

# Formulation and Characterizations of Nanoenergetic Compositions with Improved Safety

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**Abstract:** In order to improve the safety of energetic compositions, whether it has to be worked with less sensitive materials that are often less powerful or with high energetic materials crystals with improved purity and microstructure quality. A way to modify the crystal quality of an energetic material is to structure the matter on the nanoscale: the crystals size reduction should induce impurity modifications in the particles. That is one of the reasons why interest in nanoenergetic compositions that contain high energetic material ( $\geq 90$  wt-%) and an organic matrix ( $\leq 10$  wt-%) that takes part in constraining the explosive to organize itself on the nanoscale arose. The key point is to find or synthesize the matrix. In the course of this study, first ammonium perchlorate compositions structured on the nanoscale were synthesized (150 nm AP particles (80 wt-%) dispersed in an organogel matrix (20 wt-%)). The formulation

process was based on the impregnation of porous organogels with a saturated aqueous solution of ammonium perchlorate followed by freeze drying. The overall composition had an oxygen balance equilibrated towards  $\text{CO}_2$ . These AP nanocompositions show better safety behavior during combustion than their equivalent macrocompositions, while they burn more rapidly, with no degradation of their impact and thermal sensitivity properties. The formulation process of RDX nanocompositions is more complex as the solvent used is  $\gamma$ -butyrolactone which can not be directly frozen dried. However, first RDX nanocompositions were formulated and characterized using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray powder diffraction, and drop weight impact. Lately compressions of these RDX compositions were performed, prior to gap-test experiments.

**Keywords:** Nanoenergetic • RDX • AP • Sol-gel • Impact • SSGT

## 1 Introduction

In the field of insensitive munitions and energetic materials, scientists are following a permanent quest for safe matter for propulsion or explosive purposes. With the improvement of energetic devices compactness, compact and high performance energetic materials as well as alternatives to new energetic molecules which are often difficult to synthesize and costly, are searched.

In recent years, interesting works on ways to desensitize high energetic materials (HEM) by improving their purity and the microstructure quality of crystals have been described. In 2000, SNPE published first works on insensitive RDX (I-RDX) [1]. Three years later an international inter-laboratory comparison (Round Robin) on reduced sensitivity RDX (RS-RDX) was launched for three years [2].

To desensitize HEM, two ways can be followed: improvement of the crystal quality by recrystallization [3,4], or formulation of nanocrystalline high energetic material [5]. In all cases, the result is a significant desensitization of the formulations containing the improved material, towards mechanical aggressions (shock or impact).

When it was started to study nanoenergetic compositions in 2003 it was intended to reach propulsion as much as explosives applications. Therefore the idea was to find

a common way to produce compositions containing whether AP nanoparticles or RDX nanoparticles. The concept was based on the use of some kind of a mould that would guide the charge [ammonium perchlorate (AP) or RDX] dissolved in a solvent, in its nanosized pores. During drying, the charge particles, constrained by the mould walls could not grow. The key point of this concept is the mould (matrix): it has to be able to constrain the charge to organize itself on the nanoscale.

In the case of a composition for propulsion the nanostructuring matrix has to be a reductant matrix so that the mixture AP/matrix will have an oxygen balance of 0%. The aim is to improve the combustion behavior without degradation of safety. In the case of a composition for explosive application, whatever the nanostructuring matrix, the ratio

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matrix/explosive has to be as little as possible to avoid degradation of the energetic performances. The aim is to improve the safety without degradation of the performances.

In this study, compositions for propulsion containing 80 wt-% of ammonium perchlorate (AP) nanoparticles and compositions for explosive purposes containing 75 wt-% and up to 90 wt-% of RDX nanoparticles were investigated.

Below, the formulation of nanocompositions is first described. Later, the microstructural and energetic characterizations are displayed. The behaviors of the nanocompositions were compared to the corresponding macroscopic equivalents.

## 2 Experimental Method

### 2.1 Formulation of Nanocompositions

The materials prepared are nanodispersions of ammonium perchlorate (AP) or RDX nanoparticles (called charge) in a matrix.

