Rheological and mechanical behavior of coated aluminum loaded nano-composites

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Abstract
In order to improve compatibility between nanoparticles and HTPB matrix, coating with the same polymer is considered. Size distribution and stability analyses show that the best coating is obtained with 1%HTPB, mineral spirit as solvent and acetylacetone as coupling agent. Rheological tests are carried out on AP/HTPB/Al uncured formulations in which μAl is progressively substituted by coating or uncoating ALEX^{TM}. The effect of microstructure on rheology is theoretically investigated and the effects of cluster acting as micrometric particles is proposed. DMA analyses on coated-nAl loaded HTPB-based fuels show no significant effects of particle coating on viscoelastic behaviours.

1. Introduction

Metal nano-sized particles possess unique features with respect to coarser equivalent powders, and their use is in continuous growth in many industrial fields: cosmetics, pharmaceutics, energetic materials. In space propulsion applications, solid rocket propellants (SP) with total or partial substitution of micrometric aluminum with nano-sized one show a significant performance improvement: burning rate is increased while agglomeration phenomena are mitigated [1]. The addition of nanometric aluminum to Hydroxyl-Terminated PolyButadine (HTPB), used as fuel in Hybrid Rocket Engines (HRE) could represent a good pathway to solve the low regression rate problem that hindered a wide exploitation of these systems. Although nanometric powders are characterized by very attractive bulk properties, their surface interactions can avoid a total development of their potential: Brownian motion, very effective on this scale, causes particles to collide and Van der Waals forces, relevant because of the high specific surface, promote cluster formations. Moreover surface interactions among particles and hydrodynamic effects due to the nanopowder high specific surfaces cause uncured propellant viscosity increases [2], leading to difficult manufacturing and casting.
A possible solution to improve compatibility between nanoparticles and polymers is represented by surface treatment of the nano-sized powders. In this work the effect of an HTPB coating on ALEX^{TM} is considered. In order to improve the quality of the coating, particles are treated with two different coupling agents, catechol or acetylacetone, and various percentages of HTPB (up to 5%). The selection of the most promising powder is carried out with different methods: TEM images show the quality of the coating, and from size distribution analyses it is possible to evaluate clusters formation during coating. Finally the effect of the treatment on active aluminum content (Al0) and the effectiveness of the coating in improving stability to the moisture are considered.
Mechanical and rheological analyses on both solid fuels for hybrid propulsion and solid propellants containing the selected powder are carried out. Dynamic mechanical analyses are performed comparing formulations containing acetylacetone-coated ALEX^{TM} or HTPB-coated variants. HTPB/AP/Al uncured propellants are tested using a Couette rheometer. First only μAl containing formulations are considered to investigate the connection between propellants microstructure and rheological properties. The simulation of realistic heterogeneous material is demanded to a packing code, that gives the distribution of the centres of each particle in a cube centred in the origin. The obtained distribution is used to evaluate the number of fine fuel particles (μAl) around every coarse one (AP) enhancing the oxidizer fraction. The correlation between H and the number of Al particles around each AP grain is used to evaluate the number of micrometric particles in nAl/μAl containing formulations. In the hypothesis of homogeneous dispersion of NP only μAl constitutes the fine fraction, while nAl is included in the liquid phase. In case of cohesion, clusters act as micrometric particles. In this way, the correlation obtained for H can be used to predict the theoretical viscosity of a well disperse formulation. The difference between theoretical and actual viscosity is used as a method to evaluate the quality of the dispersion, comparing coated and uncoated ALEX^{TM} .

2. State of the art

2.1 Viscoelastic behavior

From the mechanical point of view, polymers are visco-elastic materials [3]: they share some characteristic with viscous materials (liquids) and some other with elastic ones (solids). In liquids shear rate is proportional to the load and energy is dissipated as heat; in solids, shear is proportional to the load and work is stored as potential energy.
As for solid materials, elastic modules can be defined for the visco-elastic polymers: Young's Modulus (E), Shear Modulus (G) and Bulk Modulus (B). In order to consider the peculiarities of visco-elastic materials also complex modules can be defined. These are composed by a real and an imaginary part [3]. The real part of a complex modulus is the storage modulus (E', G', and B') giving the in-phase response to a periodic solicitation; the imaginary part, the loss modulus (E'', G'', and B'') represents the out-of-phase component of the response. The ratio between the loss modulus and the corresponding storage modulus (e.g. E''/E') is the loss factor tanδ and can be connected to the material damping.
Polymers mechanical properties depend on many factors (e.g. chemical composition, molecular weight, crosslink and branching degree, loading with filler) [3]. Boundary conditions can also affect mechanical behavior: in particular time, frequency, temperature and stress rate can alter to the visco-elastic responses of polymers.
The consequences of adding filler to vulcanized rubber have been studied since 1960s [4][5]. In particular the effects of carbon black (CB) filled rubber were investigated. Of course at that time studies deal only with micron-sized materials. For rubber-like materials strain-stress curve is linear in a large strain range, but the presence of CB is a cause of non-linearity: dynamic modulus decreases with increasing strain amplitude, and this effect is more evident for heavily loaded rubber. In general loaded rubber E and G are higher with respect to those of the pure rubber, but part of this gain is lost at high strain levels. Moreover, at large strains the modulus becomes less strain-dependant. An explanation of this fact is given in [4][5][6]. Differences in the dynamic modulus between pure and loaded rubber are given by the superposition of three different factors: polymer network (in turn depending on material nature/crosslink density), hydrodynamic effect (due to the viscoelastic material flow and additive particles presence), and in-rubber structure (polymer-filler physical and chemical linkages). The first and second factors are present also at large strain and are responsible for the strain-independent behaviors. While the non-linear response is mainly connected to the filler network. In fact, the rubber trapped inside the filler chains loses its elastomer characteristics and reacts as filler to dynamic solicitations. Therefore, the effective volume bearing the imposed stress is reduced by filler network, resulting in an increased elastic modulus. Enhancing the strain leads to the breakdown of filler network, releasing the trapped rubber so that the effective volume fraction and hence the modulus would decrease.
Wang [7] investigated also the G" behavior for CB loaded rubber, showing an increase in G" with enhancing filler loading. This is mainly due to the hydrodynamic effect: the addition of particles in polymer matrix results in a higher viscosity compound. Moreover, a maximum is present in G" versus strain amplitude plot, corresponding to low strain values: no hydrodynamic force is responsible for this behavior, but the breakdown and reformation of filler network. After a sufficiently high strain amplitude, filler cannot recreate structures and the effects of these networks disappears. A different behavior is shown by rubber loaded with fillers that can create a stronger network, like silica: loaded formulations have always a lower tanδ. Indicating reduced dissipation by the viscous component. Mechanical properties are also affected by the dispersion degree. In [8] batches of rubber loaded with CB characterized by different mixing time are first analyzed with a microscope showing a better dispersion increasing the mixing time. Subsequently mechanical tests are carried out revealing that both in-phase and out-of-phase components of shear modulus are reduced for well dispersed formulations. This behavior can be justified considering that higher mixing time promotes weaker structure destructions.
Static mechanical tests have been performed by Pu et al. [9] considering nanometric particles (150 nm) of Silica coated with TPM in PMMA and PMA matrix. The amount of filler considered ranges from 45% to 55% of the sample mass. In particular three different batches were produced: the first one with randomly dispersed Silica, the second one with a regular arrangement of colloidal crystals, the third one with aggregates. Mechanical tests show that introduction of filler into an elastometric matrix increases its strength but decreases its extensibility, and this behavior is more evident increasing filler content. Also the toughness (the energy needed to break the sample) decreases for increasing additive percentage. In Pu et al. [9] investigation, this parameter value is lower for first and second batches with respect to pure polymer, but it is higher when nanoparticles forming aggregates. In this case Young's Modulus results higher as well.

