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► To cite this version:

Pierre Gibot, Virginie Goetz, Denis Spitzer. Spark sensitivity and light signature mitigation of an Al/SnO₂ nanothermite by the controlled addition of a conductive polymer. Chemical Engineering Journal, 2022, 427, pp.131611. 10.1016/j.cej.2021.131611 . hal-03365188

HAL Id: hal-03365188

<https://hal.science/hal-03365188>

Submitted on 5 Oct 2021

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Spark sensitivity and light signature mitigation of an Al/SnO₂ nanothermite by the controlled addition of a conductive polymer

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Abstract: (250 words)

The development of insensitive energetic composite materials is a research topic of growing interest. Nanothermites, which are described as a highly reactive mixture of metal and metal oxide, are the focus of this challenge.

In this work, the conductive polymer polyaniline (PAni) was introduced into an Al/SnO₂ energetic nanocomposite either via the preparation of a SnO₂-PAni composite or as a powdered ternary compound. Both PAni-enriched Al/SnO₂ nanothermites were characterized in terms of sensitivity (impact, friction, electrostatic discharge (ESD)) and reactive properties (combustion velocity). The two methods were compared to evaluate which one achieved the best compromise for the nanothermite in terms of performance (sensitivity/combustion properties). When the polymer is intimately structured with the oxide, it is possible to reduce the sensitivity of the energetic composition as a function of the additive amount. The polymer easily conducts the electrostatic charges through the energetic matter until the nanothermite presents no handling danger: ESD varied from 0.42 to 246.1 mJ for the safer composition (4.80 wt. % of PAni). On the other hand, when PAni powder was added to the nanothermite, the ESD threshold did not vary because no continuous conductive phase was created within the material. Concerning the reactive properties of the Al/SnO₂ energetic system, with the addition of PAni (2.04 wt. %) as an SnO₂-PAni hybrid matrix, the combustion velocity decreased from 800 to 500 m/s combined with a lower luminous signature.

The use of a structured conductive polymer as a desensitizer within nanothermites, represents a significant step forward in the development of safer and reactive energetic compositions.

Key-words:

Energetic formulations; spark sensitivity; polyaniline; microstructuring; desensitization.

1. Introduction

Over the past few decades, nanothermites - a mixture of metal (fuel) and metal oxide (oxidizer) nanoparticles - have attracted increasing attention among energetic materials. They react according to an exothermic reaction by releasing high amounts of heat at high temperatures [1,2]. However, a major hindrance for their development is their extreme sensitivity to specific external stresses. Generally speaking, nanothermites show high sensitivity to electrostatic discharge (< 0.14 mJ) and, to a lesser extent, to friction [3]. This means the energetic matter could unintentionally react to this kind of solicitations. They are particularly sensitive to electrostatic discharge (ESD) which makes daily manipulations hazardous for users because the human body discharge capacity (estimated between 8.33 and 20 mJ [4,5]) could trigger ignition. Therefore, it is significant to reduce the risks related to the extreme sensitivity of nanothermite compositions. The current challenge in the development of nanothermites is to elaborate formulations with mitigated sensitivities while maintaining high reactive properties.

The concept of nanothermite desensitization is fairly new [6] and is based on the idea of introducing a third component that raises the sensitivity threshold(s) and makes the energetic compositions as insensitive to stimuli as possible. Examples include carbon in several forms (nanofibres, nanotubes, nanodiamonds, graphene, carbon black [6-10]), metals (copper, silver [11-12]), oxides (Al_2O_3 , Fe_3O_4 , SnO_2 [13-14]) and polymers (Viton A, nitrocellulose, polyaniline [15-18]). The intensive use of carbon as an additive showed that ESD threshold is linked to the structure of carbon. For example, nanodiamonds were able to raise the threshold value to 1000 mJ with a concentration of 4.5 wt.% for an $\text{Al}/\text{Bi}_2\text{O}_3$ nanothermite [8], while carbon black did not affect the sensitivity threshold (0.14 mJ) of an Al/WO_3 formulation with 5 wt.% [10]. However, a significant reduction in reactivity was observed with the introduction of carbon nanotubes or nanodiamonds (up to 5 wt. % maximum): in both cases, combustion velocities were determined less than 10 % of the binary system's velocity (i.e. without additive) [7-8].

Using other additives like polymers could be a suitable way of achieving spark desensitization while maintaining reactivity. Because there is a wide range of polymeric compounds with different chemical structures (functional groups, heteroatoms, length of the main chain, etc.), they could be an alternative solution. For example, among energetic polymers, nitrocellulose was used to improve reactivity but its impact on the sensitivity was not noted [19-20]. Another type of polymers, the intrinsically conducting polymers, was examined for the desensitization. Adding a conductive polymer for the nanothermite electrostatic discharge desensitization is a relatively recent idea. The addition of a conductive compound would allow easier conduction of the electric energy within the energetic formulation. Among the conductive polymer, polyaniline (PAni) has been the focus of growing interest these last decades due to its easy and low-cost polymerization, as well as its attractive electrical conductive properties [21]. This polymer was already used in different forms (nanofibers, polymer matrix) as a desensitizer and showed interesting results [17-18]. The authors indicated that the homogeneity of the mixture was a significant point in achieving ESD desensitization without suppressing the reactive properties.

In this work, a comprehensive investigation was carried out to determine the impact of additive formatting on sensitivity and reactive properties of nanothermites. The polyaniline polymer was introduced into the Al/SnO₂ nanothermite using two methods. On one hand, a composite oxide-polymer (SnO₂-PAni) was mixed with aluminium to create nanothermite, and on the other, polyaniline was combined with the binary Al/SnO₂ composite. The experimental conditions were optimized (temperature of polymerization, choice of oxidant, etc.) of our previous study to reduce additive content, and elaborate a better defined and controlled polymer coating around oxide particles and thus obtain an optimized oxide-polymer composite. The reduction of polymer amount within the energetic composition allowed the determination of reactive properties as the propagation velocity of the nanothermite in confined mode.

2. Experimental section

2.1 Materials

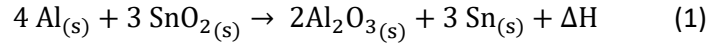
Tin (IV) oxide (SnO_2 , average particle size ≤ 100 nm), aniline ($\text{C}_6\text{H}_5\text{NH}_2$, $\geq 99.5\%$) and acetonitrile (CH_3CN , $> 99.8\%$) were purchased from Sigma-Aldrich. Aluminium nanopowder was obtained from Intrinsic Materials (pure Al wt.% of 69.3). Ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and hydrochloric acid (HCl, 37%) were purchased from Prolabo Normapur and Roth, respectively. All chemical reagents were used as received, without any further purification.

