

WEAG - Panel II - CEPA 14
ERG114.009 PARTICLE PROCESSING AND CHARACTERISATION
Part II: Particle Processing

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Abstract

The joint research project *ERG114.009 Particle Processing and Characterization* between Belgium, Germany, The Netherlands and Portugal has been started in March 2003 under the EUROPA ERG1 Arrangement with the objective to study the influence of crystallisation and processing techniques on particle quality and its implication for the formulation of plastic bonded explosives (PBX) with IM behaviour. The contribution describes the work package particle processing and provides a first raw characterization of obtained particles.

Introduction

Plastic bonded explosive (PBX) are discussed in the last years as a function of the quality of embedded energetic particles. Particularly, actual research is focussed on a sensitivity reduction of PBX by incorporating suited particle qualities. As a conclusive correlation hitherto is difficult to achieve an approach is made by Germany, Portugal, the Netherlands

and Belgium starting a joint research project entitled *ERG114.009 Particle Processing and Characterisation* under the EUROPA ERG Arrangement No 1 concerning Co-operative Defence Research and Technology Projects.

Objective and Military Relevance

The objective of the research project is to study the influence of crystallisation and processing techniques on particle quality and its implication for the formulation of plastic bonded explosives (PBX) with IM behaviour. The results of the proposed investigations are expected to lead to refined process techniques and improved qualities of particles and formulations. Besides, formulation, accelerated ageing and testing of mini and micro PBX-samples will stimulate an improvement of service life.

The most obvious advantage for military application is expected for the development of new Insensitive Munitions (IM) in accordance with STANAG 4439 and AOP-39, with the aim to reduce the probability of inadvertent initiation and severity of subsequent collateral damage to weapon platforms, logistic systems and personnel. Especially, benefits are expected for the development and testing of new ammunition, new high explosives and initiators, where appropriate crystal qualities (size, shape, defects) and processing techniques shall lead to low sensitivity products.

Cost reductions are expected by the improvement and quality control of energetic particles and formulations during the development of processing techniques and plants. Costs will also be reduced with higher shelter capacities and smaller safety distances for insensitive energetic materials and systems and with an increased service life of high explosive warheads stimulated by accelerated ageing tests of existing formulations. Besides, the development of mini- and micro-scale characterisation techniques shall increase the research and development effectiveness. The protection of resources, personnel and population combined with cost reduction shall increase the survivability of troops and platforms.

State of the Art and Modelling

As a basis for the investigations an extensive literature review has been carried out, including energetic materials, processing and crystallisation techniques, formulation techniques, binders

and additives, small scale mixer, micro scale tests for shock sensitivity and detonation performance, conditions for sample consignments and modelling of energetic materials and processing techniques. Results of the reviews are reported elsewhere (ERG-114-009 Report WP 1000: State of the art, modelling); they would exceed the frame of this contribution. Subsequently to the reviews the energetic materials HMX and RDX / RS-RDX were chosen and processing, formulation and characterization techniques have been established for the investigations.

Energetic Materials

HMX, RDX and reduced sensitivity RDX were procured from Dyno Nobel ASA, N-3476 Sætre, Norway. The specifications of the materials are summarized in Tab. 1.

HMX, delivered to ICT and TNO from the same lot, consisted of Grade B, Class 6 material. Typical particle size values for an HMX Grade B, Class 6 are: 90% point, 250 μm , 50% point, 115 μm ; 10% point, 35 μm . RDX, delivered to TNO, consisted of RDX, Type II “Standard”, Class 1 and reduced sensitivity RDX Class 1 (RS-RDX). Typical particle size values for an (RS-)RDX Class 1 are: 90% point, 325 μm ; 50% point, 130 μm ; 10% point, 50 μm .

Tab. 1: Specification of procured energetic materials

	HMX HPLC [%]	RDX HPLC [%]	Melting point [°C]	Acetone insoluble [%]	Inorganic insoluble [%]	Insoluble particles on USSS No.		Acidity [%]
						40	60	
HMX, Grade B, Class 6								
Specification	≥ 98.0	≤ 2.0	≥ 277	≤ 0.05	≤ 0.03	0	≤ 5	≤ 0.02
measured	100.0	0.0	280	0.00	< 0.03	0	0	0.02
RDX, Type II “Standard”, Class 1								
Specification	≤ 12		≥ 190	≤ 0.05	≤ 0.03		≤ 5	≤ 0.02
measured	5.9		195.6	0.00	< 0.03		0	0.00
RS-RDX, Class 1								
Specification	≤ 3		≥ 200	≤ 0.05	≤ 0.03		≤ 5	≤ 0.02
measured	0.3		203.2	0.00	< 0.03		0	0.00
	Crystal modification IR		Granulation, passing USSS No., [%]					
			12	20	50	100	200	325
HMX, Grade B, Class 6								
Specification	α -HMX not traceable		≥ 99	--	≥ 90	65 ± 15	30 ± 15	15 ± 10
measured	not traceable				100	73	21	6
RDX, Type II “Standard”, Class 1								
Specification	--		--	98 ± 2	90 ± 10	60 ± 30	25 ± 20	--
measured				100	85	46	12	
RS-RDX, Class 1								
Specification	--		--	98 ± 2	90 ± 10	60 ± 30	25 ± 20	--
measured				100	88	41	8	

