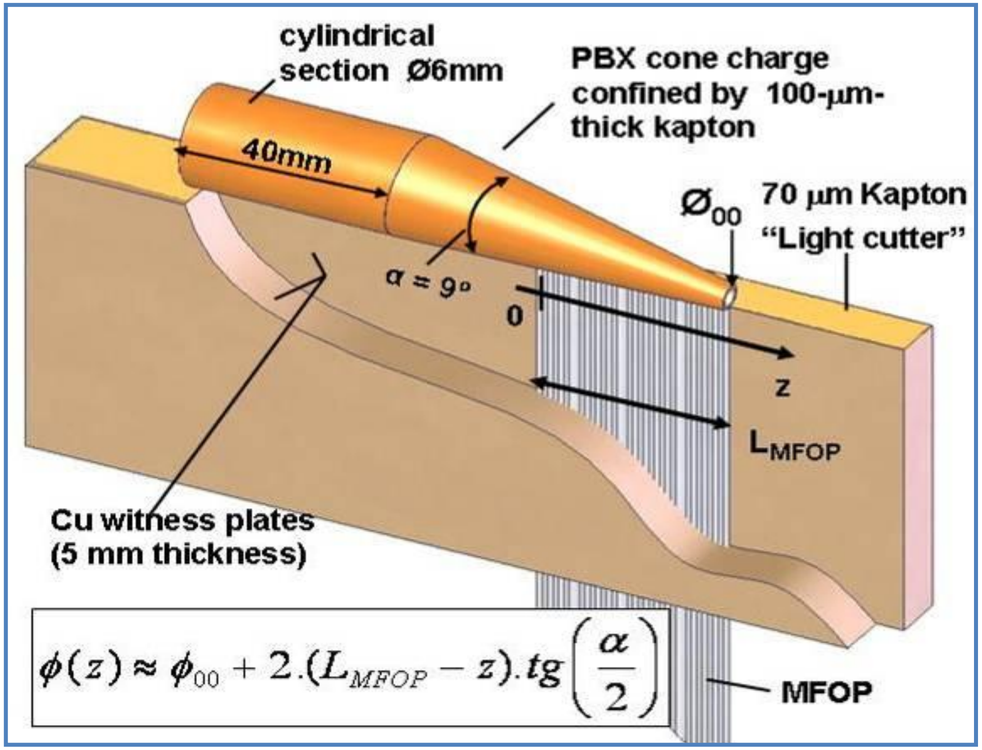


PBX b2 – “F-HMX (11.06 µm) 85/18 HTPB”-PVC SM; 985 µm-sample

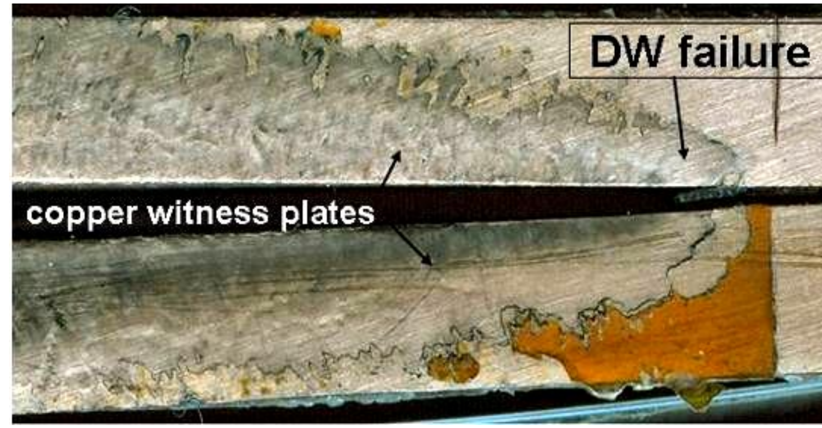


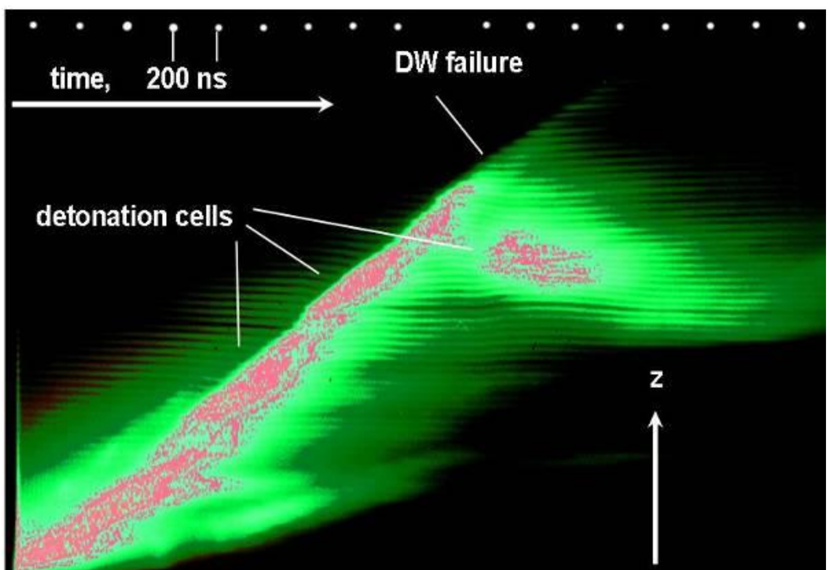
PBX b2 – “RC-HMX (130.9 µm) 85/18 HTPB”-KSM; 985 µm-sample