2.2 Synthesis of Polyaniline and SnO_2 -Polyaniline composite

The synthesis of SnO_2 -Polyaniline nanocomposites was inspired by the work of Zhang *et al.* [22]. Briefly, 500 mg of SnO_2 were dispersed in 50 mL of HCl solution (1 M) under sonication (30 min) to obtain a uniform suspension. The mixture was cooled down with an ice-bath and a certain amount of aniline was introduced under stirring. The polymerization was achieved at a cold temperature (5°C) instead of at room temperature [18] to improve the polymerization yield and favour the synthesis of a polymeric phase with enhanced conductive properties [23-24]. After one hour, the pre-cooled ammonium persulfate aqueous solution was added. Ammonium persulfate was chosen as the oxidant for the polymerization of aniline instead of potassium dichromate [18] since it exhibits high solubility at low temperature and is less harmful to users and the environment [25-26]. The molar ratio of aniline monomer to ammonium persulfate was equal to 0.9. During the oxidative polymerisation (20 hours), the colour of the solution becomes blue and then progressively dark green. The product was collected by centrifugation (4000 rpm, 4 min) and washed with demineralized water until a colourless supernatant was obtained and then twice with ethanol. Then, the product was dried under vacuum at 80°C overnight. The amount of polyaniline in the SnO_2 -PAni composites was varied from 1 to 8 wt.% with values of 1.46, 2.93, 3.92, 4.57 and 7.08 wt.%. The synthesis of the powdered polyaniline polymer was achieved following the same method except without the use of SnO_2 nanoparticles.

2.3 Formulation of the ternary PAni-doped Al/SnO₂ nanothermites

The aluminothermy reaction between aluminium and tin (IV) oxide can be written as (1):



with ΔH the amount of energy released during the reaction.

For the present study, the Al/SnO₂ nanothermite was prepared according to an equivalence ratio (ϕ) - whose formula is given in (2) – equal to 1.2 that leads to the higher combustion velocity for the investigated energetic system [27].

$$\Phi = \frac{(M_F/M_O)_{\text{exp.}}}{(M_F/M_O)_{\text{st.}}} \quad (2)$$

where M_F/M_O corresponds to the mass ratio of fuel (Al) to oxidizer (SnO₂) and the subscripts “exp.” and “st.” mean experimental and stoichiometric conditions, respectively.

The energetic mixtures composed of aluminium, tin oxide (SnO₂), polyaniline (PAni) or tin oxide-polyaniline composite (SnO₂-PAni) nanopowders were prepared by physical mixing. The nanothermite systems formulated were named according to the way the additive was introduced and its concentration (X). For a polymer inserted as a third component or by means of the synthesis of an oxide-polymer composite, the corresponding energetic composites were named Al/SnO₂/PAni-X and Al/SnO₂-PAni-X, respectively. For feature comparison, a PAni-free energetic system was also prepared and was labelled Al/SnO₂.

For example, the elaboration of 500 mg of the Al/SnO₂/PAni-2.04 thermite was performed by mixing 142.3 mg of Al, 347.5 mg of SnO₂ and 10.2 mg of PAni. The mixture was stirred during one hour with regular ultra-sonication interruptions (5 min every 30 min) before the removal of the solvent by means of a rotary evaporator (200 mbars, 80 °C, 100 rpm). The resulting energetic mixture was dried at 80°C (4 hours) before complete recovery. By analogy, for 500 mg of the Al/SnO₂-PAni-2.04 thermite, the

mixture was composed of 142.6 mg of Al and 357.4 mg of SnO₂-PAni-2.93 composite. The binary composition Al/SnO₂ was formulated with 145.2 mg of Al and 354.8 mg of SnO₂.

2.4 Characterization techniques

The polymer compound, prepared under powdered form or through a SnO₂-polymer composite, was characterised by different techniques. Fourier transform infrared (FTIR) spectroscopy was used to identify the chemical bonds of the polymer. For that, a Bruker Tensor 27 spectrometer in transmission mode (KBr disks) was selected. All spectra were recorded in the 4000 – 400 cm⁻¹ range (resolution 4 cm⁻¹) and by superposing 16 scans. Thermo-gravimetric analyses (TGA) were performed on a Seiko Exstar 600 TG/DTA 6200 to determine the concentration of polymer in the different SnO₂-polymer composites. Experiments were conducted between ambient temperature and 900 °C, under air (100 mL/min) and with a heating rate of 5 °C/min. The morphology and microstructure of the samples were investigated by a scanning electron microscope (SEM FEI Nova NanoSEM 450, FEI) working at 10 kV and by a transmission electron microscope (TEM ARM-200F JEOL, Japan) operating at 200 kV. The electrical conductivities of the polymer and SnO₂-polymer composites were determined by measurements carried out with a low conductance meter (HRLC 2, Alpha Lab Inc., Salt Lake City, USA). The sample was restrained in an insulating cylindrical matrix (inner diameter = 4 mm) to avoid any perturbations from external current. Two copper electrodes were placed on both sides of the sample to ensure the electrical conduction through the matter to be analysed. Before the measurement, the sample was pressed at 2.5 MPa over a period of one minute. The electrical conductivity (σ in Siemens per centimetre, S/cm) values were determined by using the equation (3):

$$\sigma = \frac{1}{R} * \frac{e}{S} \quad (3)$$

with R the electrical resistance (Ω), e the thickness of the sample (cm) and S the section surface (cm²) where the current passes through the sample.

The properties of nanothermites, namely the sensitivity and reactive properties were determined by specific devices.