2.2 Additive dispersion

The most explored nano-sized additive dispersion strategy is based on the ultrasonication of particle suspensions [10][11][12][13][14][15]. In this technique, the application of an ultrasound radiation source of intense power induces cavitation into the suspending fluid medium. Thus, bubbles are created, and grow till explosion. The process leading to bubble explosions yields significant temperature increases in reduced time intervals. The following cooling phase is so fast that re-crystallization is hindered, and clusters can be reduced by decreasing intermolecular and chemical bond forces [16]. Although sonication is necessary to obtain a high degree of dispersion, it is not always sufficient to completely distribute nano-particles in the suspending medium. Chemical methods are often used to disperse and stabilize NP in nanocomposite, sometimes together with the physical techniques previously mentioned. Modification of the particle surfaces to limit clustering or to functionalize NP is an important chemical challenge that can contribute to the exploitation of the unique features if nanocomposites. Various strategies, that can also be combined, have been proposed to modify nano-metals surface [17]: organosulfur compounds, like thiols and disulfides can be deposed on particles with solvents or can be added directly to the solution with precursor. Also amines can be used, but the bond with metal in this case is weaker with respect to the organosulfur compounds. In order to modify metal oxides, phosphonates have been proposed because of the connection through the oxygen of the oxide. The use of catechol to improve connection between a metal oxide and a polymer is reported in [18]. The bond between oxide and polymer is created through –OH groups and through the free electrons in the aromatic ring. Another coupling agent can be acetylacetone used in [19] to sensitize polyoxotitanate (POT) anchoring chromophores to nanocrystals.

2.3 Rheology of suspension

Detailed surveys of the rheological behavior of additive suspensions into fluid media are given by Nielsen [3], Russell [20], and Metzner [21]. Rheological behavior of energetic materials is extensively discussed by Teipel et al. [10], while the flow behavior of solid propellants was investigated by Miller et al. [22] and Muthiah et al. [23]. When dealing with rheology of suspensions, the main parameter of interest is the relative viscosity. At a given shear rate (or shear stress) this is defined by suspension and suspending medium viscosities (η_S and η_{SM} respectively) as

$$H = \left.\frac{\eta_S}{\eta_{SM}}\right|_{\dot{\gamma}} \qquad \textbf{(1)}$$

The suspension H depends on several factors, including the suspending fluid viscosity affecting the polymer-particle hydrodynamic forces [9]. Polymeric liquids loaded with additives exhibit increased viscosity. In spite of this, quantitative observations on H depends on several factors and can yield not unique results [20][21]. Einstein equation fits to experimental data for very dilute suspensions (filler volumetric fraction $\varphi \leq 0.02$), [3][10][20][21]. The latter are characterized by an almost linear H increase . The Einstein coefficient k_E can be evaluated with fair accuracy also for non-spherical particle dispersions [3]. Clustering of particles yields increased k_E values. This is related to enhanced viscosity of the considered suspension [16]. The Mooney equation [3][21] and some other relationships [3][10][21] consider φ_{MAX} as a parameter for data fitting. The latter is the maximum filler volumetric fraction. Due to particle-particle interactions and packing difficulties, clustering reduces the φ_{MAX} value with respect to the case of a well dispersed suspension. Thus, according to these equations, for clustered particle suspensions H is increased. Teipel and Forther-Barth [23] investigated the rheological behavior of ALEX^{TM} suspensions in Paraffin-oil and liquid HTPB. The tested pure paraffin oil was a relatively low viscosity medium [μ (293 K) = 198 mPa·s] and presents a Newtonian behavior. Adding ALEX^{TM} the resulting suspension exhibits a non-Newtonian, shear thinning behavior. In particular, Teipel and Forther-Barth noticed a marked H increase for $\dot{\gamma} < 1$ Hz when testing suspensions with $\varphi \geq 21.53\%$ at T = 293 K. Under the investigated conditions, for $\dot{\gamma} > 10$ Hz, the relative viscosity of the suspensions decreases due to the hydrodynamic forces induced by the flow. The HTPB resin tested by Teipel and Forther-Barth has η (293 K) = 6300 mPa·s. The viscosity of the HTPB resin is so high that induces hydrodynamic effects yielding a Newtonian behavior over the whole investigated range. Similar results are achieved by Mary et al. [25] in their experimental activity on the suspension of HTPB + ALEX^{TM} with nAl volumetric fraction up to 10%. In their work, Mary et al. evaluated the effects on H of particle surface wettability for different nAl coatings. A shear thinning behavior is achieved by their tests on a suspension of Polyethylene coated ALEX^{TM} in HTPB. This result underlines the importance of the high Ssp and surface characteristics of the nano-sized particles. As observed by Popenko et al [2], a significant increase in H of ALEX^{TM} suspensions is achieved in ES for additive mass fractions > 5%. Gromov et al. [26] investigated the behavior of micron- and nano-sized Al powders suspended in HTPB and GAP. Considering an Al mass fraction of 30% (φ = 12.5%), HTPB + ALEX^{TM} exhibits an enhanced viscosity with respect to pure HTPB and micron-sized Aluminum suspensions. This behavior, explained by specific surface of suspended particles and the hydrodynamic effect, characterizes the whole investigated $\dot{\gamma}$ and T ranges. The rheological behavior of GAP-based systems appears similar to the HTPB counterpart though some difference can be noted for $\dot{\gamma} > 100$ Hz. Under these conditions, Gromov et al. noticed a shear thinning behavior common to pure GAP as well as to GAP + Al suspensions. This behavior is addressed to some system break-up within the suspending polymer.

