Use of Nanoaluminium in HTPB/AP/Al propellants

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Abstract

The effect of aluminium size on the combustion of HTPB/AP/Al composite propellant is now widely described in the literature. This paper describes the work performed by SNPE Matériaux Energétiques on HTPB/AP propellants containing aluminium nanoparticules. Firstly, characterization of different types of nanometric particles used in propellant formulation is presented. It is shown that they differ by their passivating layer and the overall proportion of metallic aluminium. Considering the various formulations of propellants, many burning rate enhancements are observed depending on aluminium particles properties and propellant composition. The maximum burning rate increase is roughly of 80% as it is often reported in the literature. This increase is to be related to a nearly constant pressure exponent with the pressure evolution. The effect of the change of scale in aluminium size is investigated by a comparison with aluminised propellants. The introduction of nano aluminium powders can slightly modify the propellant ballistics, and for specific formulations, a 'mesa' effect, characterized by a near zero value for the pressure exponent, is exhibited. The effect of nano Al on mechanical properties is also assessed using conventional tensile experimental. The influence of the HTPB cross-linking density is examined to enhance the mechanical properties of such propellants. It is found that nanosized particles induce change in mechanical properties such as an increase of the overall rigidity.

Introduction

Aluminium powders are currently used in solid propulsion to enhance the energetic performance of the motor. The combustion of aluminium droplet leads to the formation of alumina residue with eventually unburned or not completely burned aluminium droplets. The presence of such a condensed phase can reduce the instabilities phenomena depending on the motor geometry and scale, but the accumulation of a large part of these condensed products in the motor chamber. By this way, the total weigh is increased by this additional mass which is not exhausted. With traditional aluminium particles (diameter ~45µm) combustion may not totally be completed in the chamber and especially for laboratory scaled motors. For these reasons, it seems to be interesting to reduce the particles scale in order to achieve their combustion, decrease the aluminium droplet combustion time and limit the aluminium agglomeration accruing at the propellant burning surface. First analysis on combustion residues obtained for nano-aluminised propellants can be found in [1].

Some advances on the mechanism involved in the combustion of micrometric aluminium droplet are available [2], [3], [4]. It is generally assumed that the droplets burn in the gas phase with a diffusion flame. However with the size reduction, it is more than likely that the combustion on nanoparticles changes the propellant flame structure. The mechanism is still not completely described although some pieces of answer can be found in recent papers [5], [6], [7].

The work performed at SNPE Matériaux Energétiques deals with the characterization of 4 aluminium particles types and the formulation of propellant formulated with these qualities of aluminium. Propellant formulation includes HTPB binder with ammonium perchlorate fillers. Aluminium particles used in this study are either micrometric or nanometric (cf. Table 1). Different techniques are used to determine the average particles size (SEM and TEM techniques). The thickness of the protecting layer is obtained and analysed by Electron Energy Loss Spectrometry (EELS) coupled with TEM visualisation. The oxidation in air is studied through the Thermo Gravimetric Analysis (TGA). A classical BET technique is used for the determination of the specific area.

Component analysis and propellant formulation

Aluminium characterisation

Aluminium qualities differ by the nature of their protecting layers which prevent further oxidation of the particles. For nano sized aluminium N1, an organic coating is added to the alumina layer. In the case of the nano-aluminium N2, the coating is composed by only alumina formed in a controlled environment. The aluminised components used in the propellants formulation are independently characterized and analysed. Details of the used methodology can be found in [8], however, it is interesting to recall that :

- visualisations of nanometric aluminium powders (N1 and N2) performed by SEM and TEM analysis show a multi-sized distribution with an average size of approximately 200 nm. However, some larger particles (more than 1 µm) can be observed in the sample. The larger sized micrometric powder exhibits a 6 µm diameter. Considering TEM visualisation, nano-particles N1 does not exhibit any pronounced agglomerated formation but some 'bridges' linking individual particles can be observed. In comparison, the sample N2 is characterized by a more agglomerated aspect. The nature of the coating can explain such a difference.
- The specific area is determined by a BET method based on the adsorption of nitrogen. Coupling with the average particles diameter, this analysis also provides information on microporosity in case of abnormal high value of the surface area. As expected, nano sized particles exhibits large specific surfaces.
- Electron Energy Loss Spectrometry (EELS) method coupled with TEM visualization is used to measure the thickness and composition of the protecting layer. For each type of particles, the thickness of the natural alumina layer is nearly the same and its value is 4 nm. For aluminium powder N1, an additional protecting layer covering the amorphous alumina layer, is constituted by a 2 nm thick organic coating.