To determine the sensitivity properties of energetic systems, three types of stresses were applied through impact, friction and electrostatic discharge tests. According to standard procedure, impact sensitivity was measured with a BAM fall hammer (BFH-12, OZM Research) [28]. The sensitivity was determined by the falling of a mass (1 or 5 kg) on the sample, encased in two specific cylinders. The drop height (15 to 100 cm) was adjusted to find the impact sensitivity threshold. For the friction test, the sensitivity was evaluated by means of a BAM friction apparatus (FSKM-10, OZM Research) [29]. The energetic matter was placed on a ceramic plate and a ceramic peg was used to perform the friction solicitation on the energetic matter. The friction threshold was ascertained by knowledge of the force applied on the peg. Concerning the electrostatic discharge test, the sensitivity was determined by the device provided by OZM Research (ESD 2008). A spark, generated between two electrodes, passed through a small amount of energetic matter. The intensity of the electrostatic energy is defined by the capacitance and current voltage of the device. In all tests, if the energy applied is sufficient to trigger ignition, the energetic matter reacts rapidly (fumes, sound, luminous flash, change of powder aspect, etc.). All sensitivities thresholds were determined at the highest value of solicitation when the result corresponds to six consecutive non-reaction ("no-go"). The international standards have fixed the security thresholds at 80 N and 2 J for friction and impact tests, respectively [30]. Based on the dedicated literature, the ESD reference was fixed using values corresponding to the human body discharge capacity given by Greason at 8.33 mJ [4] or by Talawar *et al.* at 20 mJ [5]. If one of these sensitivities is over the reference standards, the nanothermite could be handled or transported safely. The reactive properties (combustion velocity) of the Al/SnO₂/PAni-X, Al/SnO₂-PAni-X and Al/SnO₂ nanothermites were determined by means of the set-up described in [17-18]. The nanothermite compositions were confined in polymethylmethacrylate tubes (PMMA) (length = 150 mm, inner diameter = 3 mm) with a constant loading density all along the tube. The density of each energetic composition was calculated using the theoretical maximum density (TMD) from the equation (4) [32]:

$$TMD = \frac{1}{\sum_{i=1}^n \frac{m_i}{\rho_i}} \quad (4)$$

with i the component of the nanothermite and m and ρ , its mass and its density, respectively.

The ignition of the compositions was achieved by a laboratory-made igniter, placed in front of one extremity of the tube [32]. The combustion phenomenon was recorded using a Photron FASTCAM high-speed camera (50 000 frames per second). From these video recordings, two parameters were determined: the combustion velocity by following the front combustion traveling as a function of time and the combustion's luminosity which could be correlated to the heat released during combustion [33-34]. The high-speed camera recorded all combustion phenomena in RGB colour. The lightness is defined thanks to the HSL (Hue-Saturation-Lightness) system as:

$$L = \frac{1}{2} (M + m) \quad (5)$$

with M the largest colour component and m the smallest colour component. If L is 0, the lightness is at the minimum, the major colour is dark. If L is 1, the lightness is at the maximum, the predominant colour is white.

This lightness was calculated within a predefined area of the tube to ensure that only the luminous intensity of the nanothermite combustion itself was included. This area was predefined using two main criteria: (i) the length of the area is less than the tube's length to exclude any contribution from the igniter or its reflexion at the end of the tube, and (ii) the investigated area is at the centre of the inner tube to avoid side effects. The predefined area was then measured with a constant number of pixels regardless of the tube or the composition (*Supporting Information S1*). The average RGB values of the predefined area were obtained using GIMP software, which allowed the lightness of the image to be determined. This procedure was repeated for each combustion picture during the whole phenomenon.

3. Results and discussion

3.1 Characterization of the polyaniline and SnO_2 -Polyaniline composites

The as-synthesized PANi polymer and the different SnO₂-PANi composites were studied by thermogravimetric analysis to determine the behaviour of the polymer as a function of the temperature and its concentration within the as-synthesized composites. As the different SnO₂-PANi-X composites exhibited similar thermal behaviour whatever the polymer concentration (X) (available in *Supporting Information S2*), only the SnO₂-PANi-2.93 composite thermogram is presented in **Figure 1**, accompanied by the thermogravimetric profile of the as-synthesized polymer (**Figure 1** insert). Both thermal profiles were very similar, with two weight losses in the investigated temperature ranges (between 25-200 °C and 200-600 °C, respectively). The first weight loss comes from the removal of the water and solvent (ethanol) embedded in the polymer, and of the by-products (HCl) synthesized during the polymerization. The second (major) weight loss can be attributed to the decomposition of PANi molecular chains [35]. For the SnO₂-PANi thermal signal, no real weight loss was recorded over 600 °C suggesting both total removal of the polymer and high thermal stability of the SnO₂ material [36]. The polyaniline content in the composite was about 2.93 wt.%. For the other SnO₂-PANi composites (*Supporting Information S2*), the polymer rate was determined between 1.46 and 7.08 wt.%.

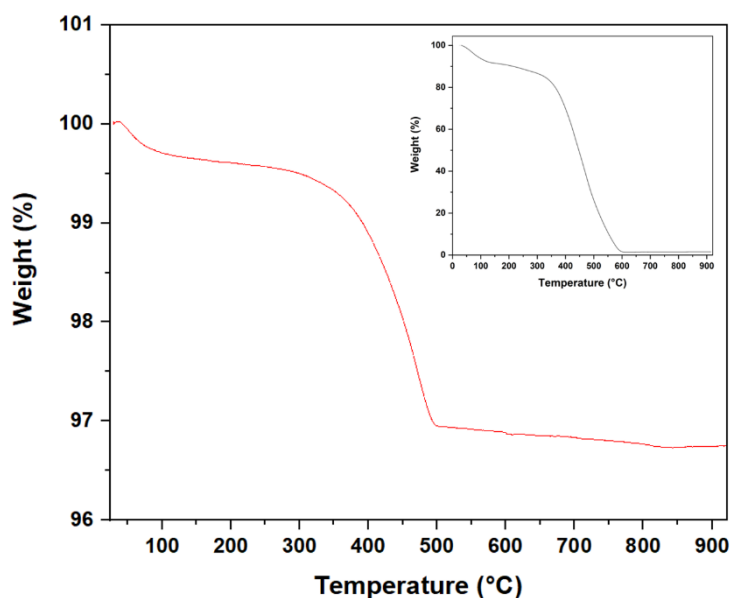


Figure 1: Thermogravimetric analysis of the SnO₂-PANi-2.93 composite. Insert: thermal profile of the as-synthesized polyaniline.

