Research paper

Effects of HTPB-coating on nano-sized aluminum in solid rocket propellant performance

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Abstract

The modification of the solid propellants with nanosized aluminum has been studied. The nanosized aluminum has been found to improve burning characteristics of the propellants. The surface treatment of nanosized aluminum has been shown to affect the processabilty of formulations prepared. The physical properties including viscosity of uncured propellant mass was studied.

Keywords : nanoaluminum powder, HTPB, ALEX, organic coating, regression rate enhancement.

1. Introduction

The enhanced reactivity of nanosized aluminum (nAl) arises interest for propulsive systems: replacing the micrometric aluminum (μAl) with nAl in solid rocket propellants leads to increase of burning rate and decrease in agglomerate formation at the near-surface zone[1].

Nevertheless, a total substitution of μAl with nAl presents brings limitations: viscosity of the uncured formulation results increased, leading to manufacture and castability problems[2,3], and active aluminum content, and as consequence, also the theoretical specific impulse is lower[4]. A partial substitution of μAl with nAl is then proposed, showing a progressive increase in performance with nanosized fraction increment[5,6].

Even in formulations containing small fraction of nanosized particles (NP), cohesion problem is relevant, and attempts to mitigate it involve different mechanisms. Sonochemistry[7], high energy mechanical systems[8] or pre-dispersion in a solvent[9] are probably the most exploited strategy. Chemical methods are often used to disperse and stabilize NP in nanocomposite, sometimes together with the physical techniques previously mentioned. Modification of the surface to fight agglomeration or to functionalize NP is an important chemical challenge that can contribute to the exploitation of the unique features nanocomposites possess. Various strategies, that can also be combined, have been proposed to modify metal NP surface[10]: organosulfur compounds, like thiols and disulfides can be deposed on particles with solvents or can be added directly to the solution with precursor. Amines as well can be used, but the bond with metal is weaker with respect to organosulfur compounds. In order to modify metal oxides, phosphonates has been studied because of the connection through the oxygen of the oxide. The use of catechol to improve connection between a metal surface and a polymer is reported in Reference.[11]. The bond between oxide and polymer is created through -OH groups and through the electron system of the aromatic ring. Another coupling agent can be acetylacetone which used in Reference.[12].

In the present work the common formulation propellants based on ammonium perchlorate (AP) and hydroxyl terminated polybutadiene (HTPB) cured by isophorone diisocyanate (IPDI) with tin based catalyst and dioctyl adipate (DOA) as plasticizer were studied. Both μAl nAl were added to formulations for enhancing the burning characteristics. nAl additives were treated with organic compounds to improve the processabilty of formulations prepared.

2. Experimental

2.1 Coating of ALEX

In order to improve dispersion degree of nAl in solid propellants and to decrease viscosity of the formulation, the coating of ALEX with the HTPB used as binder is proposed. The optimization of the coating is carried out with comparison two coupling agent, catechol and acetylacetone, two solvents, ethyl acetate and mineral spirit and various percentage of HTPB: 0, 1, 2, and 5 per cent. First, coupling agent is dissolved in the selected solvent, then ALEX is added and mixed with high shear homogenizer (HG-15D, Daihan) at 5000 rpm. After 30 min, HTPB dissolved in the same solvent is added to ALEX and the mixing continues for another 30 min. Evaporation of the solvent is carried using a rotary evaporator (Bchi Rotavapor R-200). With this procedure 16 powder samples have been prepared and compared to find the most suitable to be applied in solid propellants.

2.2 Preparation of propellant

A series of 4 propellants, obtained with a standard lab-scale manufacture procedure, is considered in this work. All formulations share the same composition reported in Table 1, but differs in the kind of aluminum additive used: HTPB coated powder (H-ALEX) is compared with uncoated ALEX and with standard 30 μm aluminum. Another formulation contains 9% μAl and 9% H-ALEX.

The binder is resin HTPB, grade R-45HTLO (Sartomer), cured with IPDI. A tin based curing catalyst is added to the formulation and DOA as plasticizer is used. In the first stage HTPB and DOA are mixed together by means of a propeller mixer. A vacuum cycle is realized to extract air bubbles. Aluminum is added and another vacuum cycle is performed. AP coarse, and then AP fine are introduced into the compound. After 10 min mixing the preparation is moved to a mechanical kneader (Braebender) for 1 hour. During this time IPDI and tin catalyst are added. The formulation is finally placed into a Teflon mold for curing.