#### 2.1.1 Matrix

The chosen matrix is a mesoporous low-density energetic organogel with a consistency that makes it possible to use to incorporate and nanostructure the necessary amount of charge (AP or RDX). This amount is limited by the density of the gel and the solubility of the charge in a solvent that will be chemically compatible with the gel. Therefore, to nanodisperse 80 wt-% AP, 75 wt-% RDX or even later 90 wt-% RDX,  $0.07 \text{ g cm}^{-3}$  gels synthesized from phloroglucinol (P) and nitrophloroglucinol (NP) as precursors and formaldehyde as reagent were used (Figure 1). The P/NP molar ratio selected was 7/3. Therefore the matrix is called P/NP(7/3)F.

The BET specific area ( $S_{\text{BET}}$ ) and the pore size distribution of the P/NP7/3F gels, preliminary dried under supercritical  $\text{CO}_2$ , were determined using nitrogen adsorption analyses

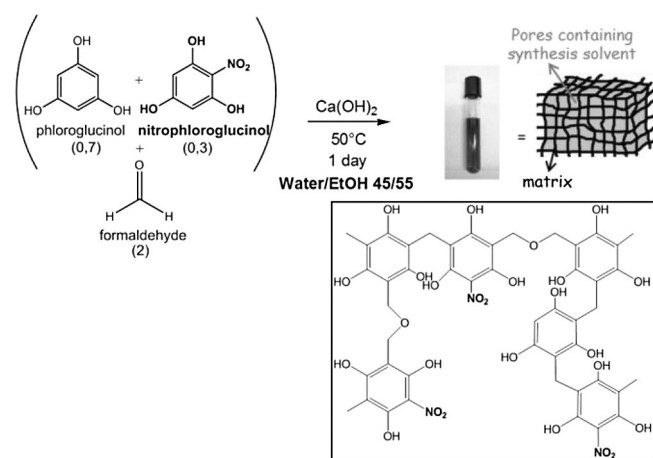


Figure 1. Synthesis of a P/NP(7/3)F matrix.

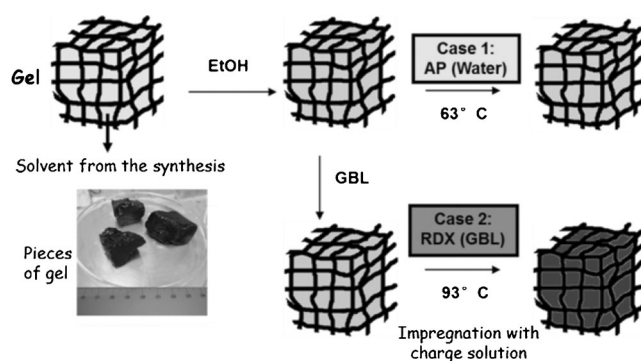


Figure 2. Impregnation process.

Table 1. Impregnation process temperature.

	Nano AP 80 wt-%	Nano RDX 75 wt-%	Nano RDX 90 wt-%
Impregnation $T/^\circ\text{C}$	63	63	93

and subsequent calculations. High  $S_{\text{BET}}$  ( $690 \text{ m}^2 \text{ g}^{-1}$ ) and a pore size range of 10 to 50 nm were observed. The synthesis of this matrix has been scaled up on a 600 g per batch scale. The matrix was used in its gel form, cut into pieces and washed with ethanol, to get rid of non reacted or partially reacted precursors.

#### 2.1.2 Matrix Impregnation with Charge in Solvent

The impregnation process consists in the immersion of pieces of gels in a saturated solution of AP (in water) or RDX [in  $\gamma$ -butyrolactone (GBL)] (Figure 2): the solution diffuses through the gel open pores network. This works well with the polar solvents used as the wall of the matrix open pores are covered with hydroxyl chemical groups. This operation can be carried out between  $63^\circ\text{C}$  and  $93^\circ\text{C}$  depending on the amount of charge inserted inside the matrix (Table 1). This process was scaled up on a 400 g per batch scale.