The chemical composition of the SnO₂-PANi-2.93 composite was investigated by FTIR spectroscopy (**Figure 2A**). For comparison, the spectra of the as-synthesized PANi polymer and the raw SnO₂ material

are also reported in **Figure 2B** and **Figure 2C**, respectively. The characteristic peaks of polyaniline and tin (IV) oxide were observed between 400 and 2000 cm^{-1} . For the sake of clarity, only this range of wavenumbers is described in **Figure 2**. The complete spectra are available in *Supporting Information S3*. The SnO_2 -PAni-2.93 composite (**Figure 2A**) showed the characteristic peaks of the two species, namely the polyaniline polymer between 800 and 1700 cm^{-1} and the tin (IV) oxide material at lower wavenumbers. The two main characteristic peaks of polyaniline (**Figure 2B**), the C=N stretching quinoid (Q) ring vibration at 1577 cm^{-1} and the C=C stretching benzenoid (B) ring vibration at 1488 cm^{-1} were observed on composite's spectrum. These peaks highlight the fact that the conductive form (emeraldine salt) is directly obtained for the composite SnO_2 -PAni [37-38]. Other peaks corresponding to the protonated form of polyaniline identified at 1303, 1247, 1144 and 821 cm^{-1} belong respectively to the C-N of secondary aromatic amine, polaron C-N⁺, typical N=Q=N stretching band of PAni and C-H band. Concerning the presence of the oxide, the characteristic peaks assigned to Sn-O band found at 650 and 520 cm^{-1} on the raw SnO_2 spectrum (**Figure 2C**) were also present on the composite spectrum at 653 and 514 cm^{-1} , respectively (**Figure 2A**) [39]. The spectra of the other SnO_2 -PAni-X composites (X = 7.08, 4.57, 3.92, 1.46) are very similar to the SnO_2 -PAni-2.93 spectrum and they are therefore not shown here.

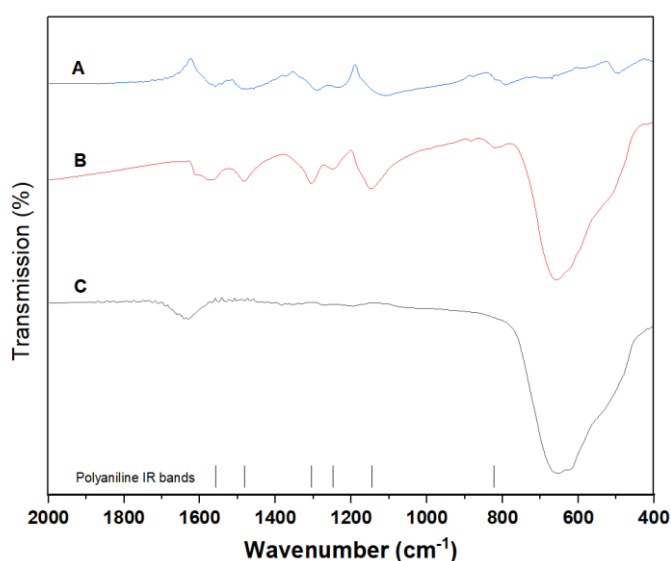


Figure 2 : FTIR spectra of the SnO_2 -PAni-2.93 composite (A), the as-synthesized powdered PAni polymer (B) and the raw SnO_2 particles (C).

As demonstrated by FTIR analysis, the polyaniline polymer within SnO₂-PAni composites is in its conductive form. Therefore, the electrical properties of the different SnO₂-PAni-X composites were determined and gathered in **Table 1**. As expected, the value of the electrical conductivity increases as a function of the concentration of PAni polymer within the composite. For example, values of 1.08×10^{-4} S/cm and 2.75×10^{-2} S/cm were determined with a PAni weight percent of 2.93 and 7.08 respectively. However, for the different SnO₂-PAni composites, the electrical conductivity is considerably lower than PAni polymer due to the low electrical conductivity of the tin (IV) oxide phase (3×10^{-9} S/cm). Concerning the conductivity of pure PAni phase, it is quite low relative to values from literature (10^0 S/cm against 10^{-1} S/cm here), which could be explained by several parameters (sample processing, method of electrical measurement...) [23]. Finally, the varying of the PAni rate conducts to the elaboration of composite materials (SnO₂-PAni) with tuneable electrical conductivity which could impact the ESD sensitivity threshold of the corresponding Al/SnO₂-PAni nanothermites.

Table 1: Electrical conductivity of SnO₂-PAni-X composites. The corresponding data of the SnO₂ (X = 0 %) and as-synthesized PAni (X = 100 %) materials are also given for comparison.

<i>X = PAni rate (wt.%)</i>	0	1.46	2.93	3.93	4.57	7.08	100
<i>Electrical conductivity σ (S/cm)</i>	3.00×10^{-9}	6.20×10^{-5}	1.08×10^{-4}	5.03×10^{-4}	5.30×10^{-3}	2.75×10^{-2}	1.78×10^{-1}

The morphology of the different SnO₂-PAni hybrid compounds was studied by SEM analysis and one example of composite, namely the SnO₂-PAni-2.93, is shown in **Figure 3A**. For comparison purposes, pictures of the PAni and SnO₂ materials are also presented in **Figure 3B** and **3C**, respectively. In the case of the SnO₂-PAni-2.93 composite (**Figure 3A**), the morphology was homogenous within the sample; there was an agglomeration of particles which are linked together by the binding agent. The contact surface between the particles seem to be the polymer which presents a porous and fibrous architecture as obviously observed in **Figure 3B**. The polymerization occurs around tin oxide particles, suggesting a structuring based on polyaniline matrix containing tin (IV) oxide particles. The particles

are not really defined (in terms of morphology, they are not perfectly spherical) and seem to be bigger than the SnO₂ particles (reference) in **Figure 3C** which are more individual, spherical and have an average particle size of 40 nm (determined by a statistical analysis based on SEM images). These different observations corroborate the successful creation of polymer's matrix around SnO₂ nanoparticles.