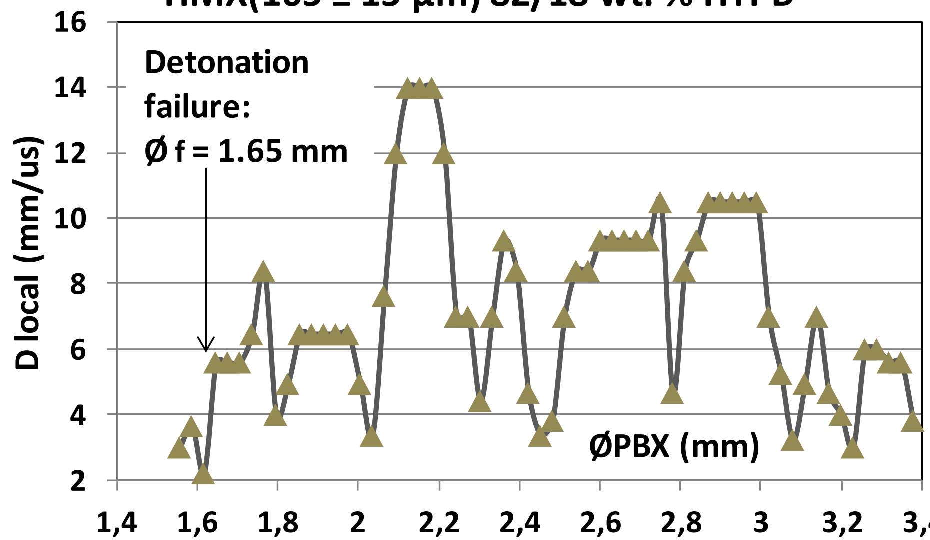
Detonation Failure Cone Test: Determination of Detonation Failure Diameter



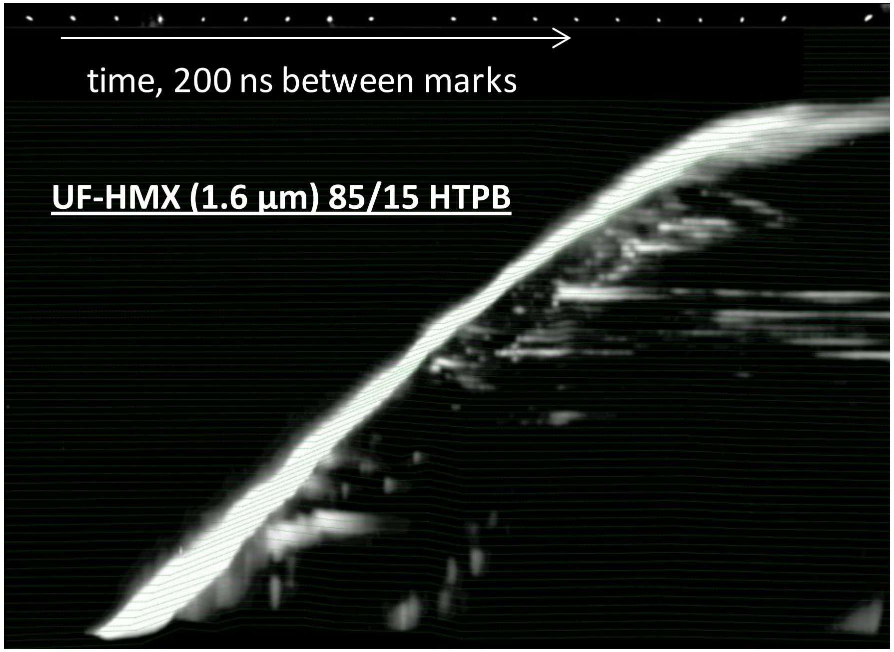
$$\phi(z) \approx \phi_{00} + 2.(L_{MFOP} - z).tg\left(\frac{\alpha}{2}\right)$$