3. ALEX^{TM} coating and samples preparation

In order to improve compatibility between nAl and the matrix, the same polymer used as fuel in hybrid systems or as binder in solid propellants is used to coat the particles. The optimization of the coating is carried out comparing two coupling agent, catechol and acetylacetone, two solvents, ethyl acetate and mineral spirit and various percentage of HTPB: 0,1,2, and 5%. First, coupling agent is dispersed in the solvent, then ALEX^{TM} is added and mixed at 5000 rpm. After 30' HTPB dissolved in the same solvent reaches the powders and the mixing continues for other 30'. Evaporation of the solvent is obtained by means of low pressure and relatively high temperature in a water bath using a rotary evaporator (Büchi Rotavapor R-200). With this procedure 16 powders are obtained and compared to find the most promising ones.

Rheological tests have been performed on uncured formulations of solid propellant. First analyses are carried out to see the effects of increasing solid fraction: in this case liquid HTPB is tested, then 18% of µAl with nominal size of 5-10 µm is added. Further samples are obtained adding to HTPB and µAl, AP with nominal size of 50 µm in percentages spanning from 5 to 60%.

Specimens with partial substitution of micrometric aluminum with nanometric one were prepared keeping constant the relative fraction among ingredients: 50% AP + 32% HTPB + 18% Al. The 18% of aluminum is obtained with different combination µAl + nAl from 17:1 % up to %:13%. A comparison between coated powders and uncoated ALEX^{TM} is carried out.

DMA analyses are restricted to fuel formulations. Three different HTPB-based compositions were tested: pure HTPB and two nAl-loaded formulations. The loaded fuels have 10% additive by mass. The DMA characterization aims at evaluating possible nAl-coating effects on cured fuel viscoelastic behaviour.

4. Experimental set ups and procedures.

The selection of the most suitable HTPB coated nAl powder is carried out considering various parameters. Size distribution is evaluated through a CPS disc centrifuge [27]. Al^0 is evaluated placing a small amount of powder in a solution 1M of NaOH. The metallic element reacts and releases hydrogen, whose amount can be measured to calculate aluminum fraction in the sample. Finally analyses to measure the stability of the powder to the moisture are carried out placing about 2 g of powders in a saturated atmosphere of sodium carbonate for at least 45 days. In this way the humidity in the closed vessel is maintained at 90%. Aluminum reacts with water vapor producing bayerite. Considering the difference in molecular weight between aluminum (26.98 g/mol) and bayerite (77.98 g/mol) it is possible to measure each day the degree of reaction (α) monitoring the increase in weight of the sample.

Viscosity measurements of uncured SP formulations are carried out using Rheotest 2.1, a Couette rheometer, whose core is composed by two coaxial stainless steel cylinders. Rheotest 2.1 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.

Dynamic mechanical analyses are carried out using TA Instruments DMA 2980 with dual-cantilever clamp. Specimens are parallelepipeds whose size is defined considering the expected elastic modulus [28][29]. Frequency and strain sweep were investigated. Frequency sweep is performed with an amplitude of 25 µm and frequencies ranging from 0.3 Hz to 30 Hz, in two isothermal conditions (40°C and 50°C). Strain sweep spanning from 0.03% to 30%, for frequency of 1 Hz and isothermal condition of 40°C are considered.

5. Results.

5.1 Powders selection

First, the 16 coated powders are compared to find the coating effect on size distribution. In Figure 1 is reported the particles population number increasing HTPB fraction. Changing solvent or coupling agent the behavior is the same.

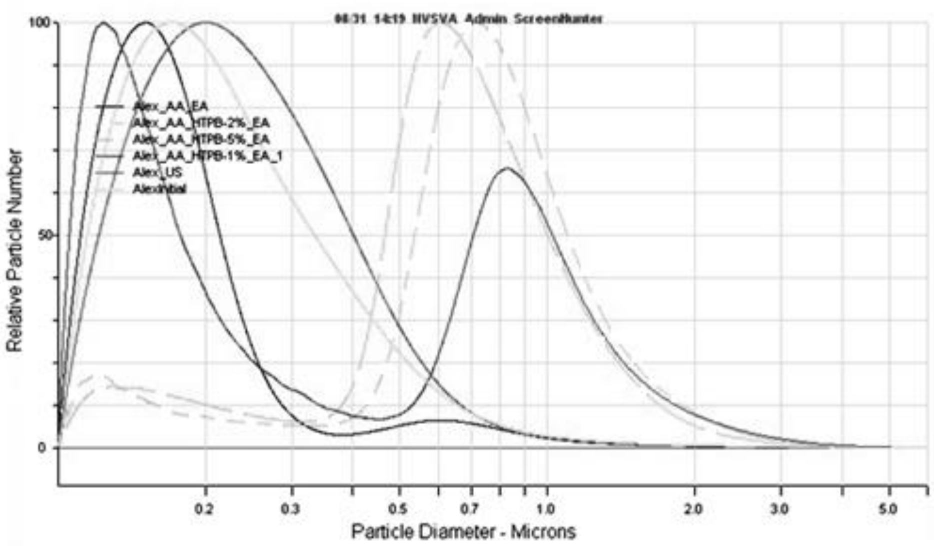


Figure 1 : Particle size distribution: ALEX™ (light gray, continuous line), ALEX™ with 0.2% acetylacetone (black), ALEX™ with 0.2% acetylacetone and various percentage of HTPB (all the curves of this group presents a peak close to 1 μm). Solvent: ethyl acetate.

Analyses carried out to find particle size distribution show that catechol or acetylacetone addition improves cluster disaggregation. The presence of HTPB coating leads to cluster formation and the higher the percentage the bigger the clusters. As it was evidenced by TEM analyses [28], some of the particles were already sintered before the coating, while in other cases is the gluing effect of HTPB that keep the particles stuck together.

Results on Al^0 are reported in Figure 2. Mineral spirit has almost no effect on Al^0, while ethyl acetate reduces active aluminum content of about 6%, but in presence of either catechol or acetylacetone the Al^0 reduction is lower, in particular powders with acetylacetone have almost the same Al^0 of original ALEX™. Both catechol and acetylacetone do not affect active aluminum content also in presence of mineral spirit, while the presence of coating reduces Al^0, probably due to the increase in size of particles and cluster formations. The lowest values of Al^0 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.

