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Curing viscosity of HTPB-based binder embedding micro- and nano-aluminum particles

Filippo Maggi*^[a]

Abstract: Aluminum is used as a metal fuel in energetic materials for the improvement of propulsion performance and density. Both nano-sized and micron-sized activated powders represent valuable options in order to improve metal combustion properties, each possessing advantages and drawbacks. These ingredients bear peculiar properties (namely, higher specific surface, coatings, or surface characteristics) which generate high mixing viscosity once suspended in a polymer as well as altered mechanical properties of the final product. The present work takes into consideration four different powders dispersed in a polymer binder and investigates the evolution of viscosity in time during the curing process. The suspending medium is represented by a mixture of hydroxyl-terminated polybutadiene (HTPB), isophorone diisocyanate (IPDI) and dioctyl adipate (DOA). Viscosity was measured for 5 hours on samples under isothermal curing at 60°C. Non-isothermal DSC kinetic analyses were also performed using the Kissinger method. It was found that, for the test conditions, a size reduction of metal particles slowed down the increment rate of curing viscosity while some peculiar coatings, such as fatty acids, introduced opposite trends.

Keywords: aluminum particles, viscosity, nanometric, micrometric, HTPB

1 Introduction

Aluminum, in the shape of micrometric particles ranging from 5 to 50 μm , represents a standard fuel for space launcher applications, being a good compromise between performance improvements, stability in time, cost, low toxicity, and availability [1]. The agglomeration attitude of these metal particles, on the burning surface, is the cause of condensed phase combustion products which are responsible for specific impulse losses due to two-phase flow nozzle expansion [2,3]. Advanced aluminum powders featuring improved reactivity aimed at easier particle ignition were and are currently developed as an answer to the need for better combustion properties [4-7].

The use of nano-sized particles in the range 50-200 nm is justified by lower ignition temperature, faster propellant burning rates, and thin flaky aggregates. The main drawbacks consist of reduced metal content, high moisture sensitivity, increased mixing viscosity, and influence on the mechanical properties of the final product [8-12]. Coatings of fatty acids (generally, stearic or palmitic), polymers, or other chemicals may be applied to the particle surface to prevent further environmental degradation or to ease dispersion [13,14]. Modeling and experimental methods to investigate nanoparticle mixing were recently published by Reese and co-authors [15].

Micron-sized particles with specific surface activations grant some reactivity benefits, but are also easier to handle and mix, with lower expected cost, and higher effective metal content. Conversely, their processing may lead to the modification of the surface composition and finishing as well as a change in the shape factor, which eventually favors higher mixing viscosity [16-19].

Hydroxyl-terminated polybutadiene (HTPB) is

a typical pre-polymer widely used in propellant formulations. The curing kinetics of the HTPB binder depends on the reciprocal concentration of NCO and OH groups. The isothermal viscosity level relates to the growth of the average molecular weight of the polymer chains and typically follows an exponential trend in the shape $\eta(t) = \eta_0 \exp(k_1 t)$ [20]. It has been observed that the solids loading has a significant effect on the process [21,22]. Papers relevant to the connection between curing viscosity and filler type were not retrieved in the open literature by the author.

The present paper addresses the isothermal viscosity of metalized HTPB-based binders filled with four different types of metal powders: two nanometric and two micrometric. The solid loading was limited to a 10% fraction by mass (about 4% by volume) in order to reduce particle-particle interaction. These formulations were not meant to be representative of optimized energetic materials characterized by higher solid loading, such as solid propellants, but were formulated to give a perspective on binder reactivity. Complex viscosity build-up in time was measured using a flat-plate rheometer in a strain-controlled oscillatory test for five hours at 60°C. Model-free curing kinetics of selected mixes were also investigated using DSC and the Kissinger method.

2 Materials

2.1 Powders and additives

The powders used in this work were characterized as part of the European FP7 project HISP (High performance solid propellants for In-Space Propulsion) and details on their physical as well as combustion properties can be found in previous works of the same research group [6,7]. A summary of nominal size, mass-mean diameter $d[4,3]$, specific surface area S_a , and active aluminum content is reported in Table 1.