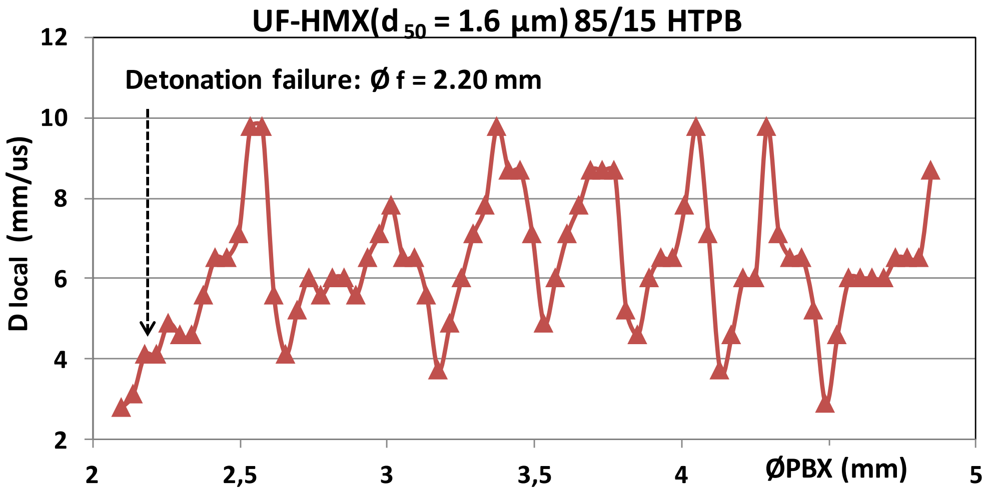


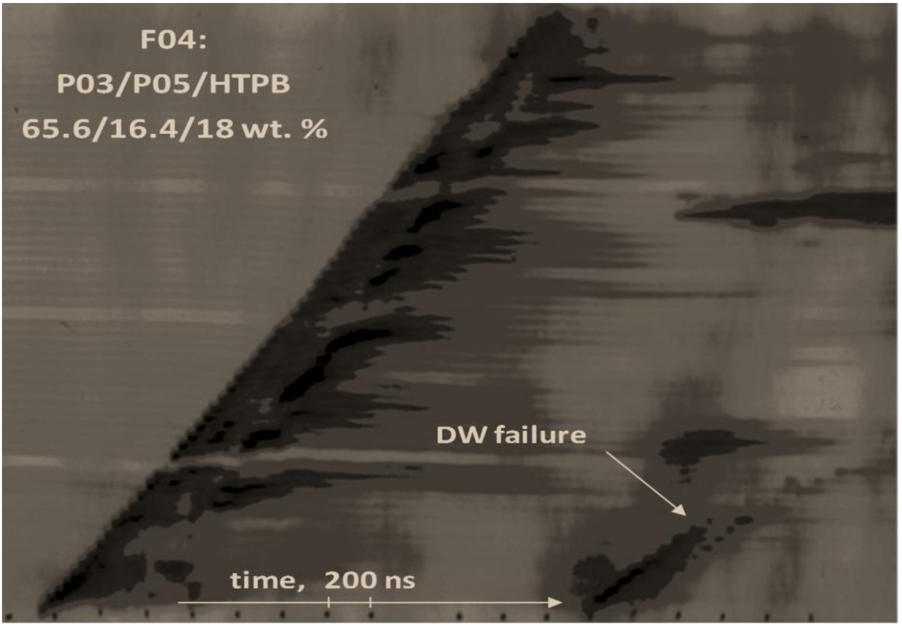


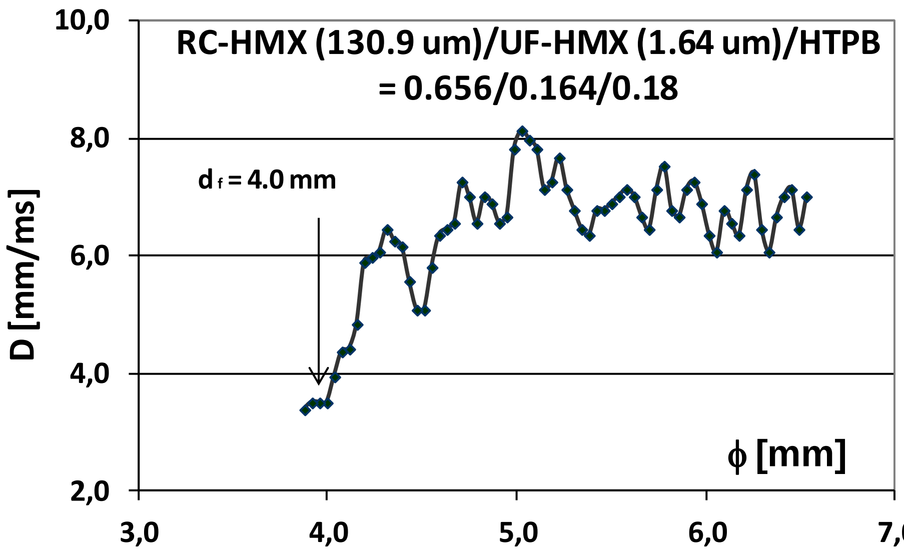


Detonation Failure Cone Test: Determination of Detonation Failure diameter