Uncured formulations with fixed proportion 50%AP/32%HTPB/18%Al for rheological analyses are prepared. A monomodal AP distribution is considered (nominal size 50 μm) and μAl (5-10 μm) is progressively substituted with nAl, comparing ALEX with H-ALEX.

Table 1 Standard composition of tested propellants.

Material	Nominal size [μm]	Mass Fraction [%]
Coarse AP	200	58
Fine AP	5−10	10
Aluminum	0, 1 and 30	18
Binder	−	14

2.3 Characterization of coated nAl

The selection of the most suitable HTPB coated nAl powder is carried out considering various parameters. Size distribution is evaluated through the disc centrifuge CPS24000 (CPS Instruments). Direct visualization of the quality of the coating is possible with transmission electron microscopic (TEM) analyses, for this purpose a FEI QUANTA 200 3D instrument is used.

Aluminum content is evaluated with volumetric measurements[13].

Analyses to measure the stability of the powders against moisture are carried out placing about 2 g of powders in a tight vessel with relative humidity 90%. Aluminum reacts with water vapor, monitoring the increase in weight of the samples makes possible to evaluate the degree of reaction α:

$$\alpha = \frac{m_t - m_o}{m_f - m_o} \tag{1}$$

where m_t is current weight of the sample
m_o is initial weight of the sample
m_f is final weight of the sample.

2.4 Burning rate and ignition delay

In order to measure the burning rate of solid propellants, strands (4 × 4 × 30 mm) are cut from the batch and treated in order to inhibit lateral combustion. Tests are performed in a tight vessel in a range of pressure from 0.2 to 4 MPa, using nitrogen as pressurizing gas. Combustion is recorded through a high-speed camera, then post-processed by an automated proprietary software, and finally burning rate results are fitted according to the standard Vieille's law:

$$r_b = ap^n \tag{2}$$

Propellant cubes with 5 mm side are used to evaluate ignition delay. Samples are placed in a tight vessel where a nitrogen atmosphere is maintained, and they are irradiated with a laser beam. The signal from a laser detector is acquired by a digital oscilloscope, together with the signal from a photo-diode, facing the window of the combustion chamber. The time between the laser firing, supplied by the laser detector, and the start of combustion, readable from the photo-diode signal, is referred to as the ignition delay.

2.5 Viscosity measurements

Viscosity measurements of uncured formulations are carried out using viscometer Rheotest 2.1 (Medingen GMBH), a Couette rheometer, whose core is composed by two coaxial stainless steel cylinders. Viscometer can measure the torque generated on the inner cylinder corresponding to various shear rate applied setting the rotational velocity. Viscosity is obtained as the ratio between shear stress and shear rate.

3. Results

3.1 Coated nAl characterization

First, the 16 coated powders are compared to find coating effects on size distribution. In Figure 1 is reported

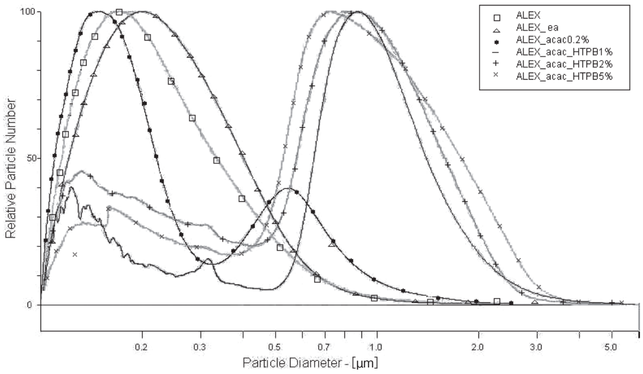


Figure 1 nAl particle size distribution.

the particles population number increasing HTPB fraction. Changing solvent or coupling agent, the behavior is the same in principle.

Analyses carried out to investigate particle size distribution show both catechol and acetylacetone addition to improve nanoparticles clusters disaggregation. The presence of HTPB coating leads to cluster reformation and the higher the percentage the bigger the clusters are. An evidence of the gluing effect of the coating is given by TEM analyses (Figure 2 (1)). From the visualization it is possible to see both particles clusters (Figure 2 (1)) and single particles well coated (Figure 2 (2)).

Results on aluminum content are reported in Figure 3. Mineral spirit has almost no effect on aluminum content, while use of ethyl acetate results in reduce the active aluminum content of about 6%, but in presence of either catechol or acetylacetone the aluminum content reduction is lower, in particular, powder with acetylacetone have almost the same aluminum content of original ALEX. Both catechol and acetylacetone do not affect active aluminum content also in the presence of mineral spirit, while the presence of coating regularly reduces aluminum content. The lowest values of aluminum content are shown by the series of powders treated with ethyl acetate and catechol, but this difference with respect to the other powders disappear for 5%HTPB coated Alex.