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Table 1. Properties of tested aluminum powders. The Al₀ fraction was quantified through hydrolysis; the procedure is described in [7]; confidence interval is 95%. (*: nominal data from supplier)

	Nom. Size μm	d[4,3] μm	S _a , m ² /g	Al ₀ , %
μAl-18	4.5	5.1	1.2	98.3±0.7
aAl-19a	4.5	5.4	2.6	93.9±0.6
nAl-01i	0.1	0.141	13.5	88.7±0.2
nAl-07e	0.1	0.149	10.5	91.6±1.1
Al ₂ O ₃	<10	8.2	N.Av.	<0.5*
AlF ₃	N.Av.	20.9	N.Av.	<0.5*

The μAl-18 powder (producer Valimet Inc., type H3) is nearly spherical with a smooth surface, naturally covered by an oxide layer.

The aAl-19a powder, shown in Figure 1, was derived from the μAl-18 batch with a process of chemical activation through a fluorine-based solution. The surface of the powder is rough after the treatment, granting a higher specific surface without altering its shape factor. The powder particle size was minimally increased by 0.3 μm. Powder processing was performed at FOI, using a method developed by Hahma [16]. The surface atomic concentration, analyzed through XPS, consisted of 58% of oxygen, 5.5% of carbon, 13% of fluorine, and 17% of aluminum in the oxidized state +3. Traces of boron (3%), potassium (1.5%), and manganese (2.1%) were identified as well. The simultaneous presence of both AlF₃ and Al₂O₃ is possible owing to detected relative concentrations.

Other compositions were formulated aiming at a better understanding of the effects introduced by these modified aluminum powders on binder curing. The metal fuel was totally replaced with aluminum oxide (alpha phase, measured d[4,3]=8.2 μm, Sigma Aldrich, lot MKBJ1604C) and aluminum fluoride (rhombohedral alpha phase, measured d[4,3]=20.9 μm, Sigma Aldrich, lot MKBP1432V), maintaining the volumetric filling factor of the initial metalized composition. Tests with pure binder and carboxyl acids were performed as well (palmitic acid lot SZBD1970V, stearic acid lot MKBM0661V, both supplied by Sigma Aldrich).

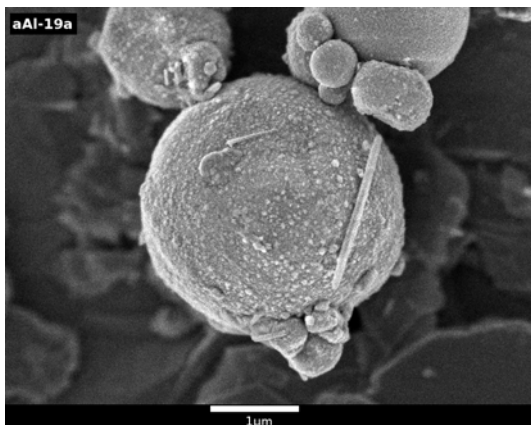


Figure 1. SEM micrograph of micro-aluminum aAl-19a (magnification 20k)

The uncoated nanoaluminum powder nAl-01i was produced using the EEW technique and was supplied by Sibthermochim (commercial name ALEXTM). The particles were spherical, smooth, and naturally covered by a passivation layer of aluminum oxide. The particle size, measured by laser granulometry using wet dispersion, was 0.141 μm.

The nAl-07e powder is a nanoaluminum whose commercial name is L-ALEXTM. It is produced by coating the surface of nAl-01i with a carboxyl acid (stearic or palmitic) to prevent further material degradation after the exposure to air and moisture. The specific melting peak of the palmitic acid coating was identified by DSC in this batch. Its mass-mean diameter was 0.149 μm, as determined by granulometry using wet dispersion.

2.2 Suspending medium

The suspending medium consisted of an HTPB-R45 oligomer by Cray Valley (lot V1501B, hydroxyl value 0.83±0.05 meqKOH/g, molar mass 2800 g/mol) mixed with IPDI, using an NCO:OH ratio of 1.04. The mass fractions of DOA and of the aluminum fuel were 13% and 10% respectively. Batches of 5 grams were mixed with a Resodyn Labram resonant mixer at about 50 g acceleration for 5 minutes under vacuum (15 kPa absolute pressure). The vessel was air-cooled to ambient temperature (21±2 °C), in order to prevent temperature rise from mixing, with a specific in-house device.