Crystallization and Processing of Energetic Particles

Crystallization from Polypropylene Carbonate (ICT)

HMX was recrystallized by cooling crystallization from propylene carbonate (PC). To obtain enough material for the characterisation and further processing to formulations, several batches were crystallized. Each batch consisted of 360 g HMX and 3000 g PC, which corresponds to a supersaturation of 1 at 75 °C. Fig. 1 shows the solubility of HMX in propylene carbonate and Fig. 2 monitors the temperature on cooling as function of time during the experiment. The nucleation was found to take place between 58 and 62 °C. After the crystallization the crystals were washed with acetone.

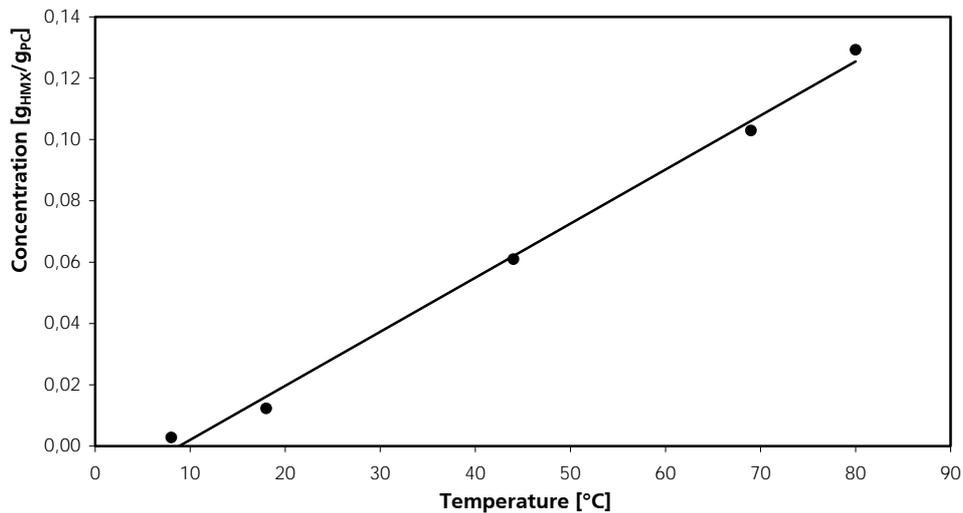


Fig. 1: Solubility of HMX in propylene carbonate PC

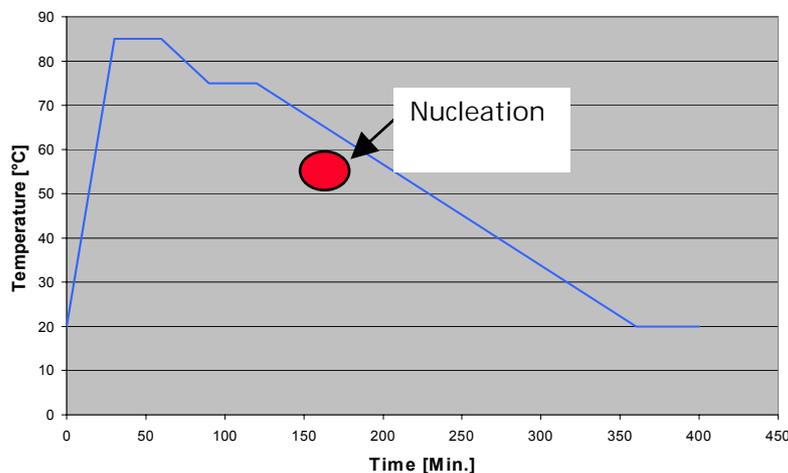


Fig. 2: run of temperature during crystallization

A first characterisation of the recrystallized sample is given in Fig. 3. It shows smooth surfaces with a lower content of defects and secondary crystals, compared to the original HMX.