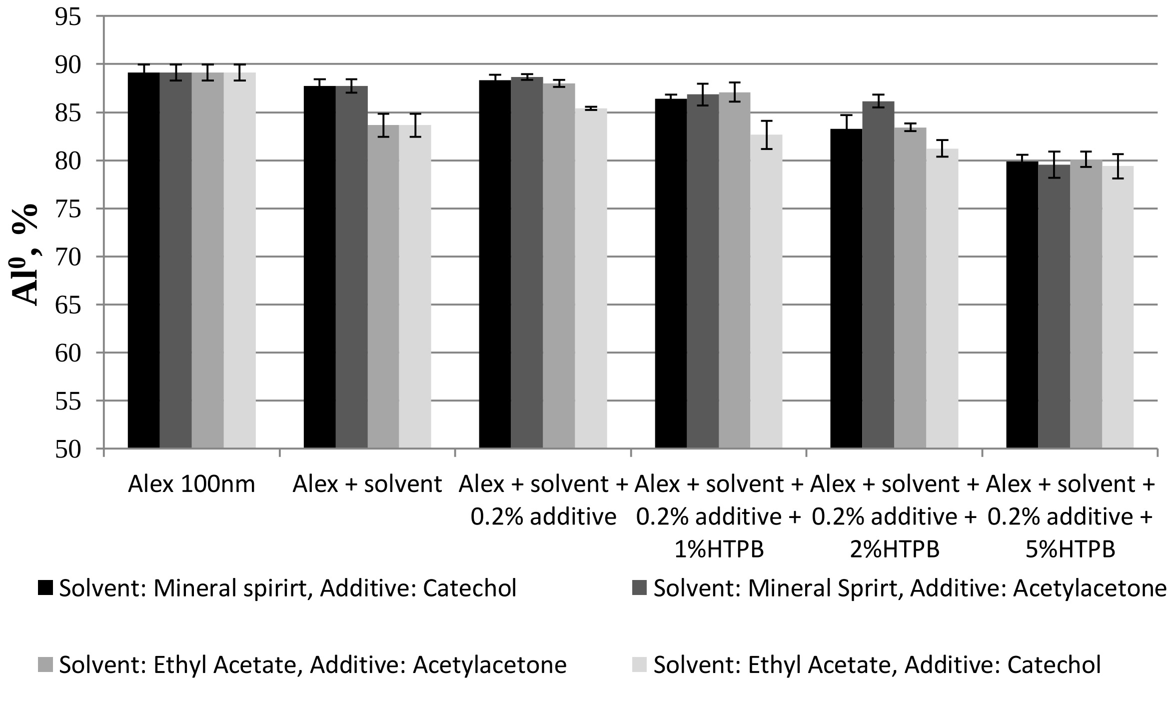


Figure 2 : Sum up of active aluminum content for ALEX™ powders coated with HTPB.

The degree of reaction of powders to water vapor is presented in Figure 3. Coating has a protective effect on ALEX™, improving the stability to the moisture. Among the tested powders the ones obtained with acetylacetone as coupling agent and mineral spirit as solvent show the highest stability.

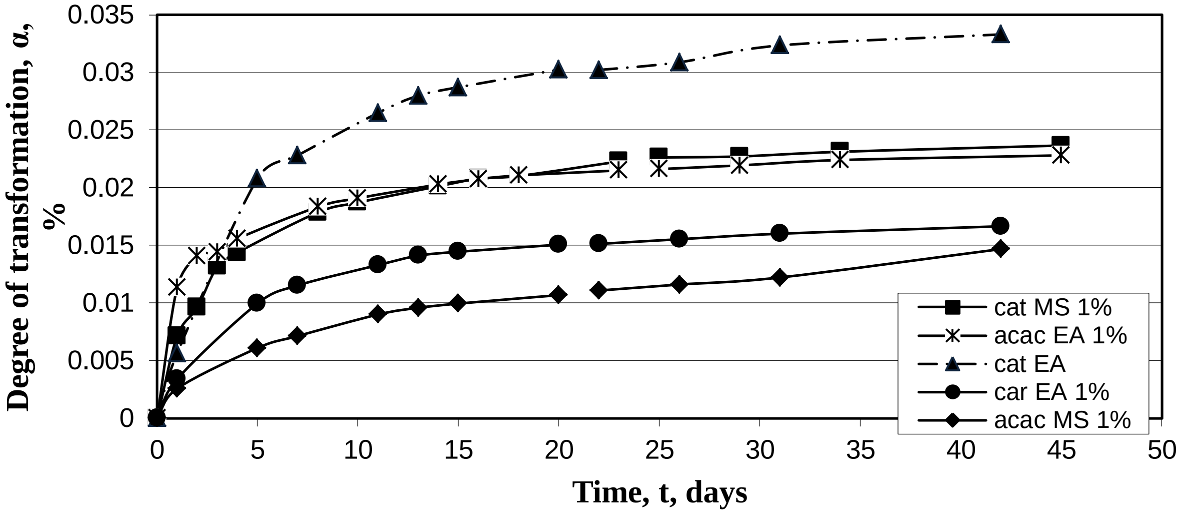


Figure 3 : Sum up of active aluminum content for ALEX™ powders coated with HTPB.

Considering all the analyses carried out, a trade off among the powders is possible and the nAl selected to be tested in the uncured propellant formulation is ALEX™ coated with 1% of HTPB using acetylacetone as coupling agent and mineral spirit as solvent. This powder, labeled H-ALEX, show relatively small clusters, a high Al^0 and the best stability to moisture. On the other hand, the powder treated by acetylacetone only, labeled H0-ALEX, presents interesting characteristics for possible applications in solid fuel formulations [29]. In particular: its particle size distribution does not exhibit marked micron-size range peaks.

5.2 Rheological analyses

From the rheological point of view, heavily loaded suspensions show a different behavior with respect to dilute ones[3][10][28][30]. As discussed in Section 2.3, compositions containing a small amount of solid particles (up to 20% in volume) exhibit moderate viscosity increases that are mainly due to the hydrodynamic particle-liquid interactions. Increasing volumetric content over 20% viscosity augments rapidly reaching an asymptotic behavior for the maximum allowable volumetric content. This behavior is verified for the uncured propellants. In Figure 4 stiffening factor as function of volumetric content is presented. First liquid HTPB is tested, showing a $\eta = 9.10 \pm 0.35$ Pa·s. Then 18% by mass of μAl is added and further enhancement of volumetric content is obtained adding AP up to 60% by mass.