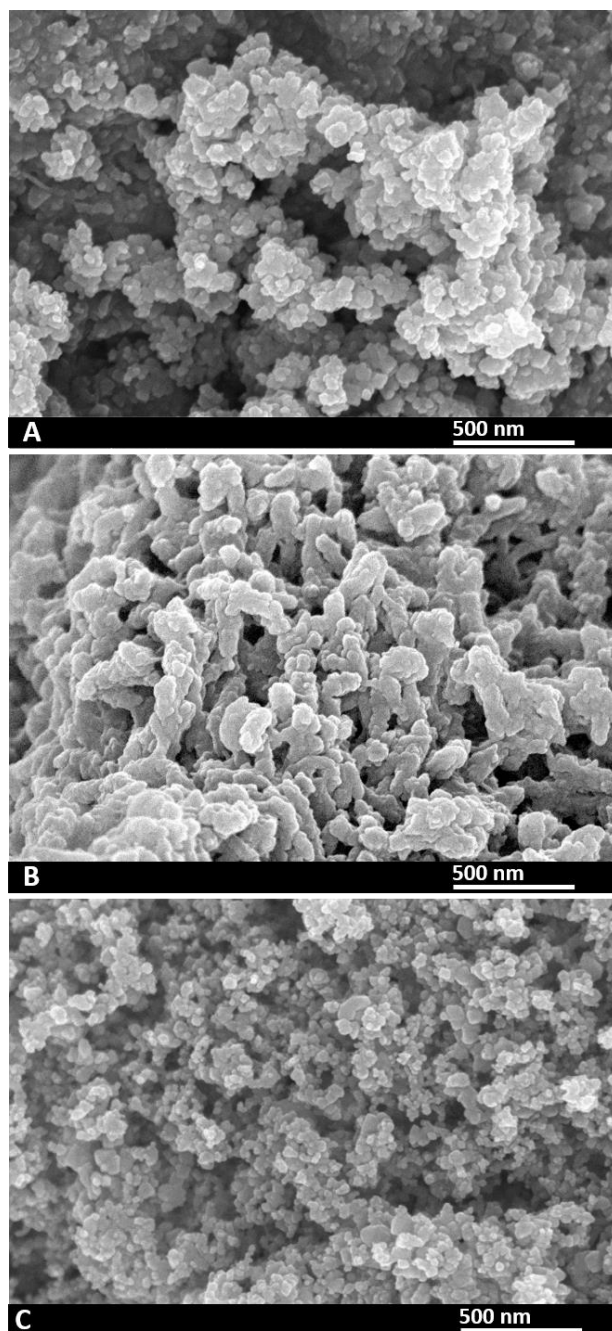


Figure 3 : SEM images of the SnO₂-PANI-2.93 composite (A), the as-synthesized powdered PANi polymer (B), and the raw SnO₂ nanoparticles (C).

Further microstructural characterizations were carried out on the SnO₂-PAni-2.93 composite by means of an HRTEM analysis (**Figure 4**). PAni polymer and SnO₂ nanoparticles are indicated on the image. Obviously, the oxide particles are linked between themselves by a binder that is consistent with the previous SEM images. This binder reflects the idea of a polymer matrix in the mixture; the polymer does not cover each particle but allows them to bind together. Compared to our previous work [18], the polymerization appears to be more controlled with a well-defined polymeric matrix and no polymer is found without physical contact with SnO₂ nanoparticles. Thus, this current study presents the elaboration of a more homogeneous oxide-polymer structure. The experimental conditions were optimized by using the common oxidant as the ammonium persulfate ((NH₄)₂S₂O₈) instead of potassium dichromate (K₂Cr₂O₇ [25-26]), and also lowering the temperature of polymerization (from room temperature to 5 °C [24]). These conditions allowed the elaboration of a more uniform coating of the polymer. Consequently, at each place where the oxide could be found, there is also the presence of the polymer.

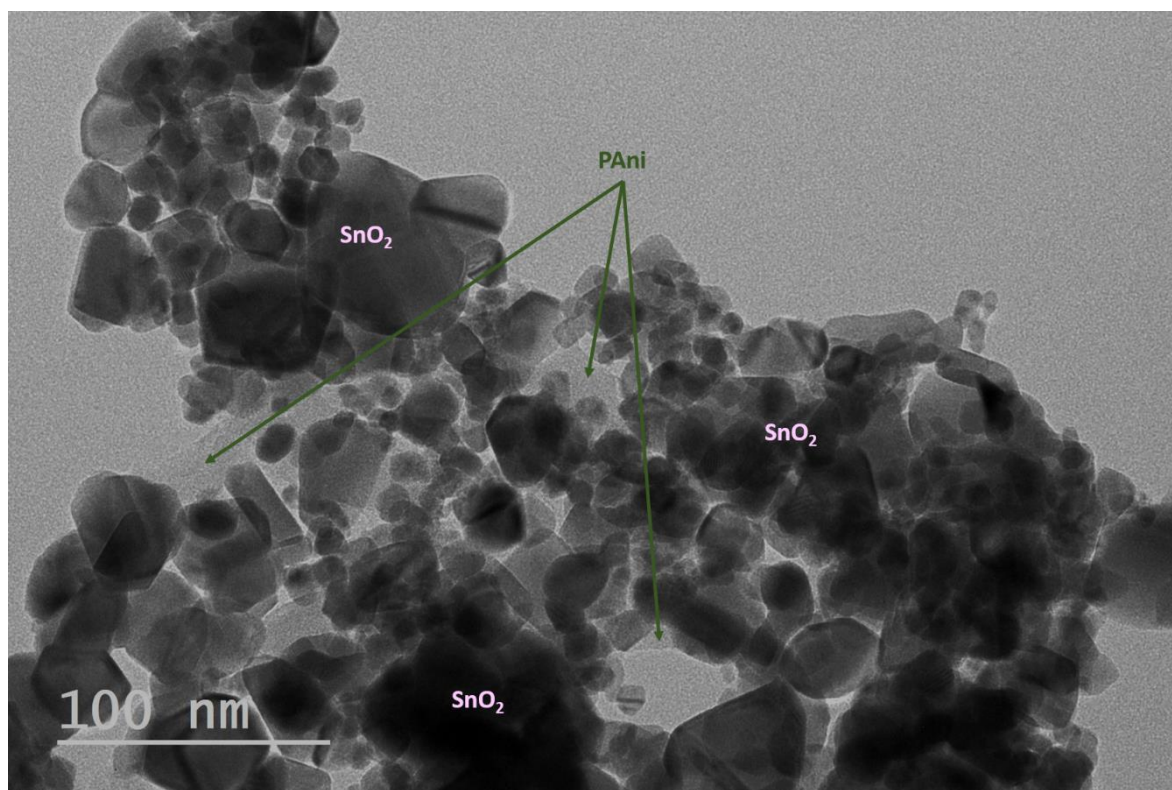


Figure 4 : TEM image of the SnO₂-PAni-2.93 composite: the dark and lighter areas correspond to SnO₂ and polymer species, respectively.

3.2 Characterization of the ternary nanothermites: Al/SnO_2 -PAni-X and $Al/SnO_2/PAni$ -X

Sensitivity tests (ESD, impact and friction)

The different Al/SnO_2 -PAni and $Al/SnO_2/PAni$ energetic formulations were characterized in terms of sensitivity and reactivity to evaluate the contribution of additive's structuring in the development of safer and reactive nanothermites. **Table 2** gathers the different values of both PAni-based energetic compositions, but also of the binary Al/SnO_2 system (reference), toward electrostatic discharge and mechanical (shock and friction) stimuli. These different results were compared to NATO's standards concerning the mechanical solicitations namely, 80 N for the friction and 2 J for the impact [30]. For the ESD stimuli, the reference values were taken to the human body discharge capacity (8.33-20 mJ) [4,5].