3 Experimental Section

The mixed samples were tested on a flat-plate rheometer (TA AR2000ex) at 60°C constant temperature. A thermal stabilization of 5 minutes was applied before starting the measurement. Complex viscosity $|\eta^*|$ was mapped during a 5-hour-long test with a 2% strain-controlled procedure under a reference frequency of 1 Hz. The strain was selected in order to operate in the linear field. The real component η' of the complex viscosity (in-phase viscosity) was observed to be much higher than the imaginary part η'' (out-of-phase viscosity, elastic behavior) for tested mixes, with the exception of samples containing a carboxyl acid. In the latter case, the suspensions approached or even crossed the gel point during the 5-hour tests, being the gel point identified by the relation $\eta' = \eta''$ [23].

Model-free apparent curing kinetics for selected mixes were investigated using the Kissinger non-isothermal method. Differential scanning calorimeter (DSC) tests were conducted at heating rates of 2.5, 5, 10, 20 K/min over the range of -20°C to 300°C on a TA 2010 DSC instrument using argon as purging gas (purity >99.995%). The activation energy (E_a) and pre-exponential factor (A) were fitted through Eq. (1) [22].

$$\ln(\beta / T_p^2) = \ln(AR / E_a) - E_a / (RT_p) \quad (1)$$

4 Results

A summary of the results obtained for the binder-fuel suspensions is given in Table 2. The isothermal build-up in time of $|\eta^*|$ is reported for all mixtures per each hour of processing, starting from the beginning of the test, after five minutes of thermal stabilization.

Table 2. Time evolution of isothermal viscosity $|\eta^*|$ for fuel-binder suspensions.

Time min	0	60	120	180	240	300
No add.	0.560	0.776	1.074	1.472	1.981	2.693
μ Al-18	0.579	0.756	0.960	1.241	1.554	1.962
aAl-19a	0.609	0.760	0.962	1.199	1.506	1.909
nAl-01i	0.854	0.936	1.108	1.383	1.714	2.134
nAl-07e	0.855	1.259	1.941	2.875	4.178	6.083
Al_2O_3	0.642	0.947	1.355	1.946	2.793	4.033
AlF_3	0.896	1.192	1.608	2.176	3.011	4.177
Palmitic	0.817	3.501	13.46	65.27	Gelled in 230 min	
Stearic	0.824	4.020	19.45	111.4	Gelled in 218 min	

4.1 Initial viscosity

The suspensions behaved like a Newtonian fluid under the conditions of the test. This was also observed by Teipel and Förter-Barth [24]. The initial isothermal viscosity $|\eta^*|$ of the mixtures increased as the specific surface area of the filler increased. The slurries filled with nanometric particles had about 50 percent higher initial viscosity than the micrometric filled samples. The mixture filled with μ Al-18 aluminum had the lowest initial viscosity. These findings are similar to those of Teipel and Förter-Barth [24] and Roscoe [25] for the nanometric based samples and Arefinia and Shojaei [25] for micron-sized powders. Based on mere size considerations, the aAl-19a and μ Al-18 can be classified as dilution fillers which contribute to viscosity mainly through hydrodynamic effects. The aluminum oxide and the aluminum fluoride also belong to this category. The viscosity of Al_2O_3 suspension was comparable to the one produced by μ Al-18, owing to similar particle size of the fillers. The higher initial viscosity of AlF_3 mixes was attributed to a different particle shape. The nAl-01i and nAl-07e powders are semi-reinforcing fillers producing particle-to-particle interaction despite the limited solids loading [26]. A high initial viscosity of polymers mixed with carboxyl acids resulted in fast curing reactions during the pre-test conditioning phase.

The aAl-19a and μ Al-18 powders have the same shape factor and almost identical particle size. The diameter of the aAl-19a powder, $D[4,3]$, increased by 0.3 μ m and an external roughness was formed due to some deposits derived from activation of the surface. Despite its more-than-doubled specific surface area, the effect on compound viscosity was only +5%, when compared to μ Al-18. This small amount may be explained by the fact that specific surface was increased by an alteration of the particle

superficial finishing, and not by the variation of shape or size. Discussions on this point are not abundant in the literature although some authors have addressed the matter. Macro-scale experiments on cements conducted by Erdoğan *et al.* did not show appreciable effects on viscosity generated by the level of superficial finishing of suspended particles for different filling factors [27]. The problem was addressed theoretically by Wilson and Davis, who found a negative contribution to the global viscosity, proportional to the square of the volume concentration [28]. The effect was negligible for suspensions with low filling factors or high roughness height and was surpassed by the effect of variation of the apparent particle diameter, which is a function of the superficial roughness of the particles.