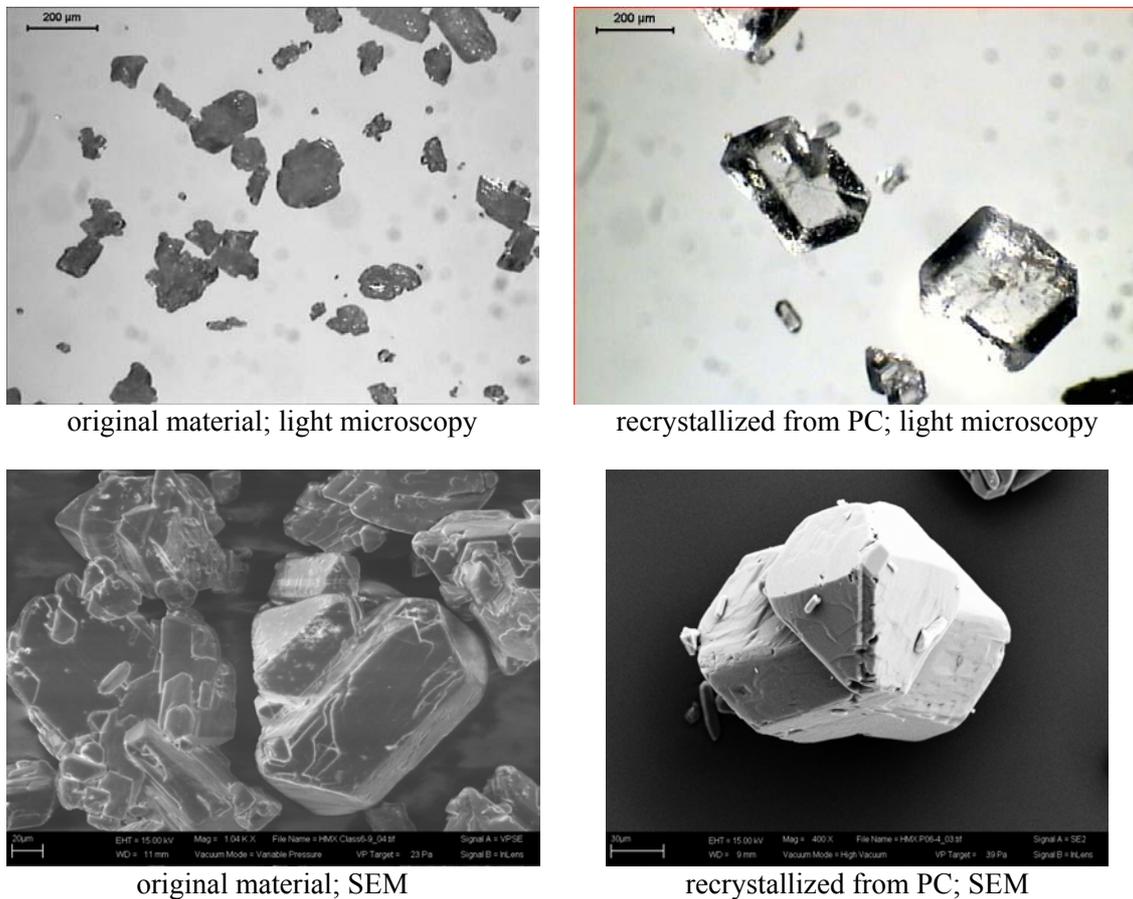


Fig. 3: Recrystallized and original HMX

Crystallization from γ -butyrolactone and acetone/ γ -butyrolactone mixtures (TNO)

The crystallization of RS-RDX and HMX from γ -butyrolactone and acetone/ γ -butyrolactone mixtures was performed in a 2 liter, jacketed crystallization vessel equipped with a draft tube and 4 baffles (made of glass) in order to improve the hydrodynamics in the solution during the crystallization process. A marine-type stirrer was used, made of steel. A computer programme is used to control a thermostatic bath with which the temperature of the solution in the crystallizer can be controlled. The temperature in the solution is measured using a thermocouple.

HMX was recrystallized from an acetone/ γ -butyrolactone mixture (1:1 molar based) on cooling. The acetone/ γ -butyrolactone mixture was used, in order to prevent the crystallization of 1:1 complexes of HMX/ γ -butyrolactone, reported in literature [1]. The crystallization process was started by using a seeding method rather than by homogeneous nucleation of crystals by slowly building up the supersaturation by cooling. After seeding, the linear cooling profile is started. When the final temperature of the crystallization process (~ 20 - 25 °C) has been reached, the crystallizer is emptied and the solids are separated from the solution by filtration over a glass filter and washed two times with demi-water. In total five recrystallization batches were performed, resulting in a total yield of ~ 1.35 kg (see Tab. 2). Fig. 4 and 5 show pictures of the HMX recrystallization process.