Table 2: Sensitivity tests results (ESD, friction, impact) for the two ternary thermites structures; Al/SnO_2 -PAni-X and $Al/SnO_2/PAni$ -X as a function of PAni concentration (X, wt.%). ">" and "<" mathematical signs correspond to maximal and minimal energy values that can be delivered by the measurement devices.

	<i>X = PAni concentration (wt. %)</i>	<i>ESD (mJ)</i>	<i>Friction (N)</i>	<i>Impact (J)</i>
Standards	0	8.33 - 20	80	2
Reference Al/SnO_2	0	< 0.21	40	47.5
Al/SnO_2 -PAni-X	1.03	< 0.42	96	> 100
	2.04	47.3	192	> 100
	2.70	78.1	96	> 100
	3.14	120.7	160	> 100
	4.80	246.4	324	> 100
$Al/SnO_2/PAni$ -X	1.03	< 0.21	160	> 100
	2.04	< 0.21	168	35

	2.70	< 0.21	160	22.5
	3.14	< 0.21	360	70
	4.80	< 0.21	192	50

First, the binary Al/SnO₂ system presented significant sensitivity to ESD with a value substantially below the reference (< 0.21 mJ vs. 8.33 – 20 mJ, **Table 2**). In the mechanical tests, impact sensitivity was not a significant problem because the value was over the standards (47.5 J vs. 2 J, **Table 2**), but friction sensitivity showed increased sensitivity (40 N vs. 80 N, **Table 2**).

The way of introducing the polymer within the energetic material had an influence on the sensitivity to impact. On one hand, complete desensitization to impact was observed in the Al/SnO₂-PAni-X system whatever the PAni concentration (**Table 2**). These values are determined at the maximum level of the impact device. The possible barrier effect played by the polymer between the aluminium and tin (IV) oxide nanoparticles and its ability to absorb energy during impact tests may explain the values obtained. The energetic composite materials thus require a higher energy to ignite. In addition, the stress level can potentially increase when the polymer concentration increases but, due to the limitations of the apparatus, it is not possible to discriminate between samples. On the other hand, when the powdered polymer is added (Al/SnO₂/PAni-X) the results are more disparate even though they stayed over the standards (> 2 J) and therefore present no handling risks. Poor distribution of the polymer within the nanothermite leading to an inhomogeneity sample could explain these disparate results. Our understanding of this random phenomenon is currently evolving.

For the friction test, both polyaniline introduction methods raised the sensitivity threshold with values of between 96 and 324 N for the Al/SnO₂-PAni system and of 160 to 360 N for the Al/SnO₂/PAni composition. For both energetic mixtures, the friction sensitivity thresholds were well over the standards enabling safer handling (**Table 3**). When the additive is introduced in the energetic mixture (whatever the introduction way), it may absorb part of the energy. The polymer could assemble freely in a linear arrangement allowing the sliding of chain during friction phenomena. This particular

arrangement could absorb part of the energy from the stimuli and thus raise the friction sensitivity threshold. A higher energy would be required to ignite the mixture [40].

Concerning ESD sensitivity, certainly the most important risk to a user, the binary system (Al/SnO₂) was particularly very sensitive to spark solicitation with a value below 0.21 mJ, far below reference's values (8.33 – 20 mJ [4-5]). Generally speaking, the high spark sensitivity of nanothermites comes from the charges' accumulation on reactants' surface which induces a thermal heating by Joule effect [41] may leading to the formation of hot spots originated of ignition of the energetic composite material considered. Herein, both polymer additive systems exhibited different ESD sensitivity thresholds. When the additive is introduced as a third component (Al/SnO₂/PAni-X system), no sensitivity mitigation is observed even with the highest concentration of PAni (X = 4.80 in **Table 2**). The additive could not prevent the charges' accumulation on reactants' surface and hence the combustion reaction could progress as the binary nanothermite system. An attempt to explain such behaviour is the poor distribution of the conductive additive within the Al/SnO₂ nanothermite. As already noted in the literature, higher additive concentrations are needed to obtain a spark desensitization (more than 5 wt.%) [6,17,42]. With an oxide-polymer structure, the Al/SnO₂-PAni-X composition displays an interesting rise in the ESD sensitivity threshold value as a function of the PAni amount (X). The behaviour of the ESD threshold is also in line with the electrical conductivity of composites. For example, the more conductive compound is present in the nanothermite, the more the system is conducting and the higher the ESD threshold is. When the polymer amount increases from 1.03 wt.% to 2.04 wt.% (x 2) the ESD threshold increases from 0.42 mJ to 47.3 mJ (100 times higher). This result can be explained by the presence of the polymer at any point in the energetic mixture. Therefore, electrostatic discharges can be easily dissipated and local heating at the Al/SnO₂ interphase is avoided or delayed [7]. It is very interesting because an early percolation threshold is obtained at only 2 wt.% (*Supporting Information S4*). This means that only 2 wt.% of polyaniline is required in the nanothermite to exceed the human body discharge capacity evaluated at close to 20 mJ [5]. With this kind of oxide-

additive structuring (Al/SnO₂-PAni-X), the ESD threshold is higher than with the powdered addition of polyaniline.

To explain the difference of results between these two additive-introduction methods, the organisation of the additive in the energetic matter was studied. The binary system as well as the systems with PAni additive; i.e. Al/SnO₂/PAni-2.04 and Al/SnO₂-PAni-2.04, were characterized by SEM analysis. The corresponding pictures are shown in **Figure 5**.

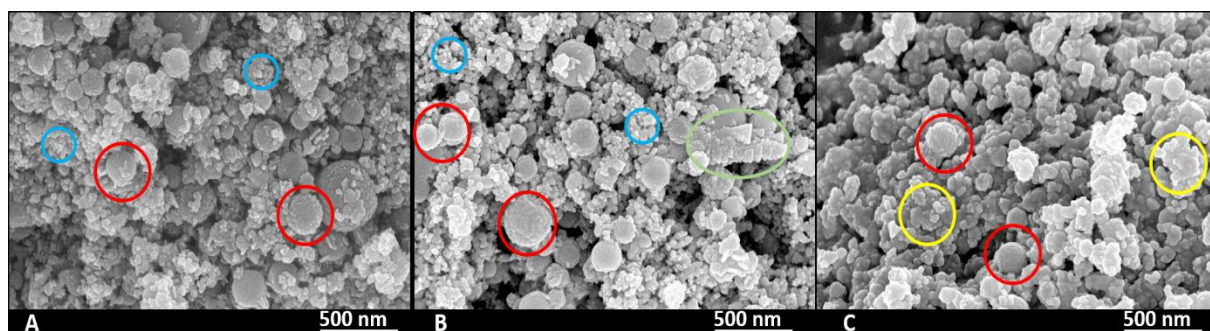


Figure 5 : SEM images of Al/SnO₂ (A), Al/SnO₂/PAni-2.04 (B) and Al/SnO₂-PAni-2.04 (C) thermites. The submicro-/nanosized spherical particles, marked with red circles, correspond to the aluminium. The SnO₂ and polymer are marked with blue and green circles, respectively. The composite SnO₂-PAni in the last image (C) is visualized with yellow circles.