The size and shape of the nAl-07e resembles that of nAl-01i, in the nanoaluminum group. The organic coating is expected to ease dispersion in a polymer matrix but it also reduces the specific surface area about 25% without appreciable influence on the compound viscosity. Similar results were found by Mary and co-authors on HDPE-coated nanoaluminum suspended in HTPB for comparable low volumetric fractions [13].

4.2 Temporal evolution of viscosity

Table 3 summarizes the parameters of the exponential function $|\eta^*| = |\eta^*|_0 \exp(k_\eta t)$ fitted to the experimental viscosity data. The constant $|\eta^*|_0$ represents the intercept at time $t = 0$, while k_η is the rate constant for the viscosity increment in time. The statistical correlation parameter R^2 is above 0.99 for all cases. Data are presented for both metal-polymer suspensions and for additional supporting analyses.

Table 3. Exponential fitting of isothermal viscosity build-up $|\eta^*| = |\eta^*|_0 \exp(k_\eta t)$.

	$ \eta^* _0$ Pa·s	k_η 1/min	R^2
No add.	0.561	0.00527	0.9994
μ Al-18	0.587	0.00407	0.9992
aAl-19a	0.598	0.00387	0.9993
nAl-01i	0.768	0.00332	0.9923
nAl-07e	0.852	0.00665	0.9989
Al_2O_3	0.654	0.00604	0.9999
AlF_3	0.862	0.00520	0.9995
Palmitic	0.791	0.02421	0.9989
Stearic	0.789	0.02700	0.9992

The slowest viscosity buildup rate was obtained for compositions containing the uncoated nanoaluminum nAl-01i. Higher rates were found for aAl-19a and μ Al-18, respectively, although the resulting k_η was still lower than the baseline polymer. The suspension containing the coated nAl-07e, in contrast, exhibited a doubled rate as compared to the uncoated nanoaluminum, and was about 20% higher than the baseline formulation.

The rate constant for aluminum oxide suspensions was found to be higher than that of the baseline composition while about the same value was found for mixtures containing aluminum fluoride. Tests performed to investigate the influence of fatty acids on the curing process showed increased kinetics, resulting in a rate constant k_n five times higher than the baseline suspension. These analyses were conducted without metal fuel, by dispersing the fatty acid in the HTPB pre-polymer. The additive mimicked the amount of the coating introduced by the nAl-07e powder. The weight of the protective layer was assumed to be the 5% of the whole particle mass, in compliance with Teipel's assertion [29].

4.3 Curing kinetics

Non-isothermal DSC analyses were performed on selected suspensions. Micrometric and nanometric uncoated aluminum (μ Al-18 and nAl-01i), coated nanoaluminum (nAl-07e) and aluminum oxide were investigated. Peak reaction temperature and Arrhenius parameters derived by the Kissinger method are reported in Table 4.

Table 4. Non-isothermal DSC peaks and fitting parameters for model-free curing kinetics.

	No add.	μ Al-18	nAl-01i	nAl-07e	Al ₂ O ₃
T_p ($\beta = 2.5$ K / min)	168.3	166.0	167.9	152.8	166.4
T_p ($\beta = 5$ K / min)	179.9	174.7	175.9	161.6	177.9
T_p ($\beta = 10$ K / min)	187.5	189.3	188.9	172.9	188.9
T_p ($\beta = 20$ K / min)	201.6	203.1	202.6	181.6	201.8
A	114.3	17.0	42.1	121.6	40.8
E_a	14.97	12.25	13.54	13.53	13.49
R ²	0.987	0.992	0.992	0.994	0.999

The activation energies were similar for all the tested compounds, regardless of the particle size or the presence of a fatty acid coating. The highest and the lowest values were obtained for the baseline binder (14.97 kJ/mol) and for the suspension embedding μ Al-18 (12.25 kJ/mol) respectively. Some differences were observed in the pre-exponent. The value of the parameter A for all uncoated metal slurries as well as Al₂O₃ suspensions was at least 5 times lower than the value obtained for the nAl-07e mix and the pure binder.

5 Discussion

All of the aluminum suspensions, with the exception of the nAl-07e mixture, resulted in a reduced viscosity build-up rate, when compared to the unloaded HTPB-based polymer. The presence of uncoated metal particles inside the polymer caused a dampening effect on the curing kinetics, resulting in a progressive decrease of the k_n parameter. A stronger reduction was obtained for the mixtures containing powders with a higher specific surface area. The fact that a micrometric filler can slow down the HTPB viscosity increment was acknowledged by Mahanta

and Pathak [22]. Another confirmation can be found in a report by McManus *et al.*, where the authors scrutinized the effect on binder curing by different propellant ingredients [30]. Kinetic tests for the specific case of aluminum were reported for different micrometric powders finding that the relative curing reaction rate increased when using particles characterized by larger diameter. The kinetic tests performed in the present work on uncoated aluminum slurries confirmed the dampening effect with respect to the baseline binder but also noted that the trend did not extend into the nanometric range.