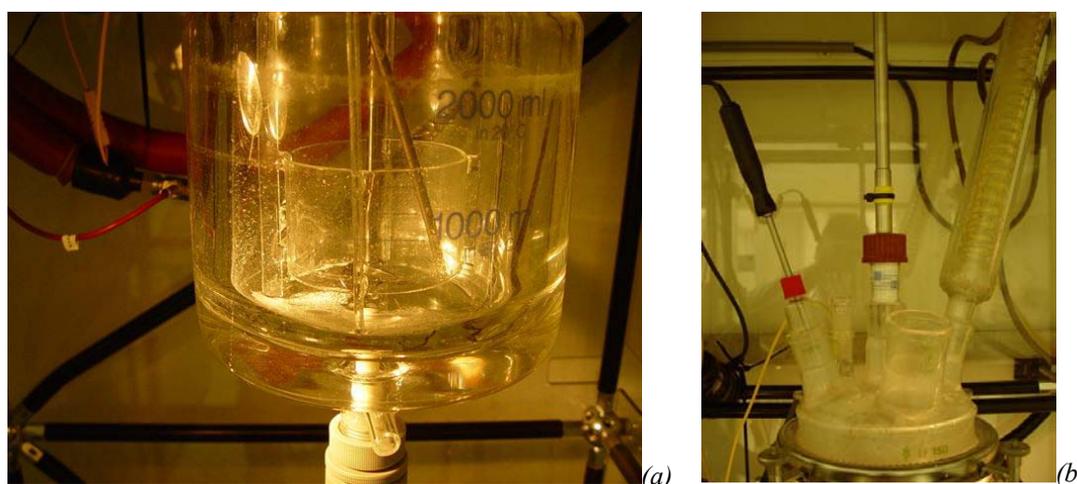


Fig. 4: (a) Crystallization vessel, showing draft tube, baffles and stirrer. (b) Top of crystallizer, showing stirrer shaft (in the middle), thermocouple (left) and reflux unit (right).

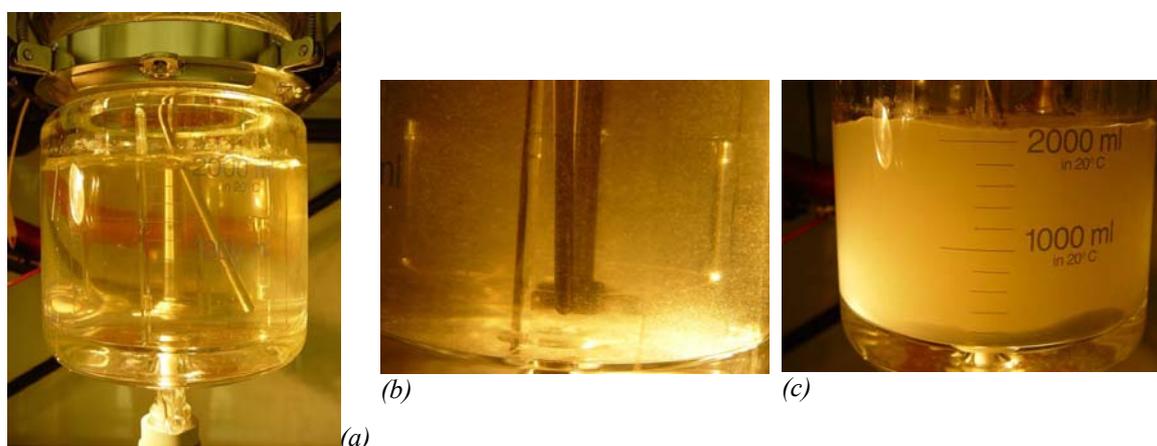


Fig. 5: (a) Crystallizer set-up after dissolution of the HMX. (b) Close-up of crystallization vessel immediately after seeding. The bright spots point at the formation of small HMX crystals. (c) Close-up of crystallization vessel after reaching the final temperature of the cooling profile.

In order to compare similar size ranges, the recrystallized as well as the original HMX were sieved (sieve fraction 75 – 180 μm , USSS No. 200 and No. 80, respectively), yielding ~525 g of HMX to be used for the characterization of particles and the PBX-formulation.