3.2 Humidity research

The degree of reaction of powders to water vapor is presented in Figure 4 and Figure 5. Coating has a strong protective effect on ALEX, suppressing the reaction with water vapor. Among the tested powders the ones obtained with acetylacetone as coupling agent and mineral spirit as solvent show the highest stability.

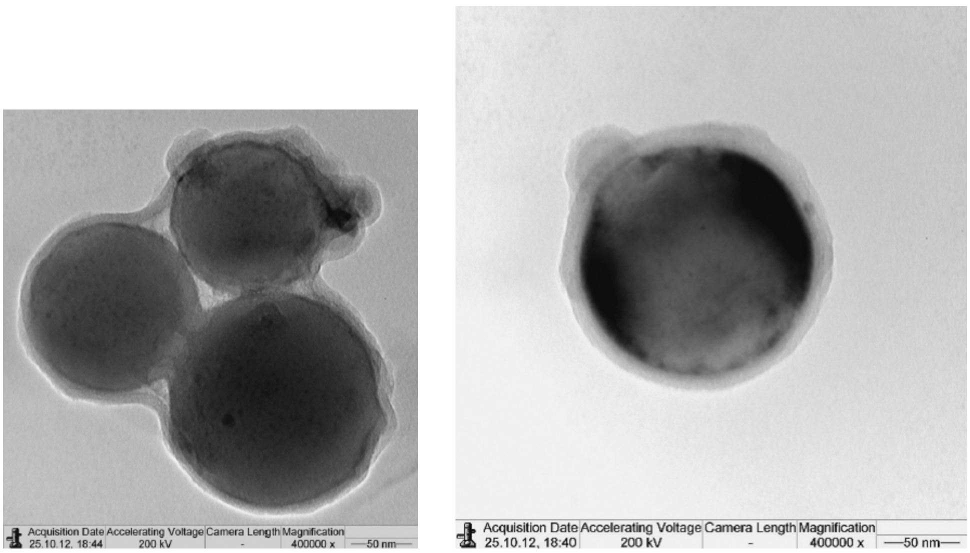
3.3 Choice of treated ALEX

Considering all the analyses carried out, a trade off among the powders is possible and H-ALEX was choiced. This powder shows relatively small clusters, a high aluminum content and the best stability to moisture. Burning rate of the P - 18H-ALEX is compared with the one of P - 18ALEX and with the 18% μAl containing SP.

3.4 Burning rate, ignition delay and viscosity measurement

Considering the bulk density of nAl and the consequent difficulty in handling the compound during the manufacture, burning rate is investigated also for a propellant containing a mixture of μAl and nAl in order to find a good compromise between increase in burning rate and manufacturability. Results are shown in Figure 6 and the corresponding Vieille law coefficient are listed in Table 2.

nAl in solid propellant lead to an enhancement of r_b up to 72% at 4 MPa. Pressure sensitivity increases as well, as it is possible to deduce from the pressure exponents listed in Table 2. The burning rate enhancement provided by H-ALEX is visible over the whole investigated range of pressure ; at 4 MPa r_b increases of 26% with respect to ALEX containing propellant and 117% with respect to the baseline. As drawback, pressure sensitivity increases as well passing from 0.42 for μAl containing propellant to 0.50 if H-ALEX is used. The pressure exponent remains



(1) Cluster of particles (2) Single particle

Figure 2 TEM of ALEX coated with 1%HTPB using acetylacetone and mineral spirit as solvent. Magnification : 400000X