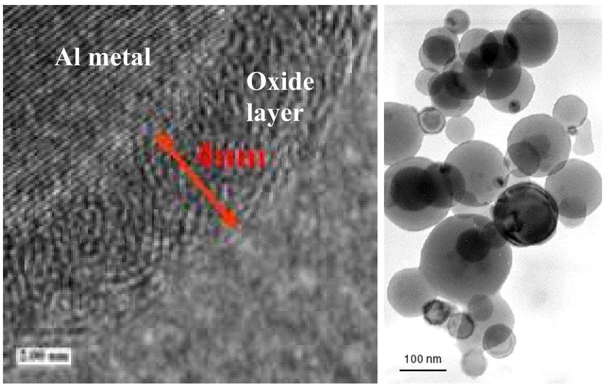


Figure 1 : examples of TEM visualisations

The Table 1 summarises the main properties observed on the different aluminium powders.

Table 1 : aluminium powders properties

	N1	N2	M1	M2
Average diameter [µm]	0.25	0.25	1.7	6
Protective layer thickness [nm]	4	4	4	4
Metallic aluminium proportion %	78	80	94	98
Specific area [m²]	11	10.9	-	-
Protecting layer and coating	alumina + organic compound	alumina	alumina	alumina

Information on the thermal behaviour of the powders can be obtained by conducting Thermo-Gravimetric Analysis (TGA) in air environment. The weight evolution for nanosized samples (N1 and N2) shows a preliminary weight loss that can be observed up to 450°C. This phenomenon is attributed to the loss of water, organic residues or contaminants present in the protecting layer. On the other hand, mass gain characterizes the powders evolution as soon as temperature is higher than 450°C. For nanosized powders, a first oxidation phase occurs until the temperature reaches 550°C, prior to the melting temperature of aluminium. The gain in weight for N1 and N2 powders is about 33% at 530°C. On the contrary, a micrometric aluminium powder of 45 µm in diameter reacts very little with a mass gain less than 1% (not used in this study but details can be found in [8]). A step can be observed at 600-630°C that is associated with the melting of aluminium (endothermic transformation). Then, a second oxidation takes place at 660°C and leads to a value 70% of mass gain for nano aluminium samples. After performing a temperature cycle, *i.e.* increase up to 850°K, EELS analysis reveals only the presence of oxygen, without any trace of nitrogen. This result is in accordance with those of Larichev [9] and confirms the hypothesis that only oxidation phenomena occur. The mass evolution of the micrometric aluminium presents a totally different aspect and only the second oxidation seems to occur. At 1000 K, the total mass gain for this 45 µm sized particles is only 8% which lets us presume a rather low oxidation. This process seems to be linked with the low specific area which is a prime of importance parameter in the oxidizer diffusion through the protecting layer [10].

Propellant formulation

Propellant formulation used in this study is chosen to be comparable of those traditionally used in solid rocket motor. The formulation is referred as a mix of 68% in mass of Ammonium Perchlorate with 17% of aluminium powder. In the purposes of comparison, several types of aluminium particle, presented in Table 1, are considered to precise the influence of the particle size on both ballistic characterisation and mechanical properties.

In the frame of this study, six HTPB/AP/Al (15/68/17) propellants are tested. Their composition is presented hereafter in Table 2.

Table 2 : formulation of studied propellants

Component Mass proportion	Binder 15%	AP distribution 68%	Aluminium 17%
Propellant 1 (P1)	R45HT	Trimodal	Coated nano powder N1
Propellant 2 (P2)	R20LM	Bimodal	Coated nano powder N1
Propellant 3 (P3)	R45HT	Bimodal	Coated nano powder N1
Propellant 4 (P4)	R45HT	Trimodal	Uncoated nano powder N2
Propellant 5 (P5)	R45HT	Trimodal	Uncoated micro powder M1
Propellant 6 (P6)	R45HT	Trimodal	Uncoated micro powder M2

The main problem encountered with mixing HTPB/AP propellant with nano-aluminium particles is due to the elevated viscosity [5], [11]. For this reason, a special HTPB binder (R20LM), with a relatively low molecular weight, was used in a first stage of the study. This is a characteristic of propellant P2. It presents a homogenous aspect without any appearing default such as cracks as it can occur for higher nano-aluminium proportion [11]. In a second time, an adaptation of propellant manufacturing methodology was proceeded : the standard binder replaced the previous one in order to achieve standard Solid Rocket Motor formulation (referred as P1, P3-P6 in this study).