In scientific literature the effect of volumetric fraction on viscosity is widely investigated. In this work a correlation with the microstructure of the mixture is explored, in order to find the effect of interactions between particles on rheological properties.
The simulation of realistic heterogeneous material is demanded to a packing code, Polipack [31], that gives the distribution of the centres of each particle in a cube 2x2x2 centred in the origin (Figure 5). Data obtained from the code are elaborated in order to find, for every composition, the number of aluminum particles surrounding each AP crystal. In Figure 6 the number of Al particle centres are plotted as function of the distance from AP expressed in number of aluminum radii, normalized with respect to μAl radius.

Selecting a distance it is possible to evaluate the number of particles inside the region, correspondent to the various AP fraction. From a rheological point of view the most interesting region is the one closest to AP surface, where the interactions between particles can play an important role. In Figure 7 results for particles distances lower than 1.5 or lower than 2 radii are reported.

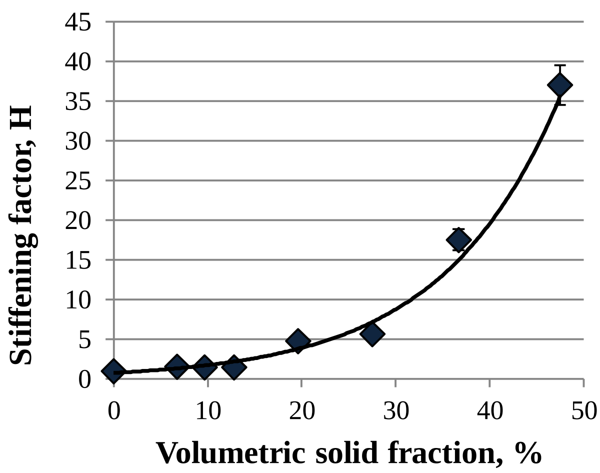


Figure 4 : Stiffening factor as function of volumetric solid content of uncured propellant for $\dot{\gamma} = 1$ Hz.

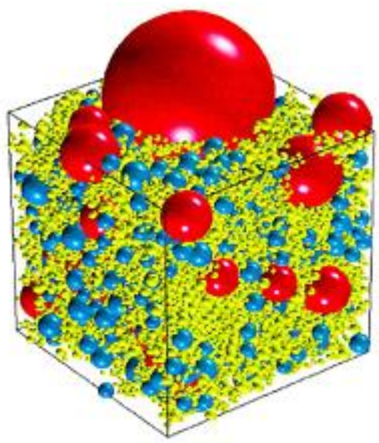


Figure 5 : Simulation of heterogeneous structure by a packing code.

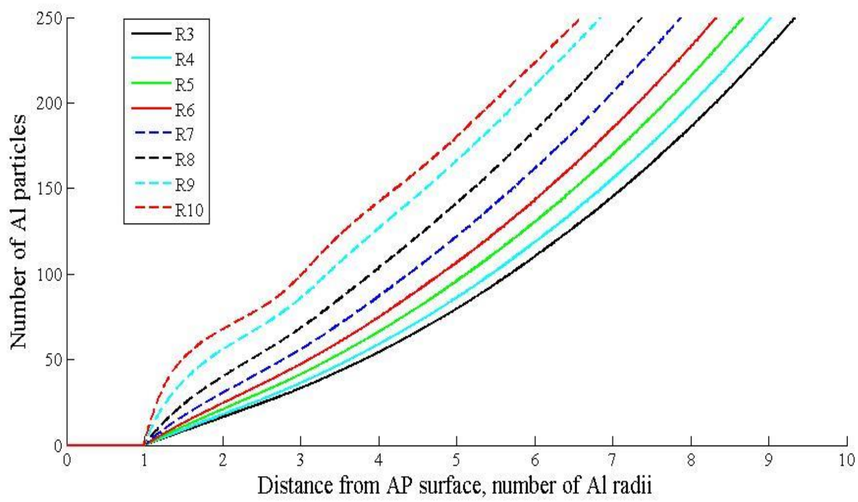


Figure 6 : Number of aluminum particles as function of distance from AP crystal, expressed in normalized number of Al radii.

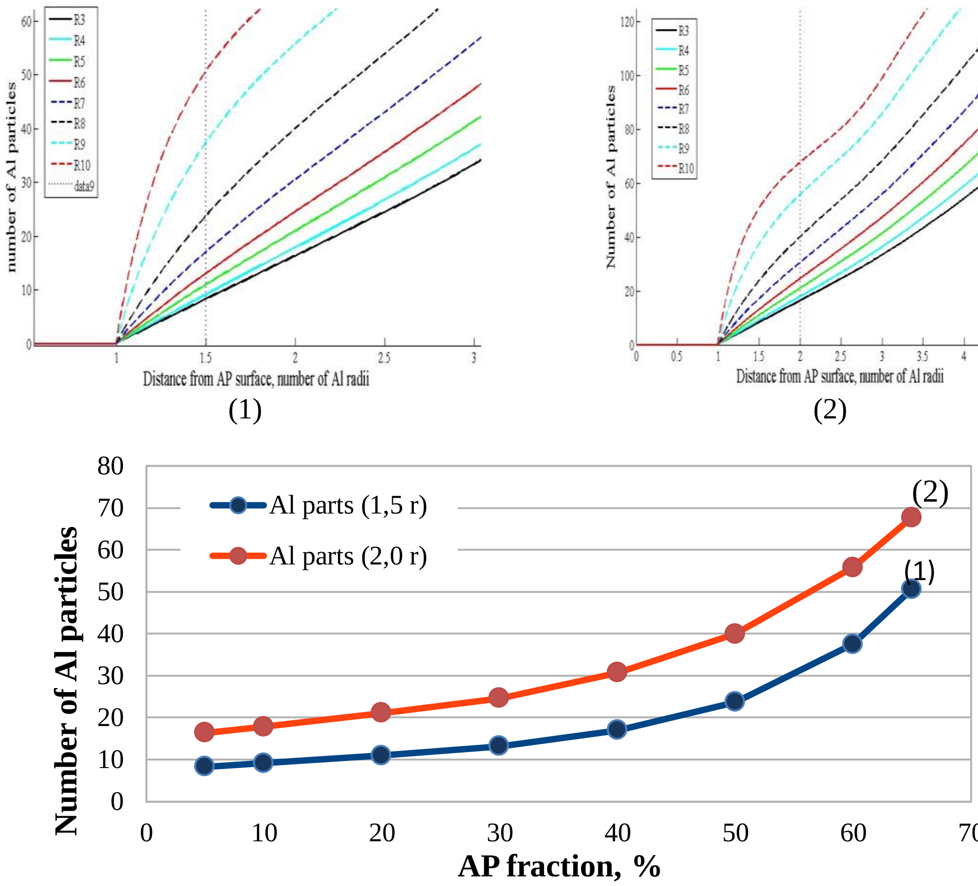


Figure 7 : Number of Al particles as function of AP mass fraction inside the region at 1.5 Al radii (blue curve) and at 2 Al radii (red curve).