The curing of the Al₂O₃ suspension featured a viscosity build-up rate almost double that of the aluminized compositions. Alumina is known to increment the polymerization rate in other polyaddition processes, such as the epoxy-amine reactions [31]. However, no peculiar behavior was observed from a kinetic standpoint. It should be noted that all uncoated metal particles are covered by a natural layer of amorphous aluminum oxide which might behave in a different way with respect to the alpha phase of the tested Al₂O₃ additive. A definitive explanation for the dampening effect is not yet available and is beyond the scope of this paper, however, both mobility depression of the molecular chains by the filler and more complex chemical interactions with the suspended particles cannot be excluded.

Surface particle treatment of the μ Al-19a did not produce significant modifications of the curing reaction with respect to the original μ Al-18 powder, limiting its action on a variation of the initial viscosity. The tests on suspensions of AlF₃, present on the activated surface, did not demonstrate peculiar behavior. The rate constant k_n was similar to the one observed by the baseline polymer, owing to the fact that the AlF₃ additive was relatively coarse.

Interesting properties were shown by ALEX nano-powders. The dampening effect on the curing rate of the uncoated nAl-01i was the strongest. The presence of an organic layer on the surface of nAl-07e did not contribute to the reduction of the initial mixing viscosity but delivered higher $[\eta^*]$ increment rate. Also the kinetic pre-exponential parameter was higher with respect to the other metal powders. Such behavior may be attributed to the presence of the acid-kind protective coating. Baseline compositions embedding palmitic or stearic acids demonstrated a substantial increase in the reaction rate, with no difference between the two materials. The result was expected, since it is known from organic chemistry that carboxyl acids react with NCO groups of isocyanate forming amides. However, further reactivity with the aluminum carboxylate, present at the first atomic layer of the coated particle, might also be possible [33,34].

6 Conclusion

This paper addressed the isothermal viscosity buildup of a HTPB-based binder embedding micron- and nano-sized particles with different surface treatments. The analysis showed that, under the tested

conditions, metal-polymer curing kinetics was reduced using uncoated aluminum powders. Particle size was observed to play a role in this respect finding a slower reaction rate for higher specific surface area. The origin for this effect, observed for both nanometric and micrometric powders, has not been yet fully understood. Both mobility depression of the molecular chains by the filler and more complex chemical interactions with the suspending material cannot be excluded so far. A high viscosity level and development rate was observed for the nanoaluminum coated with fatty acid resulting in a final value three times higher than the uncoated variant. Reaction between isocyanate and fatty acid, or isocyanate and carboxylate product of the coating process, is the possible reason. Finally, it should be underlined that results were retrieved under a condition of low filler volume fraction, in order to minimize the particle-particle interaction effect. Extrapolation to highly loaded compositions, typical of propellants, might not be straightforward.

Symbols

A Arrhenius pre-exponential factor, 1/s
 $d_{[4,3]}$ Mass-weighted mean diameter, μm
 E_a Arrhenius activation energy, kJ/mol
 k_n Rate constant for viscosity buildup, 1/s
 R Universal gas constant, 8.314 J/(mol K)
 R^2 Coefficient of determination
 S_a Specific surface area, m^2/g
 t Time, s (if not differently stated)
 T_p Peak temperature, K
 x', x'', x^* Real, imaginary and complex value of x
 $|x|$ Modulus of x
 β Heating rate, K/s (if not differently stated)
 η Viscosity, Pa·s

Abbreviations

Al_0 Active aluminum content
 aAl Activated aluminum
 BET Brunauer-Emmet-Teller
 DOA Dioctyl adipate
 DSC Differential scanning calorimeter
 EEW Electrical explosion of wires
 FOI Swedish Defense Research Agency
 HDPE High density polyethylene
 HTPB Hydroxyl-terminated polybutadiene
 IPDI Isophorone diisocyanate
 nAl Nano-sized aluminum
 No Add. Baseline formulation
 SEM Scanning electron microscopy
 XPS X-ray photoelectron spectroscopy
 μAl Micron-sized aluminum

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