Tab. 2: Information on the crystallization of HMX

Solution	
HMX [g]	498
Acetone [g]	331
γ -Butyrolactone [g]	1,469
Process conditions	
Cooling profile	From 80 °C to ~20-25 °C in 240 min (linear)
Stirrer rotation rate [rpm]	450
Seeding [yes/no]	Yes (see text)
Yield after crystallization [g]	
	1,351 (~ 54%)
Sieving	
	75 – 180 μm , USSS No. 200 and 80
Yield after sieving [g]	
< 75 μm	59.0
> 75 μm and < 180 μm	525.2
> 180 μm	765.9

Tab. 3: Information on the crystallization of the RDX batches.

Solution	
RS-RDX [g]	585
γ -Butyrolactone [g]	1,456
Process conditions	
Cooling profile	From 80 °C to ~20-25 °C in 240 min (linear)
Stirrer rotation rate [rpm]	450
Seeding [yes/no]	Yes (see text)
Yield after crystallization [g]	
	1,917 (~65.5%)
Sieving	
	75 – 355 μm , USSS No. 200 and 45
Yield after sieving [g]^a	
< 75 μm	~ 6.5
> 75 μm and < 355 μm	851.6
> 355 μm	962.4

^a Due to the fact that several sieving trials were applied, some of the material was lost.

The RS-RDX grade was recrystallized for testing whether a new RDX grade with improved properties (particularly regarding its shock initiation properties when incorporated in a PBX) compared to the RS-RDX grade could be produced. Details on the crystallization batches are summarized in Tab. 3. The procedures applied were the same as with the HMX batches. In

total five recrystallization batches were performed, resulting in a total yield of ~ 1.9 kg (see Tab. 3).

In order to avoid differences in particle size distribution, which might affect the shock initiation properties on the level of PBXs, also the recrystallized RS-RDX and the original RDX and RS-RDX batches were sieved.

Milling by rotor-stator-system (ICT)

HMX was comminuted in a rotor-stator-system (fig. 6) in an aqueous system with 10 w% HMX four hours. Fig. 7 shows SEM pictures of the rotor-stator milled and the original HMX. The obtained particle size is about 10 μm with a comparatively wide size distribution. Due to mechanical attrition the comminuted particles have a spherical like shape.

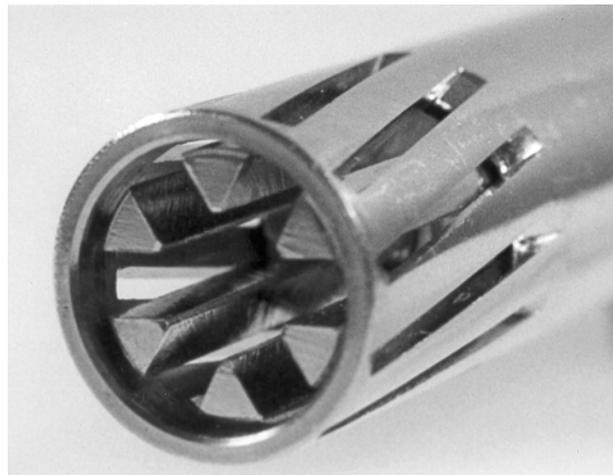
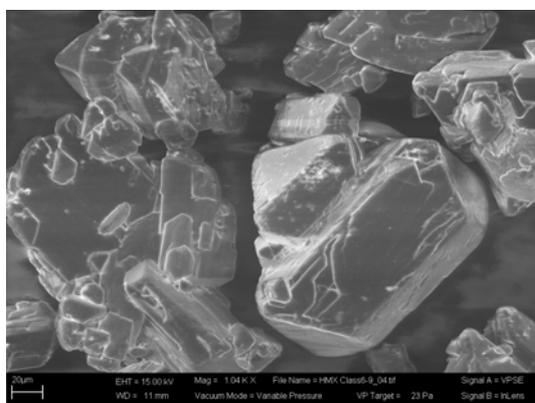
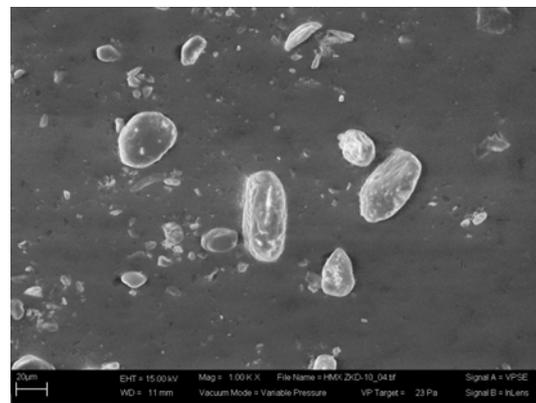


Fig. 6: Rotor-stator system



Original HMX



Comminuted HMX

Fig. 7: Comparison of original and rotor-stator milled HMX

Milling by annular gap mill (ICT)

HMX was comminuted in a quasi-continuous annular gap mill shown in fig. 8. The aqueous suspension with 10 w% HMX is pumped through the system. The gap is filled with milling balls which consist of ZrO_2 , SiO_2 and other oxides as Al_2O_3 . The product passed the mill 20 times; the frequency of the mill was 8000 rpm.