Ammonium Perchlorate size distribution was also chosen in a first time to reduce the viscosity during manufacturing (i.e. before curing). In association with binder R20LM, a bimodal AP characterised fine and coarse particles is considered. In a second time, modifications and improvements were adopted to achieve a trimodal AP distribution (propellants P1, P4-P6).

Combustion tests

It is often reported in the literature that replacing micrometric aluminium by nanometric aluminium leads to a dramatic change in the propellant ballistics. Although propellants described in the literature do not present the same composition as the ones studied in this work, the combustion is characterized by a more or less important increase of the burning rate which can reach 100% [5], [6], [11]. A change of the pressure exponent is also observed and visualizations always show a flame characterised by a higher luminosity [5], [6], [7]. Although the combustion mechanism is not clearly understood (although some promising ways are provided in [1], [8], [12]), it is supposed that the combustion of nano particles strongly affects the propellant flame structure. These changes affect the burning rate which is measured by currently used technique of Ultra-Sound method for a pressure range of 1MPa up to ~25 MPa. All results plotted in the two following figures are obtained by this experimental way.

Early work performed at SNPE Matériaux Energétiques exhibits an amazing effect of aluminium powder in specific composite propellant [8]. It consists in a "mesa" effect in the burning rate evolution with the pressure as it can be seen on Figure 2. The burning rate evolution with regard to the pressure can then be divided into three specific ranges. A first one is characterised by P between 1 and 7 MPa and a monotonous increase of the burning rate with the pressure. The second one is the mesa effect for P lower than 15 MPa. The last one exhibits an increase of the burning rate for P larger than 15 MPa. Considering the propellant formulation, this effect seems to be related to the low molecular weigh of the binder as indicates the comparison of the curves plotted on Figure 2. Such an effect characterised by a rather low or negative value of the pressure exponent was also observed by Zarko but HMX and AP containing propellants were considered and burning difficulties sometimes leading to a mass burning were also reported in this case.

As it can be show on Figure 2, the modification in the nature of the components, but with keeping the same proportions, leads to significant variation of the burning rate.

- The first appreciable change consists in the disappearance of the "mesa" effect by replacing the R20LM binder by the R45HT binder. However, further developments on the combustion mechanisms and the effects of nano aluminium particles in association with R20LM binder would have to be conducted to explain the quasi-constant burning rate in the 7 to 15 MPa pressure range (propellant P2). The action of nano sized particles on R20LM binder still remains not clearly understood.
- The comparison between P2 and P3 results shows that reducing the AP distribution size induces a significant increase of the burning rate. Such a behaviour can be explain by considering a modification of the diffusion flame structure at the propellant surface, but also in limiting the agglomeration of aluminium particles. It follows that aluminium particles burn or are oxidised very close from the surface and then enhance the heat flux feeding back to the surface [7].

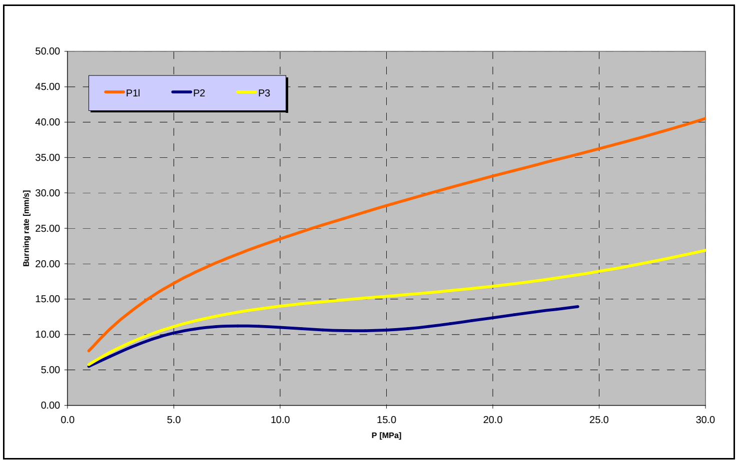


Figure 2 : effect of components nature on burning rate

On Figure 3, burning rates of several propellants is plotted. These propellants respectively correspond to P1, P4, P5, P6 where the formulations differ only by the type of aluminium powders. As it is often reported in the literature the higher burning rate is obtained for nano-aluminised propellants. For the two nano-sized powders, the uncoated particles provide the highest rate for all pressure range.