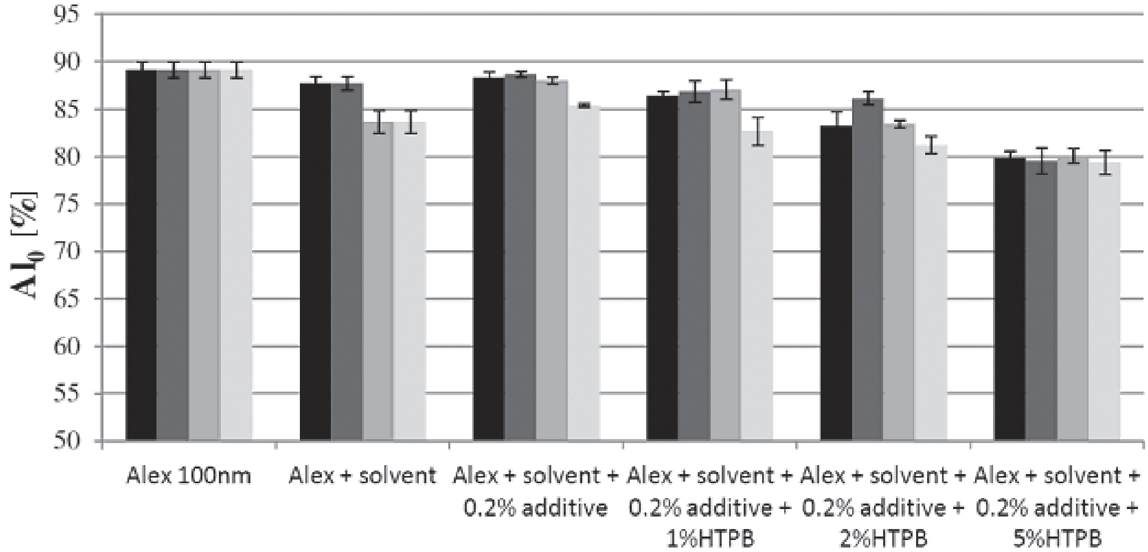


Figure 3 Comparison of active aluminum content for all the aluminum powders coated with HTPB.

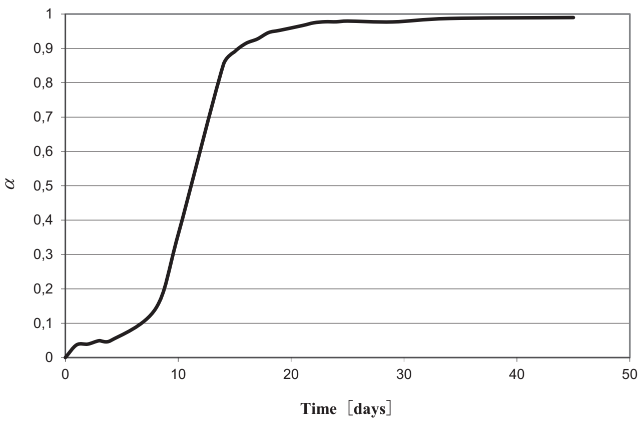


Figure 4 Sum up of inactive aluminum content for ALEX.

relatively high even if H-ALEX is mixed with μAl. Nevertheless the increment in burning rate obtained with the mixture μAl/nAl is about 65% at 4 MPa.

Ignition delay as a function of radiant heat flux for all the propellant considered in this work is reported in Figure 7.

The higher reactivity of nAl leads to a faster ignition of the propellant. Moreover formulations with 18% H-ALEX presents the lowest ignition delay. Mixing μAl with H-ALEX makes possible to obtain a propellant with ignition

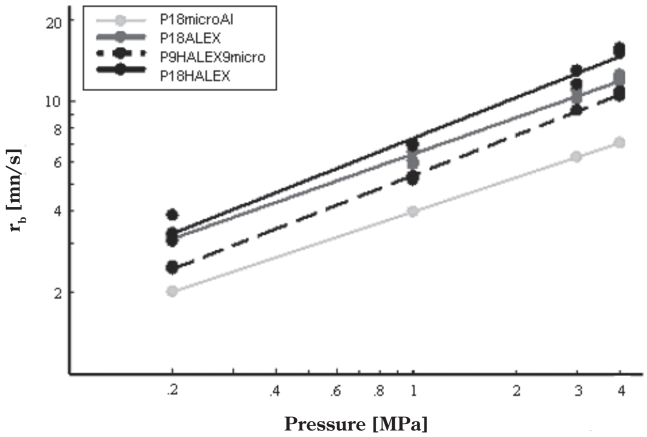


Figure 6 Steady burning rate for 18% Al containing propellant.

Table 2 Coefficients of the Vieille equation.