The first thing worthy to be underlined is the linear growth of the number of particles with AP fraction, up to 30% in mass, corresponding to about 20% in volume. In this range the Einstein equation [28] is valid, that states a linear relation between viscosity and the number of solid particles into a fluid. For diluted formulations, in fact, interactions between particles are not presented, being too far from each other, and the only responsible for increase in viscosity enhancing the amount of filler is the hydrodynamics force that rise between the solid fraction and the liquid matrix. For higher percentages of solid content the deviation from linear behavior becomes clear and the number of Al particles around each AP grain increases faster and faster with AP content.
For further analysis only the region closest to AP surface is considered, selecting 1.5 radii as limiting distance. So only Al particles with the center inside this region are taken into account.
The stiffening factor found through the experimental investigation is plotted in Figure 8 as function of the number of Aluminum particles in the considered region.

As it is possible to see in Figure 8 the stiffening factor augments with the number of particles with a cubic dependence.
The results obtained show the great importance of particle-particle interactions on the micro-scale in determining the viscosity of a heavily loaded suspension. The relation obtained between H and the number of particles (n), reported in equation (2) will be used to estimate the effect of nanosized particles addition.

$$H = 0.0016n^{3.21} \quad \textbf{(2)}$$

A comparison between HTPB-coated and uncoated ALEX^{TM} is carried out in formulations with partial substitution of μAl with nAl. Results increasing ALEX^{TM} fraction are reported in Figure 9 for 2 different shear rate. As can be seen in Figure 9, formulations containing nAl shows lower viscosity with respect to uncoated ALEX^{TM} loaded ones for almost every amount. The only exception is visible in the plot obtained for a shear rate of 3 Hz where the difference start to became visible in the composition 3% ALEX^{TM} + 15% μAl. An explanation for this behavior can be given considering that coated particles should better disperse inside the liquid matrix. The contribution of clusters to the viscosity enhancement is theoretically analyzed considering the microstructure of the uncured propellant.

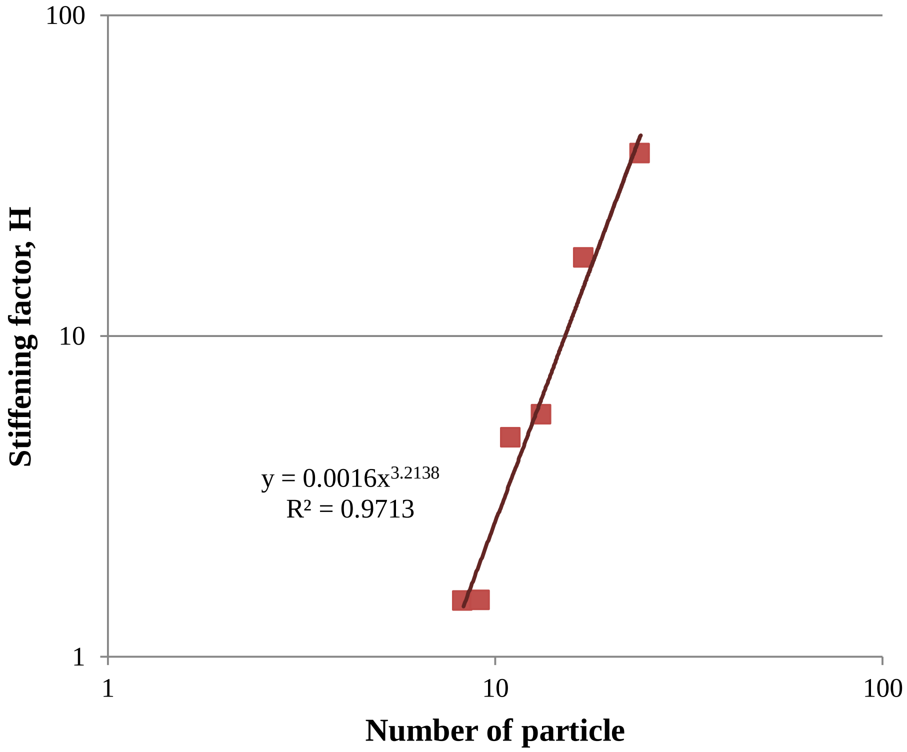


Figure 8 : Stiffening factor as function of number of particles in the region at 1.5 Al radii around AP crystals.

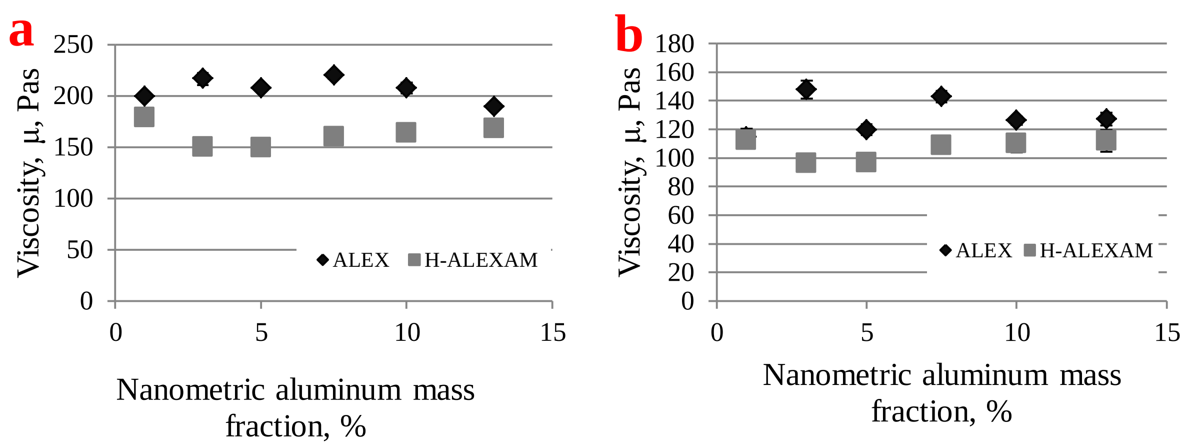
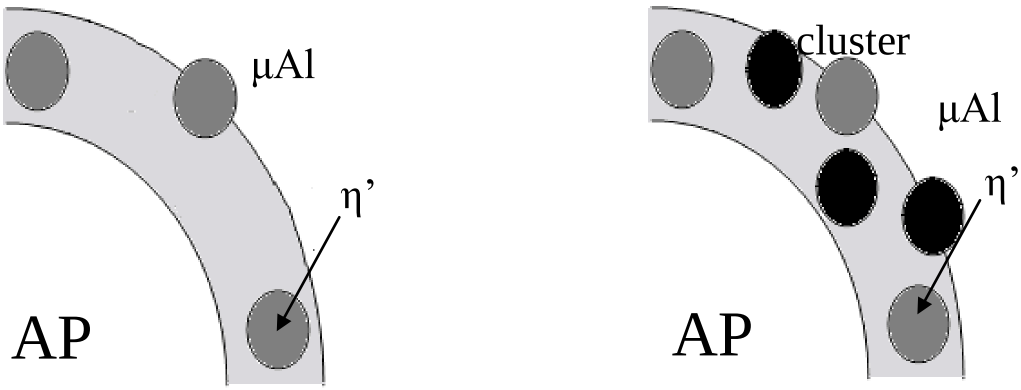