#### 2.1.3 Charge Crystallization and Drying Process

After impregnation, the saturated solution residues present on the gel pieces are delicately and quickly mopped up before cryotransfer in liquid nitrogen. At that time, numerous charge (AP or RDX) crystal nuclei are formed. These nuclei can not grow as they are not surrounded with charge solution. Therefore the charge particle size reached during the cryotransfer designs the final size of charge particles in the P/NP(7/3)F/charge nanocomposition.

If crystallization and drying process is very simple in the case of AP charge (cryotransfer and freeze-drying, Figure 3), in the case of RDX things are more complicated: the solvent used is  $\gamma$ -butyrolactone and it can not be directly frozen-dried.

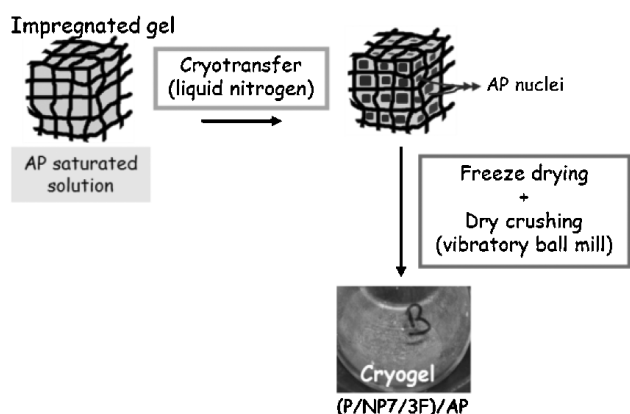


Figure 3. AP crystallization and drying process.

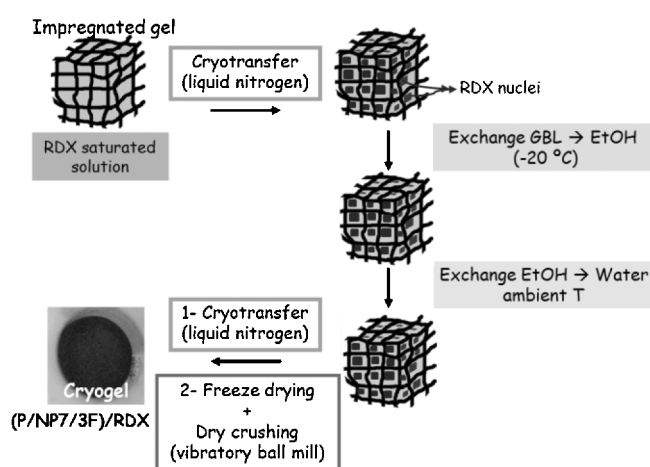


Figure 4. RDX crystallization and drying process.

GBL has to be exchanged with water, which is the only industrially freeze dryable solvent. The challenge is to reduce as much as possible the growth of RDX nuclei during the solvent exchange. Therefore it was decided to perform a first exchange with ethanol at  $-20^{\circ}\text{C}$  and secondly carry out the exchange with water at ambient temperature (Figure 4).

After freeze-drying, the cryogels are mildly crushed in a vibratory ball mill and subsequently characterized. The crystal size distribution of the crushed powder is  $50\text{ }\mu\text{m}$  to  $200\text{ }\mu\text{m}$ . Therefore it is assumed that crushing does not disturb the organization of the charge nanoparticles inside the protective matrix. This process has been scaled up on a 125 g per batch scale in the case of AP nanocompositions and on a 50 g per batch scale in the case of RDX nanocompositions. The RDX nanostructuration process could be improved in terms of duration and efficiency: at present it is aimed for a way whether to substitute the last cryotransfer and freeze drying by a classical drying at ambient pressure and temperature or to introduce RDX during gelation.

Equivalent AP and RDX macrocompositions were prepared by mixing powders of P/NP7/3F frozen dried gel and AP  $3\text{ }\mu\text{m}$  or RDX  $0\text{--}100\text{ }\mu\text{m}$ .

## 2.2 Characterization Methods

All nanocompositions were characterized using elementary analysis, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray powder diffraction and impact response. 80 wt-% AP nanocompositions were additionally characterized using combustion tests and 90 wt-% RDX nanocompositions were additionally characterized using small-scale gap test. For all these tests, comparisons of the nanocompositions with their macroscopic equivalents i.e. powder mixtures with the same weight ratio were done.