Fig. 9 compares original and by annular gap milled HMX. The comminuted particles are spherical like and narrowly distributed with a mean particle size is about $1\ \mu m$. We found some contamination of the particles after milling, being abraded from the milling balls. The product contained 0.07 w% zirconium, 0.05 w% silicon and 0.02 w% aluminium.

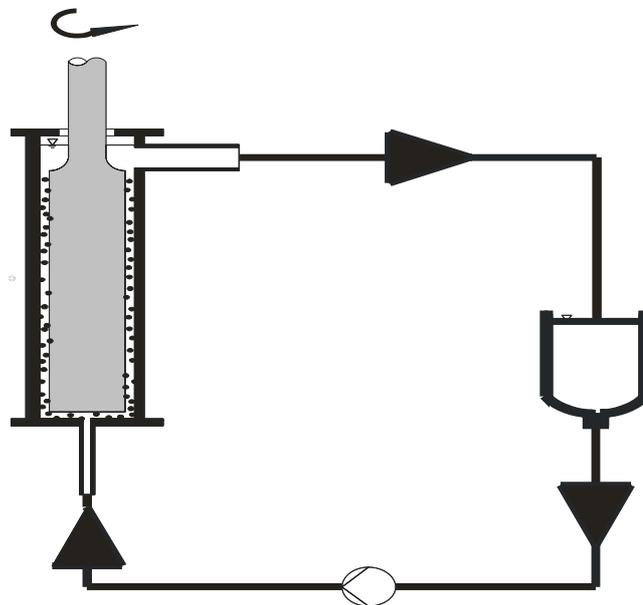
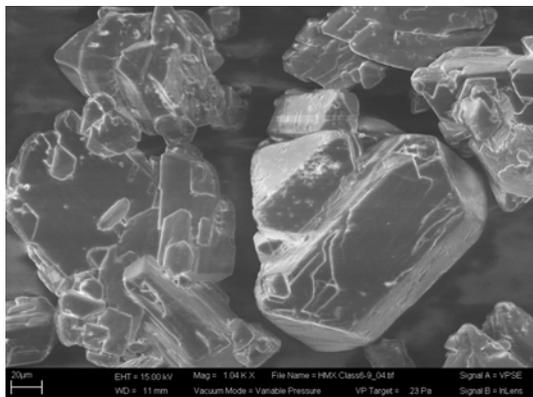
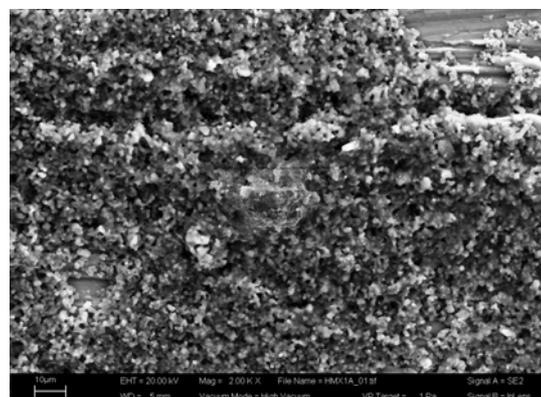


Fig. 8: Annular gap mill



Original material



Comminuted HMX

Fig. 9: Comparison of original and annular gap mill comminuted material

Storage in isopropanol (ICT)

A sample of the rotor-stator milled HMX was stored for 7 days at 20 °C in isopropanol in order to improve the crystal quality of the rotor-stator-milled HMX. It was expected that storage in a nearly anti-solvent would have some healing effect on the crystals by diffusive material transport. Fig. 10 shows SEM pictures of the rotor-stator milled and the afterwards in isopropanol stored material. A significantly higher amount of small particles in the micro or sub micro range were found in the stored samples agglomerating with the larger particles.