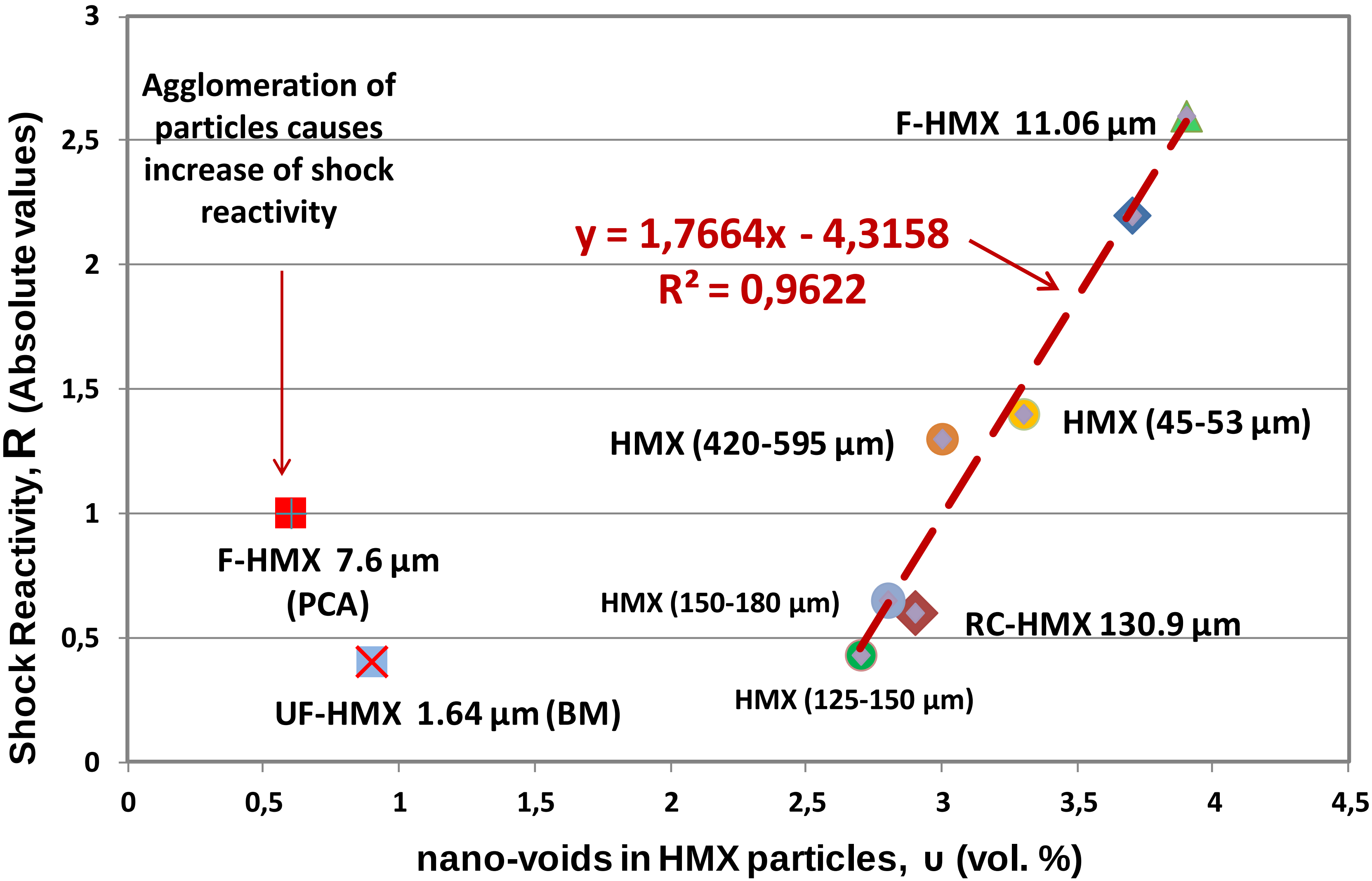


The RS-PBX "RC-HMX/UF-HMX/HTPB 65.6/16.4/18 wt.%" is possessing the Detonation Failure diamete on the level of the purified TATB explosive material of 0.97 TMD (LASL data)