The impact response of the studied materials was investigated using a drop-weight system. This apparatus consists of a 10 kg mass, which drops from a height up to 2.5 m on a 30 mg sample. The height  $H_{50}$  for which 50% of impacts lead to a decomposition is evaluated by the classical up-and-down method. In addition, the maximal pressure  $P_{\text{MAX}}$  released by the decomposition gases is measured in the closed impact chamber of the apparatus. These pressure values were used to estimate the impact reactivity of the sample.

Combustion tests were performed in a closed-vessel apparatus. Pellets of 2 g were ignited with a small quantity of black powder and pressure in the closed-vessel of  $64\text{ cm}^3$  was monitored during the combustion. In addition, measurements of the linear combustion rate were done at the National Center of Aerospace Research (ONERA) by means of an ultrasound method on 10 g pellets.

In order to quantify initiation behavior under shock, small-scale gap tests (SSGT) using M702 detonator (Nexter Munitions) as a donor and aluminum alloy Au4G as a barrier were performed.

## 3 Results and Discussion

### 3.1 First Characterizations

Elementary and thermal analyses were performed on the nanocompositions charged with AP and RDX. Elementary analysis is a mean to estimate the amount of charge crystallized inside the matrix: the cryogel matrix is first analysed alone, followed by the nanocomposition. Table 2 summarizes

Table 2. Elementary analysis on nanocompositions.

Sample	P/NP(7/3)F [wt-%]	AP [wt-%]	RDX [wt-%]
P/NP(7/3)F/AP	$20 \pm 3$	$80 \pm 3$	–
P/NP(7/3)F/RDX	$30 \pm 5$	–	$70 \pm 5$
P/NP(7/3)F/RDX	$10 \pm 3$	–	$90 \pm 5$

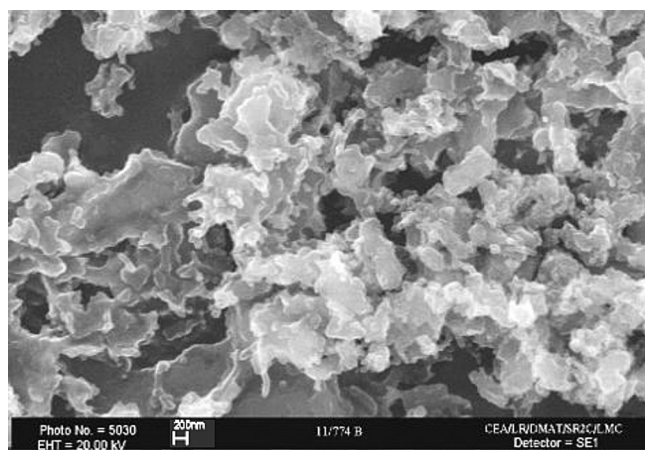


Figure 5. SEM image of 80 wt-% AP nanocryogel.

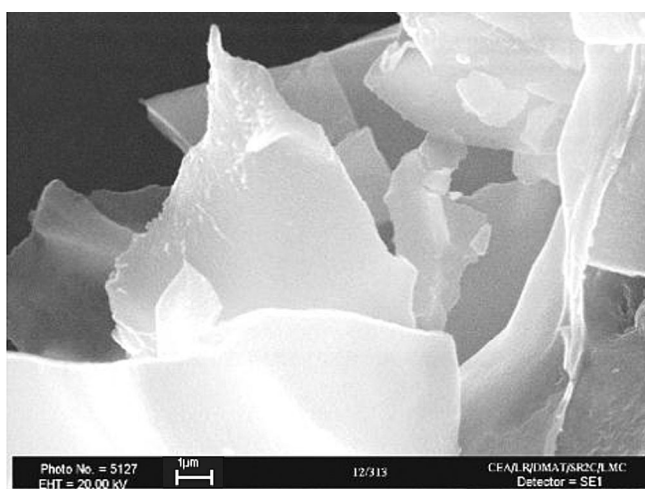


Figure 6. SEM image of 90 wt-% RDX nanocryogel.

es results obtained on the three nanocompositions groups studied.