Considering the micrometric propellants P6 as reference, the gain on the burning rate can be analysed. An important increase is observed with a maximum value obtained at a pressure of 7 MPa for both nanometric propellants (P1 and P4). For the propellant with uncoated aluminium (P4), the increase reaches 80% of the reference burning rate (P6) whereas the increase is limited to 50% for the propellant P1. This indicates the significant influence of the aluminium quality, and especially of the coating, on the burning rate. For higher pressures (i.e. larger than 7 MPa), the gain collapses. For instance, at 20 MPa, it falls to 24% for P1 and 61% for P4 (the reference burning rate is always with propellant P6).

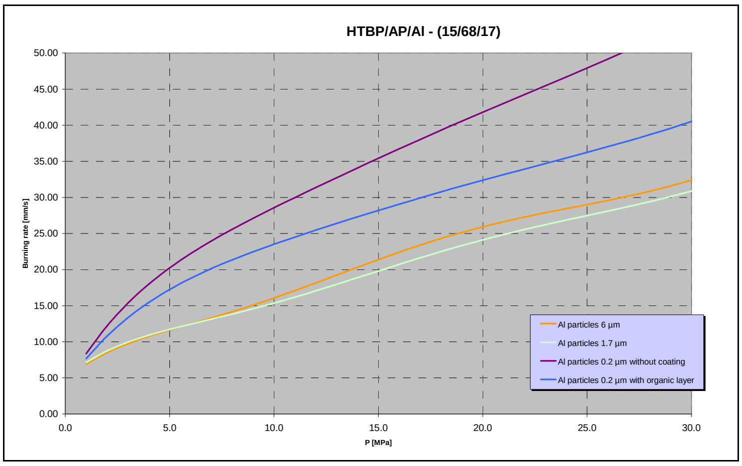


Figure 3 : burning rate for different aluminium powders

It is also interesting to note the quasi identical burning rates for micro-sized propellants. Referring to Trubert's analysis [12], this behaviour can be explained by considering the agglomeration phenomenon. The AP distribution in sizes exhibits that smallest AP particles have an average diameter close to 10 µm. The application of agglomeration pockets theory provides the possibility of forming aluminium agglomerates of that diameter. It results in the combustion of large aluminium droplets which size is comparable to the 6 µm particles used in the propellant P6. By this way the effect of aluminium size on burning rate remains limited due to the AP size distribution.
By modelling the burning rate with a classical Vieille Law ($r_b = aP^n$), a second observation can be made due to the presence of nano aluminium particles. The evolution of the pressure exponent *'n'* with the pressure remains nearly constant with a value of 0.5 with a pressure spreading from 1 MPa to 10 MPa. Such a behaviour is not observed for microaluminised propellants.

The explanation of the effect of nano powders on ballistics is not clearly understood (and especially on the value of the pressure exponent). Visualizations of the burning surface show a more luminous flame with a possible heat feed back to the surface by radiation. Probable changes of the flame structure are proposed by several authors [5], [6], [7], [8].

Mechanical properties

Mechanical properties are estimated through the well known tensile test which gives the strain through the stress applied to the propellant. They are based on an average of three tensile measurements conducted at 20°C with a velocity of 50 mm/min. The objective is to compare the mechanical behaviour of propellants differentiated by the nature of aluminium used in their formulation. A specific focus is made on the cross-linking of the polymeric chains : three cross-linking rates are investigated conducting in the formulation of three types of propellants based on P4 propellant : the values are 0.85, 0.9 and 0.95.