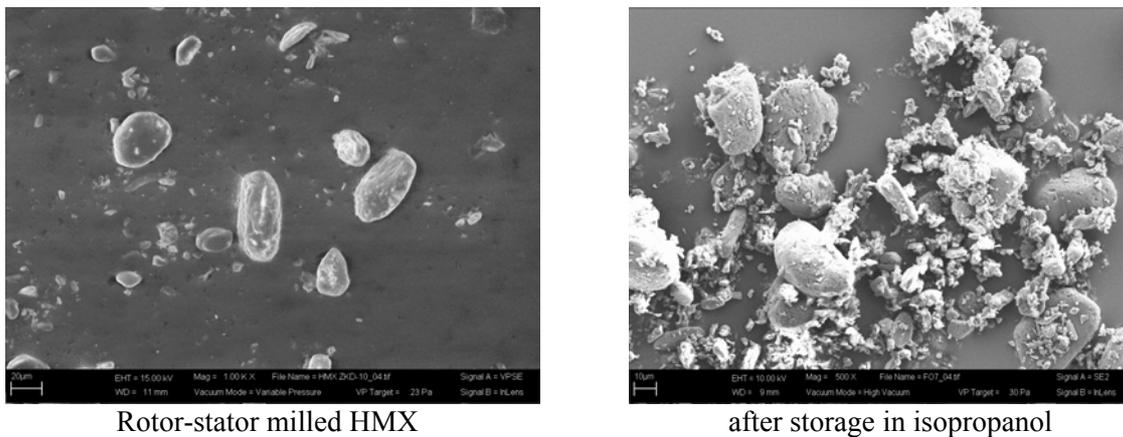


Fig. 10: Comparison of rotor-stator milled and afterwards in isopropanol stored HMX

Preparation of highly homogeneous samples (LEDAP)

For the investigation of particles and bi-modal PBX formulations with a mass ratio up to 90/10 “filler/binder” particularly by micro scale detonation tests, highly homogenous samples are required. Therefore a technological preparation procedure has been developed.

The procedure implies formation of a “slurry” by adding of a liquid, vaporizing agent that is non-solvent for HMX but solvent for binders. Applications, for instance, of ethyl acetate alcohol revealed positive results in “slurry” preparation from dry fine or ultra-fine HMX particles. Ethyl acetate is a perfect vaporizing (intermediate) agent, and at the same time represents a solvent for binders (HTPB, epoxy resin and GAP). Mixing of HMX particles with the ethyl acetate, in mass ratio 1/1, allows obtaining of highly homogeneous “slurry” and avoiding the hazardous effects of static electrifying.