DSC is used as a safety test. No evolution of the thermal stability of nanocompositions compared to macrocompositions could be observed; both have such a high thermal stability that the matter can be handled.

X-ray diffraction measurement confirmed that AP or RDX particles dispersed in all P/NP(7/3)F cryogels have an average size of about 100–150 nm. The SEM images show a good homogeneity of the AP and RDX cryogels microstructure (Figure 5 and Figure 6).

The AFM image of RDX nanocryogel shows that main particles are divided into fine entities on the hundred nanometer scale (Figure 7).

Impact results for P/NP(7/3)F/AP formulations containing 80 wt-% (Table 3) show that AP nanocompositions are less sensitive than mixture of powders (macrosized formulation). Moreover, during decomposition, the pressure released by the decomposition process is higher in the case of nanosized formulations.

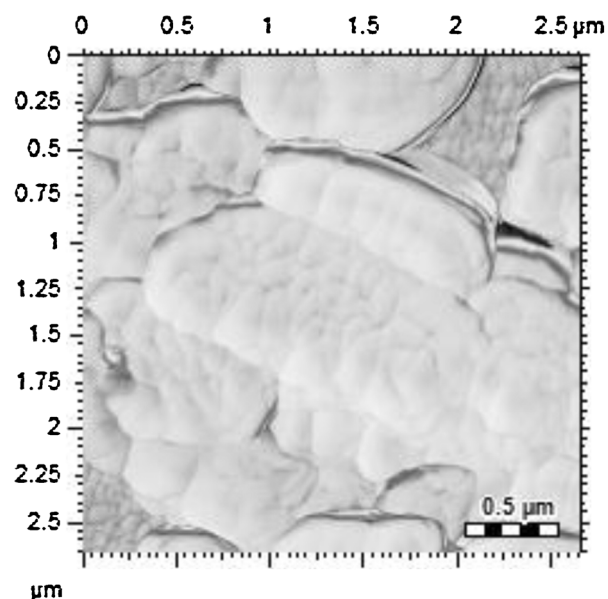


Figure 7. AFM image of 90 wt-%RDX nanocryogel.

Table 3. Drop-weight results on AP formulations.

Sample	Impact ( $H_{50}$ [mm]/ $P_{MAX}$ [MPa])	
	Macro	Nano
P/NP(7/3)F/AP 20/80	215/0.106	500–700/0.2–0.33

Table 4. Drop-weight results on RDX formulations.

Sample	Impact ( $H_{50}$ [mm]/ $P_{MAX}$ [MPa])	
	Macro	Nano
P/NP(7/3)F/RDX 25/75	138/0.211	130/0.148
P/NP(7/3)F/RDX 10/90	170/0.485	99/0.460
RDX various crystal sizes	100 to 150/ $\approx$ 0.5	–

Table 4 describes the drop-weight results for P/NP (7/3)F/RDX formulations containing 75 and 90 wt-%. Sensitivity of nanosized formulations are the same as sensitivity of macrosized and even of intrinsic RDX ones. When the RDX weight percentage is under 90, the pressure released by the decomposition is lower in the case of nanosized formulations. The better dispersion/dilution of RDX in the matrix in the case of nanocompositions (better matrix coating) can explain this phenomenon. When increasing the part of intrinsic explosive of the composition up to 90 wt-%, sensitivities and reactivities of macro and nanoformulations are all the same and they are close to the pure RDX reactivity.

### 3.2 Combustion Behavior of AP Formulations

#### 3.2.1 Closed-Vessel Combustion

These tests were performed on nanocryogel and mixture of powders. After a few preliminary tests on mixtures of pow-

ders, a pressing sequence of  $3 \times 100$  MPa with a temperature of  $60^\circ\text{C}$  was selected to obtain pellets of nanocryogels and macrocryogels with a density of  $1.65\text{ g cm}^{-3}$  from powders issued from dry crushing and powder mixing. For these experiments, two different nanostructuring matrixes were tested [6]: a PF matrix synthesized from phloroglucinol (P) and formaldehyde (F) and the P/NP(7/3)F matrix described in the first part of this article. Whatever the matrix, the nanoformulation process was the same as described in the Experimental Part above.