The volume variation of samples is also examined thanks to Farris tensile test allowing to access the following quantities (cf. Figure 4 for the meaning):

- the tensile modulus E_{tg},
- the maximum stress S_l before breaking,
- the maximum strain e_l,
- the tangent α,
- binder/load bonding limit e_d,

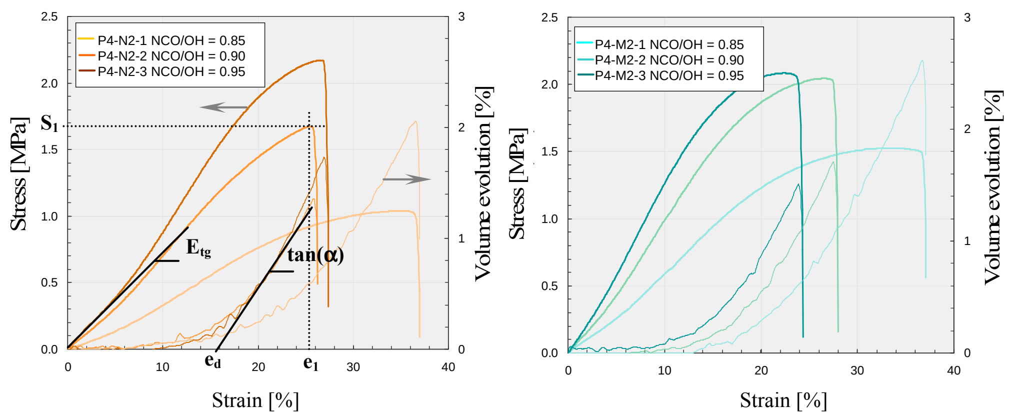
The Table 3 presents the propellant definition and the corresponding mechanical properties obtained.

Table 3 : tested propellants definition and mechanical results

	Cross-linking	HTPB %	PA %	Al %	E_{tg} [Mpa]	S_1 %	e_1 %	tan(α)	e_d %
Nanometric Al				**N2**					
P4-N2-1	0.85	15	68	17	4.06	0.97	29.5	0.081	18.8
P4-N2-2	0.90	15	68	17	7.92	1.70	24.1	0.112	13.9
P4-N2-3	0.95	15	68	17	11.0	2.14	23.7	0.131	14.5
Micrometric Al				**M2**					
P4-M2-1	0.85	15	68	17	6.32	1.47	31.5	0.127	18.1
P4-M2-2	0.90	15	68	17	9.88	2.03	25.4	0.126	14.9
P4-M2-3	0.95	15	68	17	12.6	2.10	21.6	0.115	12.9

On Figure 4 are plotted the experimental studied quantities before the sample broke. Corresponding data are summarised in the Table 3. From these curves analysis, the main issues are :

- Elastic modulus and the breaking stress increase although the maximal strain decreases
- The bonding limit appears faster with the sample rigidity icreases
- For micro-aliminised sample, the volume expansion rate is independent from the cross-linking, whereas an increase is observed with the nanosized aluminium particles.
- A limit in term of strain is observed for nanometric aluminised sample
- A limit in term of maximum stress is observed for micrometric aluminised sample



a) nanosized aluminium *b) microsized aluminium*

Figure 4 : traction test and Farris results

It is interesting to present the results by plotting the maximum stress before breaking in function of the corresponding strain as it is shown on Figure 5. For a given family of propellants, all dots are located on a same curve which generally is an hyperbole considering the assumption that the formulation differences do not modify the binder matrix. The deviation from this curve is representative of the matrix perturbation due to either different cross-linking rates or different specific areas in the AP loading. Two ways of action are then identified : the influence of the nano sized aluminium particles is located either in the matrix network itself or at the binder/loading interface. The volume evolution should give indication on which phenomenon happens.