The Al/SnO₂ binary system in **Figure 5A**, showed good dispersion of the two reactants; i.e. oxide and aluminium nanoparticles. When the polymer was added in the nanothermite as a third component (Al/SnO₂/PAni-2.04 **Figure 5B**), the SEM image was very like the binary system with the polymer only visible in some parts of the frame (right part of **Figure 5B**). No direct contact between the additive and one of the reactants is visible. Without any conductive pathway within the composition, electrical conduction cannot be provided in all points of the nanothermite. This is in accordance with the low ESD threshold determined for this energetic system (**Table 2**). With the Al/SnO₂-PAni-2.04 nanothermite (**Figure 5C**), the SnO₂ particles' morphology was not as well-defined as in the Al/SnO₂ energetic system (**Figure 5A**). That implies that the polymer is present at the surface of all the SnO₂ nanoparticles, as previously demonstrated in the SnO₂-PAni composite, and therefore throughout the

entire energetic formulation. With the conductive polymer present in each point of the nanothermite, the electrostatic charges can dissipate more easily and rapidly [7].

Combustion tests in confined mode

The reactive properties were studied in confined mode (tube experiments) on nanothermites doped with 2.04 wt.% of PANi polymer and on the binary system. The loading densities were about 0.664 g/cm³, 0.541 g/cm³ and 0.745 g/cm³ for the Al/SnO₂ binary system and the PANi-doped Al/SnO₂ ternary systems, respectively, representing 13.7 %, 11.5 % and 15.8 % of their respective TMD.

Figure 6 shows the combustion reactions of the three systems: the Al/SnO₂ binary thermite in frames **A** and the Al/SnO₂/PANi-2.04 and Al/SnO₂-PANi-2.04 ternary thermites, in frames **B** and **C** respectively. The three combustions were followed by the luminous signature all along the tube. Depending on the composition, differences in the propagation of the reaction were easily observed.

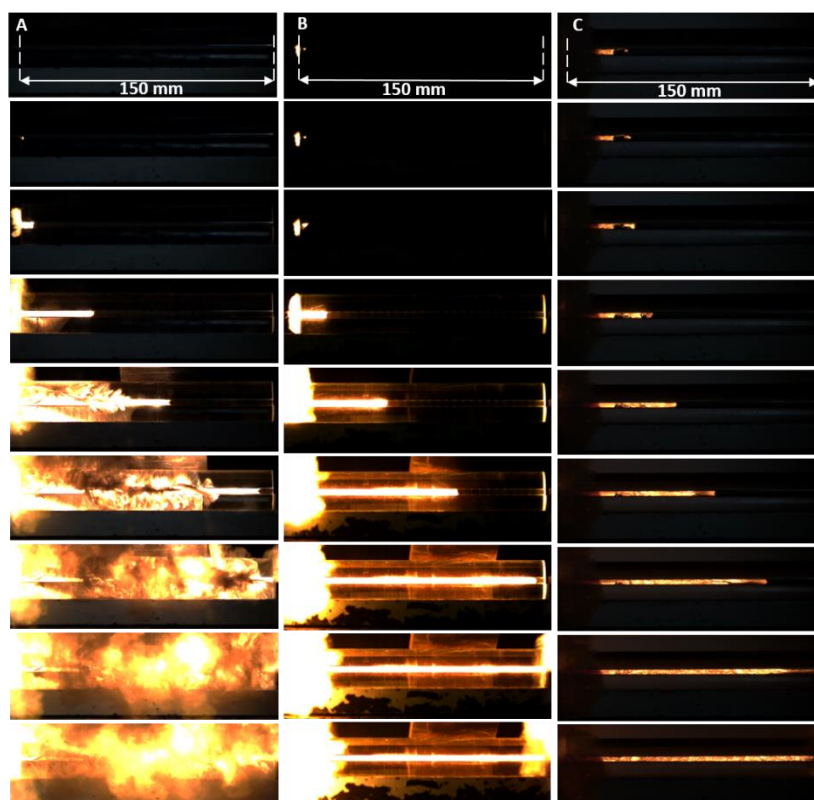


Figure 6 : Selected frames of the combustion of thermite in tubes: the Al/SnO₂ binary thermite (A), the Al/SnO₂/PANi-2.04 (B) and Al/SnO₂-PANi-2.04 compositions (C). 60 μ s elapsed between each picture. First picture of C is taken 35 ms after ignition.

The combustion phenomenon of the Al/SnO₂ binary thermite was continuous and fast (**Figure 6A**). On the contrary, when the polymer was present within nanothermites, the combustion took place in several steps. A longer ignition delay was observed with the polymer, whatever the introduction method (**Figure 6B** and **6C**). The assumption is that the polyaniline could be a thermal barrier storing the energy to a certain point. Then, the additive degrades gradually all through the tube and thus delays the combustion propagation. After a long ignition period, the Al/SnO₂/PAni-2.04 system in **Figure 6B** shows the similar combustion propagation trend to Al/SnO₂ system. In the case of the oxide-polymer composite (**Figure 6C**), the reaction seems to be slower than the previous additive-rich system, based on a rapid comparison of numbers of pictures between **Figure 6C** and **6B**. Furthermore, mitigation of the signature lightness was clearly observed between the binary Al/SnO₂ composition and the composition desensitized with 2.04 wt. % of polymer (**Figure 6A** and **6B**, respectively). The loss of lightness in the polymer-doped energetic formulation can be explained by a lower burning temperature since the polymer absorbs part of the energy for its own decomposition. The lightness measurements over time for the Al/SnO₂ and Al/SnO₂-PAni-2.04 are displayed in **Figure 7**.