For all the different formulations, the linear combustion rate was estimated as a function of pressure making strong assumptions on the burning surface of the pellets during the test. Results are presented in Figure 8.

Whatever the pressure and whatever the type of structuring matrix, the burning rate of nanosized formulations is about two or three times higher than the one of mixtures of powders and the combustion is regular. These results are in agreement with drop-weight tests: nanostructuration allows a significant improvement of the decomposition by combustion of the formulations. In addition, nanostructuration guarantees a stable combustion all over the explored pressure range (pressure exponent  $< 1$ ).

The two nanosized formulations burn regularly. But, for one of the mixtures of powders (PF/AP), the well-known phenomenon of deconsolidative burning above a critical pressure of 5 MPa despite the high density of the pellet occurs. The pellet cracks due to thermal stress during the combustion inducing a sudden increase of the burning surface, which is materialized by a break-up of the pressurization speed slope above a certain pressure. It is not the case with P/NP(7/3)F as a matrix probably because of its different thermomechanical properties.

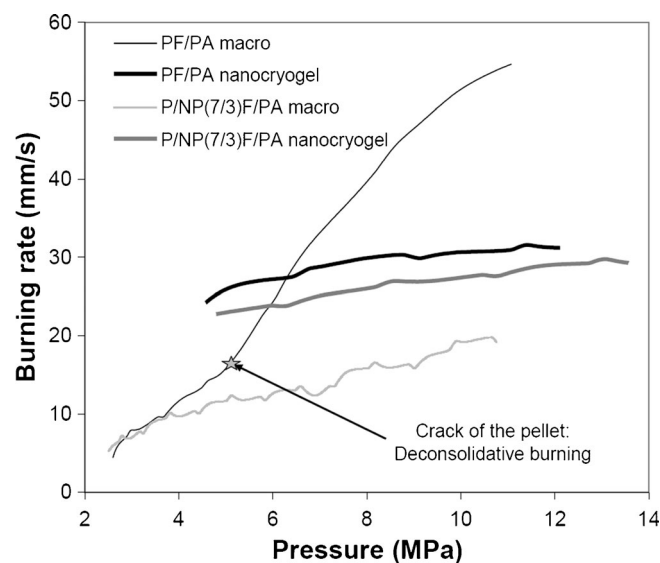


Figure 8. Closed-vessel: burning rate vs. pressure.

### 3.2.2 Ultrasonic Method

The ultrasound method used by ONERA is similar to the classical emission/reception non-destructive technique [7]. An ultrasound transducer emits a mechanical wave, which travels through the sample. This wave is reflected on the burning surface and comes back to the transducer. A specific electronic device allows one to follow the displacement of the burning-surface echo from its initial position up to the end of burning. Therefore, it is possible to get in one shot the linear combustion rate of solid propellants vs. pressure in a large range. For this experiment the cylindrical surface of the pellet is inhibited with a resin.

Such experiment was performed on nanocryogel P/NP(7/3)F/AP (20/80 wt-%) and equivalent mixture of powders under pellets form. To obtain pellets (10 g) of 16 mm diameter with a density of  $1.78\text{ g cm}^{-3}$ , a pressing sequence with a temperature of  $60^\circ\text{C}$  and triple cycle pressure was applied. The pressure was 110 MPa for nanocryogels and 150 MPa for macrocryogels. No binder was used. The density of the pellets is different than the one of closed-vessel pellets because it is needed to reduce as much as possible the residual porosity to prevent the penetration of the resin in the pellet.

The results obtained (Figure 9) confirm the closed-vessel experiments ones: the burning rate of the nanosized formulations is about two or three times higher than the one of mixtures of powders and the pressure exponent is lower in the case of nanosized formulations all over the explored pressure range. In the case of mixture of powders, the heterogeneities of the matter induce noise in the burning rate measurement.