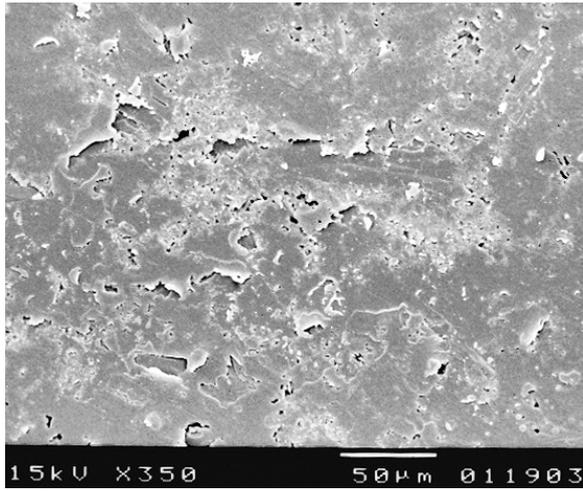


Fig. 11: HMX/Epoxy (85/15), incl. original HMX

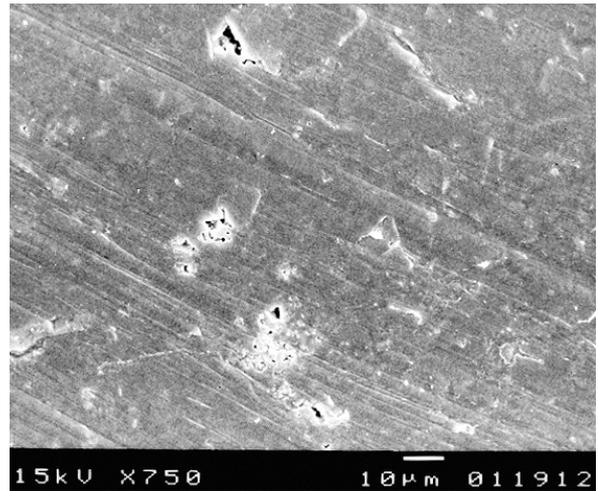


Fig. 12: HMX/Epoxy (85/15), incl. recryst. HMX from acetone/ γ -butyrolactone

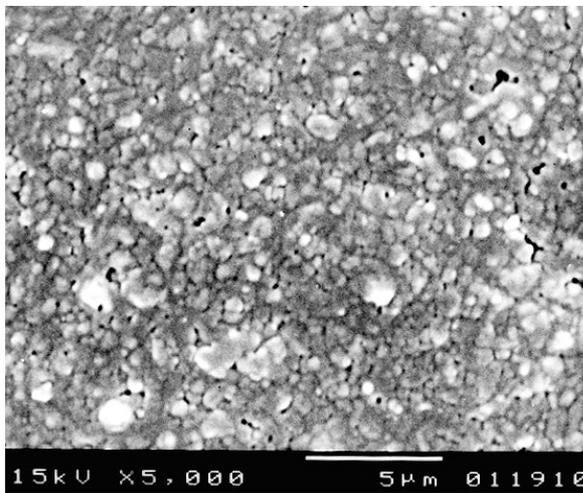


Fig. 13: HMX/Epoxy (85/15), incl. annular gap milled HMX

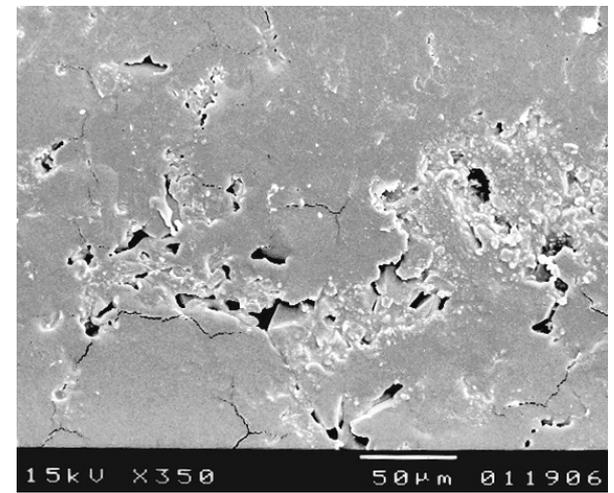


Fig. 14: HMX/Epoxy (85/15), incl. recryst. HMX from propylene carbonate

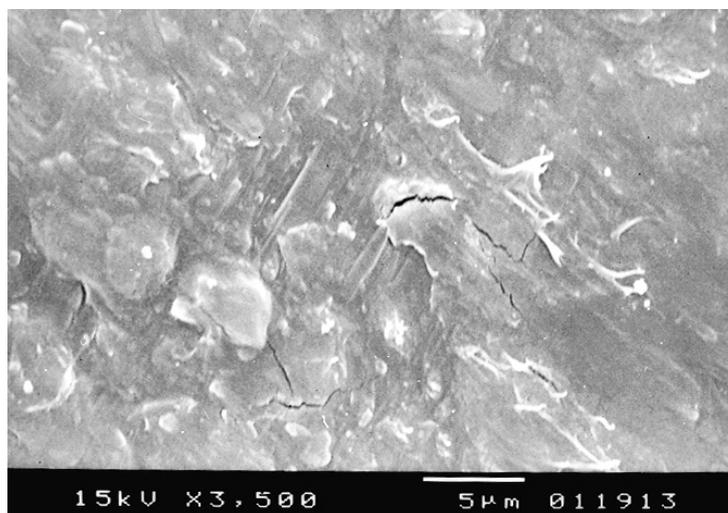


Fig. 15: HMX/Epoxy (85/15), incl. rotor-stator milled HMX stored in isopropanol

The “slurry” technology was applied to the fine and ultra-fine HMX particles provided by the crystallization and comminution techniques described above. The HMX particles were bonded by Epoxy resin Araldit® in mass ratio 85/15. Low-pressure pressing technique combined with a vacuum facility has allowed performing low-porous solid samples of 0.99 TMD. SEM photos of samples are presented in Fig. 11 to 15.

Conclusions and Outlook

On the basis of an extensive literature review energetic materials and crystallization, formulation and characterization techniques have been chosen, that are in the scope of actual scientific research. Moreover, the energetic materials HMX, RDX and reduced sensitivity RDX are commercially available and used in industrial applications.

Within the work package *Particle Processing* these energetic materials were procured and a variety of particle processing techniques was applied including cooling crystallization from different solvents, comminution techniques, particle treatment in an anti solvent and a “slurry” technique. Thus, a sample portfolio was produced including different qualities of fine and coarse lots of HMX and RDX suited for mixing of defined bimodal PBX formulations and homogeneously in resin distributed particles suited for micro scale investigations.

The samples have been distributed for the subsequent work packages *Particle Characterization*, *Formulation of PBX* and *Characterization of PBX*. It is expected that correlating results of these work packages with the reported particle processing parameters endorses advanced particle production for PBX with IM behaviour.

References

- [1] L. Svensson, J. Nyqvist and L. Westling, “Crystallization method for HMX and RDX”, US patent 4,638,065; 1987