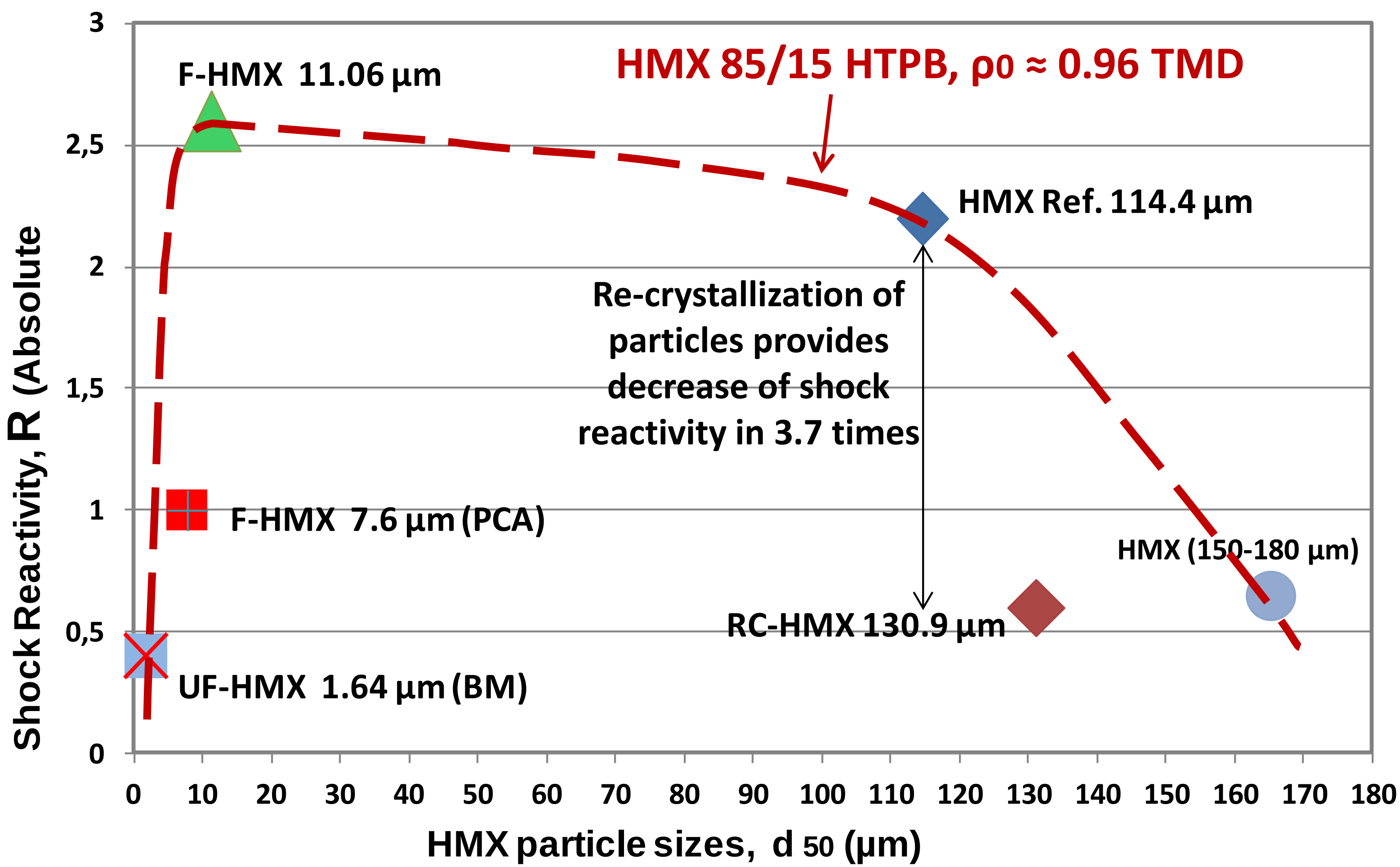
Shock Reactivity of PBXs vs. HMX-particles Morphology: Data Summary for PBXs "HMX (82-85 wt. %)/Epoxy" & "HMX (85-90 wt. %)/Epoxy"