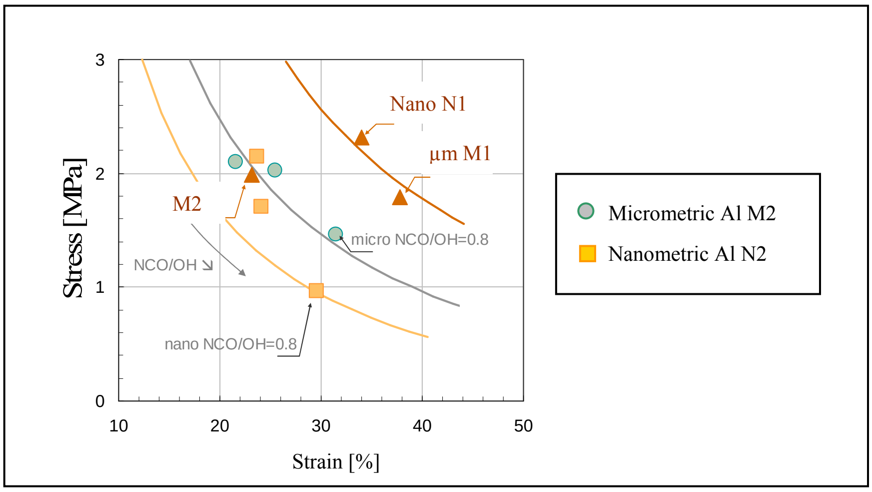


Figure 5 : stress vs. strain

Considering the micrometric propellant, it is observed that the increase of the cross-linking rate leads to a decrease of the breaking strain. This increase of the rigidity is naturally associated with a reduction of the e_d limit. The tan(α) parameter remains nearly constant, which suggests no significant modification of the binder/AP bonding. For nanometric aluminium loaded sample, the tan(α) parameter increases with the cross-linking (cf. Figure 6). This indicates that the overall damaging is limited and that the interaction of the nanoaluminium is preponderant at the binder/AP interface where it takes place.

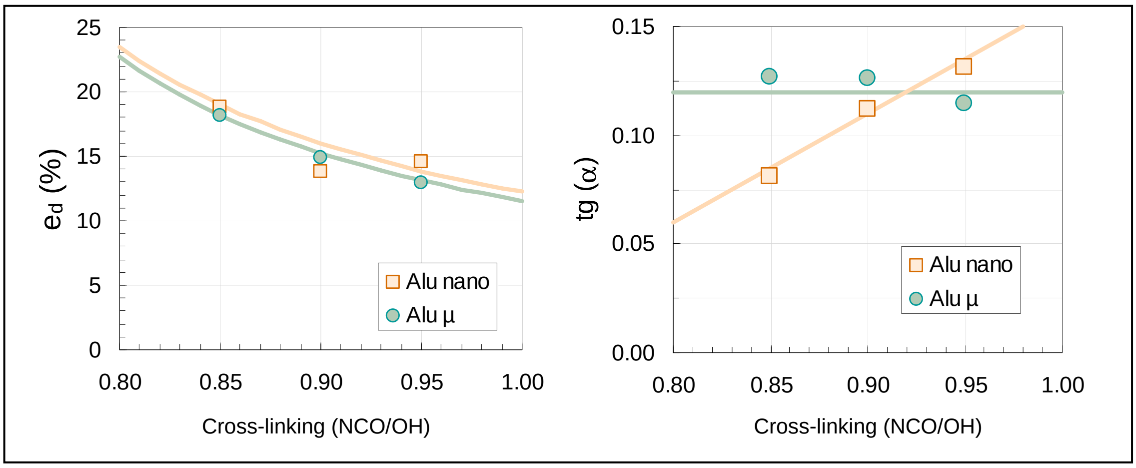


Figure 6 : effect of the cross-linking evolution

CONCLUSIONS

Different nano sized aluminium powders are analysed through advanced methods. Visualizations by SEM and TEM reveal an initial agglomeration phenomenon. The mean particle diameter is evaluated at 0.2 µm although a multi-sizes repartition is clearly shown. The thickness of the protecting layer is nearly 4 nm. The thermogravimetric analysis proves that two oxidation steps up to 1000 °C can be identified for nanoparticles. Studied propellants are formulated in order to avoid the apparition of defects and guarantee a homogeneous grain. First experiments on evaluating the mechanical properties gave interesting results. They show different behaviour by considering nano or micro sized particles. For nano particles, their interaction seem to be located at the binder/AP load interface. From the ballistics point of view, replacing traditional micrometric aluminium increases the burning rate up to 80 % for moderate pressures (i.e. 7 MPa). Results are more contrasted for a higher pressure range (15-20 MPa) with lower gain. The nature of the protecting layer is also a parameter controlling the ballistic. For nano particles, a 'mesa' effect can be observed between 7 and 15 MPa. This interesting ballistic behaviour seems to be dependant on the binder nature.

These results are encouraging. They show how promising can be the use of nano aluminised in propulsion by providing large burning rate with a low pressure exponent variation (n~0.5). However, an important work is still necessary to understand its influence on combustion phenomena and its effect on the mechanical properties. Mastering of such composite propellants in operating conditions remains a challenge.

ACKNOWLEDGEMENTS

The authors would like to thank the French MoD Procurement Agency (DGA) for funding this study. The authors would also thank the Madirel Laboratory (University of Provence) for its participation in the physico-chemical analysis and the thermal analysis.

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