Figure 9: Comparison between HTPB-coated and uncoated ALEX^{TM} for increasing nano-sized aluminum fraction: (a) $\dot{\gamma} = 1$ Hz and (b) $\dot{\gamma} = 3$ Hz.

The main idea is that, if the nanosized fraction is homogenously distributed into the matrix, down to the nanoscale, it has no interactions on higher level (microscale) that can improve viscosity. In other words, in the stiffening factor H, a ”new” fluid with viscosity η’ is considered. Clusters act on the micro scale, behaving like micrometric aluminum particles. The correlation between H and the number of micrometric aluminum particles in the region close to AP surface is considered. In case of cohesion clusters behave like μAl, artificially increasing the number of particles around each AP crystal (Figure 10).



(1) No cluster formations (2) Clusters presence

Figure 10 : Aluminum particles in the region delimited by 1.5Al radii, with and without clusters.

First the number of Al particles around each AP grain is evaluated simulating the distribution of the particle with the packing code Polipack. The homogenous distribution of nanosized aluminum in the matrix is supposed and according to previous statement is considered void, as HTPB.
Results for the various formulations as function of distance from AP surface, expressed in normalized Al radii are presented in Figure 11, where it is possible to see that the number of Al particles around each AP crystal increases going far from the oxidizer surface. For formulation containing low fractions of μAl the increment in particle number is low, while in case of 15% or 18% of micron-sized Al particles the growth is quite fast. Setting a reference distance, it is possible to compare the various formulations.
Considering the equation (2) connecting the number of μAl particles around AP crystals with the stiffening factor it is possible to determine the expected H for every condition. These values are compared with the ones achieved for tested formulations, considering $1s^{-1}$ as reference shear rate.

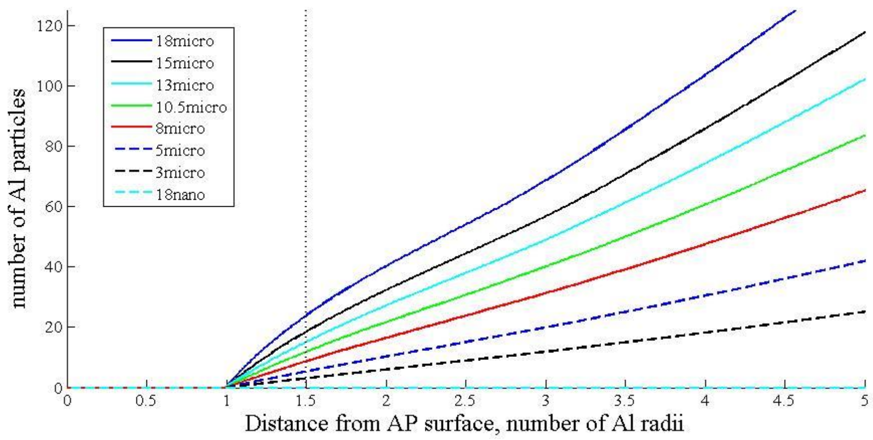


Figure 11 : Number of micrometric Al particles as function of distance from AP crystal, expressed in normalized number of Al radii for nAl containing formulations.

The viscosity η' is obtained considering the mass ratio between nano-aluminum and HTPB in the investigated conditions interpolating the results in [29]. The viscosity obtained for HTPB+ALEX^{TM} suspensions are reported in Table 1 as function of the relative mass fraction. Only values up to 30% are considered, being not confirmed the linearity obtained from the interpolation for higher level of loading. The comparison between expected H and real values is presented in Table 2. With the only exception of the value for H-ALEX in the formulation containing 3%nAl and 15%μAl, which can be seen as an experimental singularity, all the values from the tests are higher. The explanation for the difference can derive from cohesion: clusters acts as micrometric particles. Considering the relation (2) between H and the number of particle it is possible to calculate the correspondent micrometric population around AP grains for any of the investigated formulations. The theoretical number of μAl particles, the global quantity, obtained from calculated H and the amount due to cohesion are reported In Table . As it is possible to see in

Table 3 clusters are present almost in any case, but their influence is higher for uncoated ALEX^{TM} and increasing nanosized fraction.

Table 1**:** Suspension viscosity as function of ALEX^{TM} in the suspension

ALEX^{TM} mass fraction in the propellant, %	ALEX^{TM}/HTPB mass ratio, %	η'@ 1 s-1
1	3.1	8.9
3	9.4	12.6
5	15.6	16.1
7.5	23.4	20.6
10	31.2	25.1

Table 2**:** Comparison between the expected values of H and the real ones obtained for propellants containing nanosized Al.

nAl mass fraction in the propellant, %	Expected H	H for ALEX^{TM} containing suspensions	H for H-ALEX$_{AM}$ containing suspensions
1	19.47	19.91	22.25
3	17.96	11.92	17.23
5	9.43	9.24	12.82
7.5	4.38	7.75	10.65
10	1.62	6.50	8.25

Table 3**:** Comparison between the theoretical number of micrometric particles around each AP crystal and real values obtained for various formulations.

nAl mass fraction in the propellant, %	Theoretical number of µAl particles	ALEX^{TM} containing suspensions		H-ALEX$_{AM}$ containing suspensions	
		Micrometric particles	Clusters	Micrometric particles	Clusters
1	19	20	1	19	0
3	18	18	0	16	N. Av.
5	14	17	3	15	1
7.5	12	16	4	14	2
10	9	14	5	13	4

5.3 Dynamic Mechanical Analysis

Results achieved from the DMA tests are presented in Table 4, Table 5 and Figure 12. The achieved data show a storage modulus increase for nAl-loaded formulations with respect to HTPB. This is clearly connected to the presence of a filler in the binder matrix. For an operating temperature of 40°C at 1 Hz, the storage modulus of HTPB + H0-ALEX is 46% higher than the non-loaded formulation, while the H-ALEX formulation achieves a +50%. Similar, considerations can be done for the 50° C data (see Table 5). The loss modulus exhibits no significant variation in the investigated conditions. The highly similar behavior of the two investigated nAl formulations is well shown by the data for the strain sweep at 1 Hz and 40° C presented in Figure 12. While storage modulus remains constant over the tested strain range, loss modulus exhibits faint increasing behavior due to the strain growth.