ID - HMX particles, d_{50}, d_{min} & d_{max}		ρ_0 [g/cm^3]	nano-Porosity, υ [vol. %]	R: Shock Reactivity	Failure diam., d_f [mm]	Relative Shock Sensitivity, S
HMX ref. (114.408 um)		1.877± 0.005	3,7	2,2	n/a	≡1
RC-HMX (130.9 um)		1.895± 0.007	2,9	0,6	n/a	0,3
F-HMX (11.06 um)		1.874±0.008	3,9	2,6	n/a	1,2
UF-HMX (Ball Milled), d_{50} = 1.64 um		1.9330.005	0,9	0,4	2,2	0,2
F-HMX PCA, 7.6 um		1.939	0,6	1	n/a	0,5
Fractions of HMX Class-3 particles	HMX (420-595 um)	1.893±0.012	3	1,3	2,52	0,6
	HMX (180-210 um)	n/a	n/a	n/a	1,55	n/a
	HMX (150-180 um)	1.896	2,8	0,65	1,65	0,3
	HMX (125-150 um)	1.899±0.001	2,7	0,43	n/a	0,2
	HMX (63-90 um)	n/a	n/a	n/a	1,55	n/a
	HMX (45-53 um)	1.886± 0.019	3,3	1,4	1,38	0,6