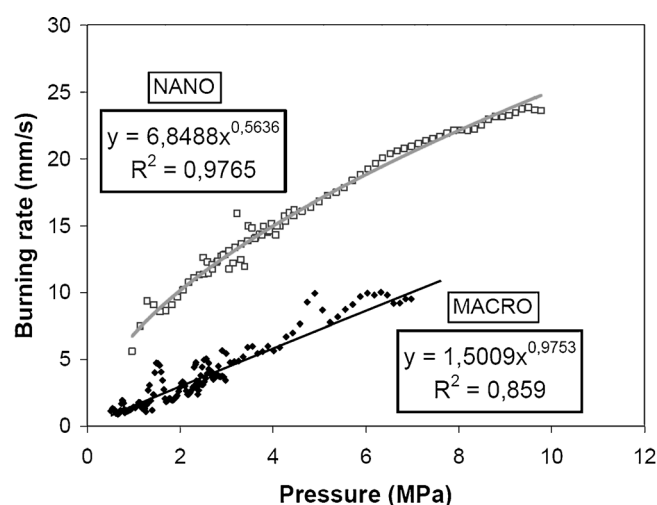
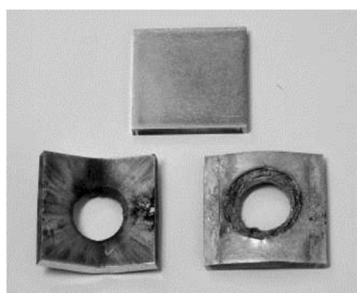
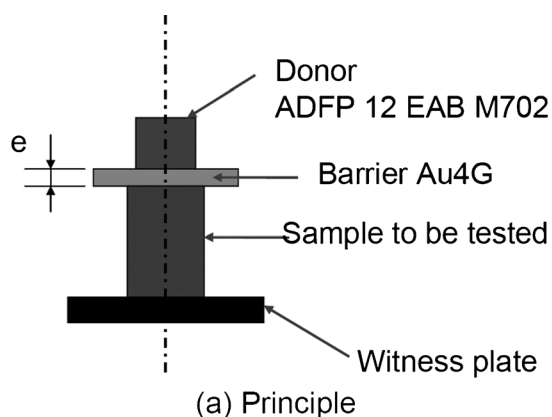


Figure 9. Ultrasonic method: burning rate vs. pressure.



**Figure 10.** Experimental device for SSGT. (a) Principle. (b) Witness plate before and after a positive shot.

### 3.3 Small-scale Gap Tests (SSGT) on RDX Formulations

The SSGT is performed using the experimental device described in Figure 10. The donor is a 7 mm diameter detonator and the sample is a 10 mm diameter pellet.

The key point of this device is the barrier that isolates the donor from the explosive sample. The sample itself lies on a witness plate. The barrier is characterized by its thickness ( $e_{50}$ : the thickness, for which 50% of the donor shock wave induces the initiation of the explosive sample). The evaluation is normally performed by a classical up-and-down method on 30 samples. The smaller the  $e_{50}$ , the less sensitive is the composition.

Each sample tested was preliminary processed into pellets. The challenge was to define the residual porosity volume of the compositions since it is the key-point for initiation studies. It was decided to set it to 5%, which corresponds to a density of  $1.65 \pm 0.02 \text{ g cm}^{-3}$ . Pellets of 10 mm diameter of nanocryogel P/NP(7/3)F/RDX (10/90 wt-%) and equivalent mixture of powders were obtained by uniaxial pressing without any additional binder. A pressing sequence of  $5 \times 200 \text{ MPa}$  was applied on nanosized formulations and  $1 \times 150 \text{ MPa}$  on the macrosized ones. The temperature was  $60^\circ\text{C}$  for both sequences. For each formulation, eight pellets were prepared.

Table 5 summarizes the gap test results for nanosized and macrosized 90 wt-% RDX compositions free of binder, compared with results obtained previously on a formulation containing HMX, TATB, and a fluorinated binder.