Propellant	a	n
P −18μAl	1.50 ± 0.03	0.42 ± 0.01
P − 18ALEX$_{TM}$	2.31 ± 0.07	0.45 ± 0.01
P − 18H-ALEX	2.32 ± 0.12	0.50 ± 0.02
P − 9H-ALEX/9μAl	1.73 ± 0.03	0.49 ± 0.01

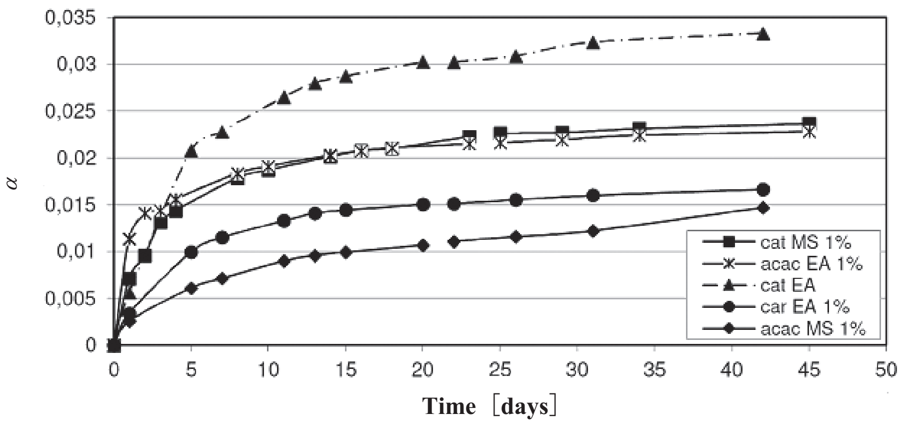


Figure 5 Sum up of inactive aluminum content for ALEX powders coated with HTPB.

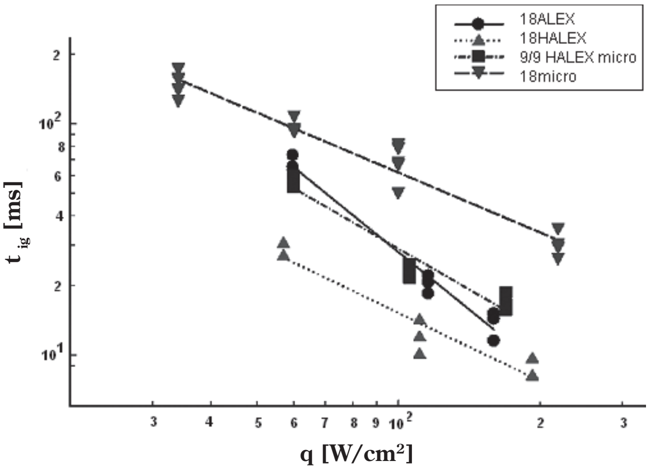


Figure 7 Ignition delay for 18%Al containing propellant.

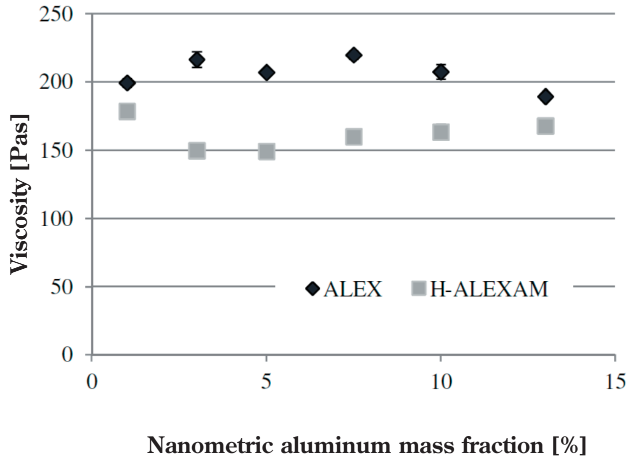


Figure 8 Viscosity as a function of nanosized aluminum amount.

delays similar to P-18ALEX but with a lower flux sensitivity.

In Figure 8 the viscosity as a function of the nAl content for a shear rate of $1s^{-1}$ is reported, comparing also in this case ALEX with H-ALEX.

Formulation containing ALEX shows higher viscosity with respect to the one loaded with H-ALEX for all the compositions. The difference in viscosity is reduced when the substitution of μAl with nAl is minimum or almost complete. In formulations of varying ratio μAl to nAl with total aluminum content being constant, the viscosity reduces considerably.

4. Conclusions

In order to improve the dispersion degree of nAl in propellants, a HTPB coating is proposed. Different coupling agents and solvents are compared; best results are obtained with acetylacetone and mineral spirit. The obtained powders are used in propellants resulting in the burning rate enhancement and to the ignition delay reduction with respect to both μAl and ALEX. Castability is improved as can be seen from the reduction in viscosity. A good compromise between performance in combustion and castability is obtained mixing μAl and H-ALEX.

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405

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