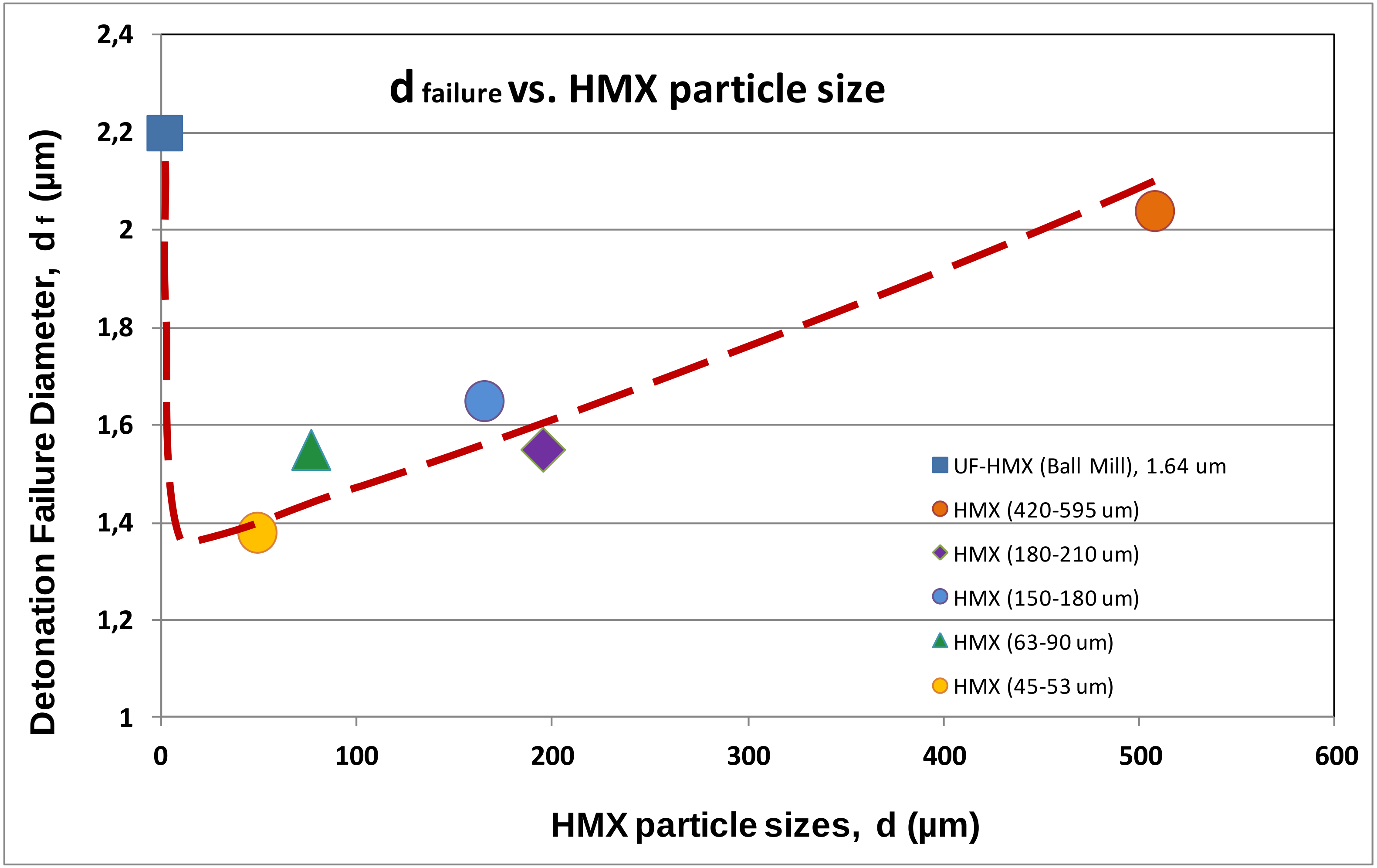
Shock Reactivity of PBXs vs. nano-porosity of HMX particles: Data Summary for PBXs "HMX (82-85 wt. %)/Epoxy" (0.96-0.98TMD) & "HMX (85-90 wt. %)/Epoxy" (0.99TMD)



Shock Reactivity of PBXs vs. HMX-particle size: Data Summary for PBXs “HMX (82-85 wt. %)/Epoxy” & “HMX (85-90 wt. %)/Epoxy”



Detonation failure diameter of PBXs vs. HMX-particle sizes
Data Summary for PBXs “HMX (82-85 wt. %)/Epoxy” & “HMX (85-90 wt. %)/Epoxy”



Conclusive Remarks

➔**Kinetic Rate/Reaction Radiance Test** and **Detonation Failure Cone Test**, both instrumented with **Multi-Channel Optical Analyzer *MCOA-UC*** produce quantitative data on reaction rate in PBX-samples subjected to shock or detonation.

➔Very small amount of test material (KR-RR Test: 20mg, Detonation Failure Test: 800 mg) is required for tailoring PBXs on shock sensitivity.

➔Role of HMX-particles morphology in shock sensitivity of PBXs is quantitatively described.

➔Basic "morphological factor" determining a shock reactivity of HMX-particles is a nano-porosity of crystalline structure of the particle's surface layer.

➔HMX-particles of micron/submicron size demonstrate a shock reactivity in 5-7 times lesser than larger particles, having 100-10µm sizes. Experimental data are in good correlation with Kenneth Graham's results

➔In this context, shock reactivity data 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.

➔ PBX-formulations composed with the re-crystallized particles, a micron-size particles and HTPB in ratio 65.6/16.4/18 wt. %" is possessing the insensitivity to shock on the level of the TATB.