**Table 5.** SSGT results.

Formulation		$e_{50}$ [mm]	Confidence limits
P/NP(7/3)F/RDX (10/90) 95 % TMD	Macro	2.70	[2.52–3.01]
	Nano	1.84	[1.51–2.22]
HMX/TATB/technoflon (65/30/5) 98 %TMD		1.88	[1.78–2.00]

Despite large confidence limits, due to the reduce number of pellets available, it can be asserted that pellets of nanocryogel are significantly less sensitive than the equivalent pellets of mixture of powders. When RDX is nanosized,  $e_{50}$  decreases: the smaller the RDX particles, the safer the RDX composition is. It is expected that such behavior is partly related to the smaller void size remaining in the nanosized RDX particles as described by Stepanov et al. [8]. But, these results need to be confirmed and additional experiments such as critical diameter determination have to be carried out. It is known that the critical diameter of the RDX, near its theoretical density, is about 1 to 2 mm. If the values of  $e_{50}$  of Table 5 are considered, the SSGT will not be biased by troubles of propagation in the pellet just after the gap if the critical diameter of the tested compositions is the same than RDX. But, if it's not the case, gap test with a higher diameter to confirm these first results would have to be performed.

The RDX crystals of the macrocompositions can be damaged during the pressing sequence because of the lack of binder and the size of the crystals. Some additional defects can be introduced, which can sensitize the macrocompositions pellets to shock and then amplify the measured  $e_{50}$  difference between macro and nanocompositions. Nevertheless, the pressing sequence of the nanosized formulations needs more pressure and more cycles to obtain the same pellet density so it remains difficult to conclude about the effect of pressing on shock response.

That's why the pressed nanocryogel containing 90 wt-% nanosized RDX (nitramine), no binder and 5% residual porosity was compared with a pressed PBX formulation containing HMX (similar nitramine as RDX on a shock sensitivity point of view), 30 wt-% TATB, and only 2% residual porosity. Their sensitivity thresholds are nearly similar and thus provide good illustration of the potential of high energetic material nanostructuration to reduce the shock sensitivity.

## 4 Conclusions

A nanodispersion process allowing nanostructuration of up to 90 wt-% charge (AP or RDX) in an organogel matrix was developed. XRD and SEM analysis were used to demonstrate that the charge is homogeneously nanodispersed. The potential of this process is its changeability: in case of

propulsion application it is possible to change the amount of AP depending on the expected oxygen balance. In the case of explosive applications, it is possible to adapt the process conditions (temperature, duration, drying, and solvent) to change the charge nature or increase its ratio. It could also be interesting to mix different charges in a same matrix, or even improve the intrinsic energetic performances of the matrix.

On an energetic point of view, when organogels impregnation is performed with saturated solution of AP, the impact sensitivity of dried nanoformulation containing 80 wt-% charge is significantly lower than macroformulation one and their decomposition is more powerful. For RDX nanoformulations, the impact sensitivity is equivalent to macroformulations whatever the RDX wt-%, but the reactivity is lowered as soon as the RDX wt-% is below 90.

According to the results obtained using the closed-vessel experiment or the ultrasonic method (ONERA), 80 wt-% AP nanocompositions show a stable increase in the burning rate compared to their macro equivalent. Thus, it could be demonstrated that AP nanoenergetic materials have an interesting energetic potential compared to their macroscopic equivalent.

In the case of RDX, the work performed on 90 wt-% nanoformulations proves that RDX nanostructuration induces a significant benefit in terms of safety towards mechanical aggressions of the formulation. Next, the steady-state detonative behavior of the 90 wt-% RDX compositions (nanosized and macrosized) will be studied (critical diameter, detonation front curvature, pyrometry,...).

The 90 wt-% RDX nanoformulations are produced today as macroscopic powders. These powders could be used directly without further processing in detonators. To enlarge the use of these desensitized high energetic materials in boosters or as loading explosives, the mechanical properties of the formulations will have to be improved using a binder. Therefore, it is intended to have a look on the formulation of plastic-bonded explosives containing 90 wt-% RDX nanoformulation. Moreover it is expected to compare as soon as possible the behavior towards shock of a PBX formulation containing nanosized 90 wt-% RDX and an

equivalent PBX formulation containing reduced sensitivity RDX [9].

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