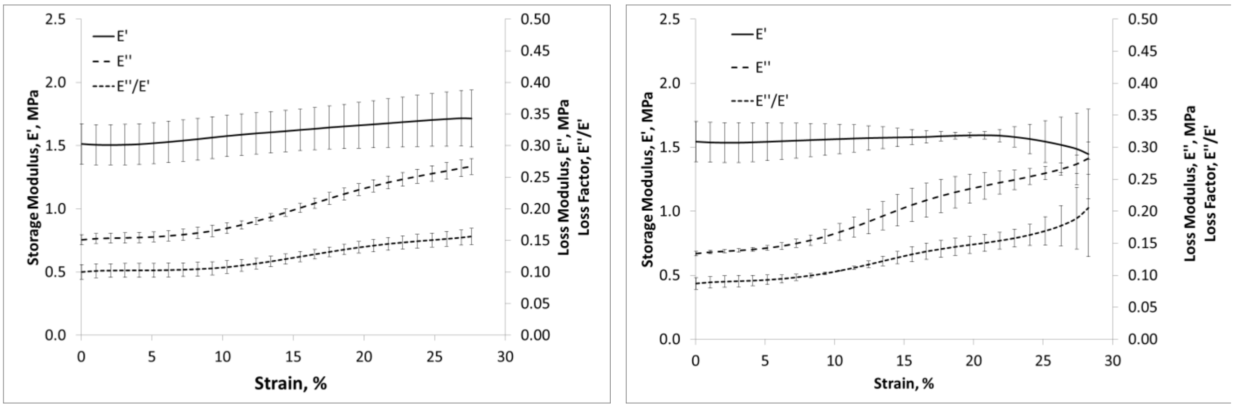
Table 4**:** Frequency sweep data for the tested HTPB-based fuel formulations at 40°C.

Fuel Formulation	**Frequency, Hz**	**Storage Modulus, E', MPa**	**Loss Modulus, E'', MPa**	**Tan(δ) = E''/ E'**
HTPB	1	0.83 ± 0.07	0.12 ± 0.03	0.14 ± 0.4
	10	0.98 ± 0.07	0.20 ± 0.04	0.20 ± 0.4
HTPB + H0-ALEX	1	1.43 ± 0.34	0.16 ± 0.01	0.11 ± 0.03
	10	1.71 ± 0.34	0.27 ± 0.01	0.16 ± 0.04
HTPB + H-ALEX	1	1.47 ± 0.28	0.14 ± 0.01	0.10± 0.02
	10	1.71 ± 0.25	0.25 ± 0.01	0.15 ± 0.03

Table 5**:** Frequency sweep data for the tested HTPB-based fuel formulations at 50°C.

Fuel Formulation	**Frequency, Hz**	**Storage Modulus, E', MPa**	**Loss Modulus, E'', MPa**	**Tan(δ) = E''/ E'**
HTPB	1	0.81 ± 0.06	0.10 ± 0.02	0.12 ± 0.3
	10	0.93 ± 0.02	0.18 ± 0.04	0.19 ± 0.4
HTPB + H0-ALEX	1	1.23 ± 0.23	0.14 ± 0.01	0.11 ± 0.02
	10	1.46 ± 0.22	0.24 ± 0.01	0.16 ± 0.03
HTPB + H-ALEX	1	1.33 ± 0.38	0.12 ± 0.00[a]	0.09± 0.03
	10	1.53 ± 0.38	0.21 ± 0.00[a]	0.14 ± 0.04

[a] Uncertainty is lower than 0.01.



a **b**

Figure 12 : Strain sweep for nAl loaded fuels, HTPB + H0-ALEX (a) and HTPB + H-ALEX (b).

6. Conclusions and future developments

In order to improve compatibility between nanoparticles and HTPB matrix, coating with the same polymer, used as fuel in hybrid rocket systems and as binder in solid propellants is considered. Size distribution and stability analyses show that the best coating is obtained with 1% HTPB, mineral spirit as solvent and acetylacetone as coupling agent.
Another promising solution to improve dispersion is given by the coating of acetylacetone alone, due to the fact that it reduces the average size of particles and does not promote cohesion. Rheological experimental investigations on formulations containing HTPB, AP and 18% of μAl confirm the increment in formulation viscosity due to AP volumetric fraction increase with an asymptotic behavior, in agreement with literature data. The correlation between rheological properties and microstructure of the compound is researched, finding a cubic dependence of stiffening factor with the number of aluminum particles around each AP grain.
Experimental tests on formulations containing nanosized Al confirm the effectiveness of HTPB coating in improving compatibility between ALEX^{TM} and the polymeric matrix. In the theoretical analyses the homogenously dispersed nanopowders are supposed not to affect the increment in viscosity due to interactions at the micro-scale: the effect of nAl is only in the nanoscale and a fluid with modified viscosity is considered. On the micro-scale, the difference between the value of H obtained from experimental analyses and the theoretical one, obtained from the correlation with the number of aluminum particles around each AP grain, is connected to cluster presence.
The calculated clusters number shows a major presence if uncoated ALEX^{TM} is used and for relatively high nanosized fraction. The dependence with nanosized fraction can be explained considering that particles are closer and attractive forces are more effective.
DMA tests conducted on HTPB-based solid fuels loaded with acetylacetone-coated ALEX^{TM} and HTPB-coated ALEX^{TM} revealed no significant differences in formulation viscoelastic behaviors. Due to the presence of the energetic filler storage moduli of the tested metallized fuels result higher than the one of the baseline HTPB formulation over the whole frequency and strain investigated ranges. Tested fuels viscoelastic behavior is not influenced by solicitation frequency and strain amplitude under the investigated conditions. The presence of clusters highlighted by particle size distribution by centrifuge tests (see Figure 1) produces no significant effects on storage modulus and loss factor.
Recommended developments of the present work include a detailed analysis of possible non-inert coatings granting good compatibility with HTPB fuel/binder formulation, reduced cluster formations and low viscosity. In particular, while clustering/cold cohesion can affect solid fuels ballistics due to the limitation of powder reactivity [32], inducing negligible changes in solid fuel mechanical properties and propellant burning rates [33].

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