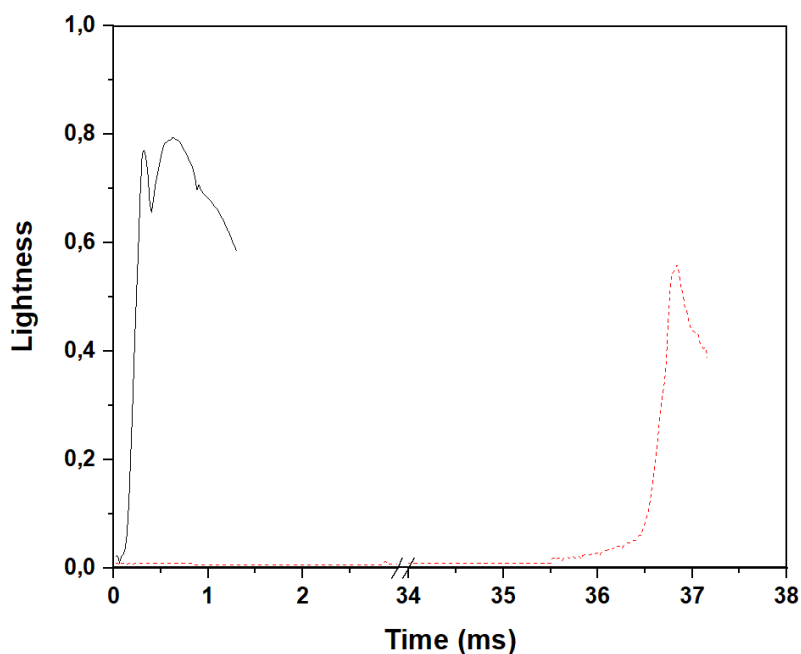


Figure 7 : Lightness of the Al/SnO₂ binary thermite (solid black) and Al/SnO₂-PAni 2.04 composition (dash red) as a function of time. The beginning is taken at the igniter triggering.

The binary Al/SnO₂ thermite presents an intense luminosity (about 0.77 in lightness) very rapidly (only 0.32 ms) after ignition. This significant light, characteristic of nanothermite reaction [43], is present for nearly 0.86 ms before gradually extinguishing. It is noted that the first loss of intensity corresponds to the breaking of the tube, which is visible as the dark part in the seventh picture of **Figure 6A**. The nanothermite-polymer composition, on the other hand, required significant ignition time (35.66 ms) before the increase in lightness. When the reaction took place, the lightness increased to a maximum of 0.55 and then decreases rapidly. In this case, the lightness was 30 % lower than in the binary thermite. This is due to some dark shapes (part of the degraded conductive polymer [17]) visible during the reaction propagation along the whole tube.

The combustion velocities were determined from video frames. The data was determined between 65 mm to 135 mm from the beginning of the tube since the travelling speed was constant in this interval. The combustion speeds were averaged in two tubes for each investigated formulation. The highest combustion velocity was obtained for the binary system with a velocity of 798 ± 73 m/s. With equal levels of polyaniline in their composition (2.04 wt. %), the combustion velocities of the PAni-doped Al/SnO₂ systems presented different results. For the Al/SnO₂/PAni-2.04 composition, the propagation velocity was similar to the binary thermite with a value equal to 779 ± 17 m/s, unlike the Al/SnO₂-PAni-2.04 composition which was more decelerated with a velocity of 483 ± 12 m/s. These data were consistent with observations from **Figure 6**. The combustion behaviour is influenced by the way the polymer is introduced into the energetic composition.

For the Al/SnO₂/PAni-2.04 system, the reactive behaviour – which is as impressive as that of the Al/SnO₂ binary nanothermite - can be explain by the fact that the aluminium is almost always in contact with oxidizer particles since the addition of PAni was not homogeneous throughout the mixture as previously demonstrated in **Figure 5B**. Thus, fuel and oxidizer particles can easily react since their contact surface is as high as for the binary system. For this reason, the propagation velocity of the Al/SnO₂/PAni-2.04 is similar to the one of the binary composition (Al/SnO₂). For the Al/SnO₂-PAni-2.04 composition, where the PAni polymer was introduced by preparing a SnO₂-PAni composite, the

combustion reaction performs differently. The reaction between the aluminium and the oxide is moderated by the polymer which homogeneously coats the tin oxide particles (**Figure 5C**). The polymer acts as a thermal barrier and must be decomposed to make the oxide accessible for the classical combustion reaction. This could be a logical explanation of the loss of velocity recorded in this kind of PANi-doped Al/SnO₂ nanothermite, compared with the two other energetic systems (Al/SnO₂ and Al/SnO₂/PANi). When the polymer is present in the composition, the reaction seems to follow a multi-step combustion process with a first step of difficult ignition (decomposition of polyaniline) followed by the propagation of the combustion all through the tube. The delayed ignition and, by extension, the combustion velocity, are largely influenced by the formatting of the additive in the energetic composition. The polymer decomposition has also an influence on the combustion's luminosity, reducing the luminous signature of the nanothermite (**Figure 7**). The combustion is less detectable, which could be interesting for cover-up applications.

3.3 Discussion and comparison with the literature

The concept of nanothermite desensitization by adding a third component was developed using several different kinds of additives, for example carbon, metals and polymers species [6-16]. To compare these developments precisely with our system, we only describe the introduction of polymers within nanothermites in this section.

The first introduction of polymer for the purposes of nanothermite desensitization concept was conducted by Apperson et al. [44]. Carboxyl terminated butadiene acrylonitrile (CTBN) was able to raise the ESD sensitivity threshold by adding 5 wt. % of polymer (**Figure 8, black-square**) and still preserve good combustion velocity. Energetic polymer, Viton A and nitrocellulose (**Figure 8, blue-sphere and green-triangle respectively**), were also used to desensitize nanothermites, but a relatively significant amount of additive (more than 5 wt.% of additive) was required for a material impact on ESD sensitivity [15,16]. The polyaniline conductive polymer, with a fibrous morphology, was added as a third component in an Al/WO₃ nanothermite by Gibot et al. [17]. These long fibres significantly

reduced electrostatic discharge sensitivity of the mixture by creating a three-dimensional conductive network. In this way, the ESD threshold increased from < 0.14 to 120 mJ by adding only 5 wt. % of PANi (**Figure 8, purple-hexagon**). Other authors [18] suggested the coating of tin (IV) oxide particles with the conductive polymer to enhance homogeneity of the ternary mixture by a better distribution of the polymer within the energetic medium (compared to [17]). The elaboration of a composite oxide-polymer was also less time-consuming than the synthesis of PANi fibres (31 h [18] vs. 72 h [17]) as reported by the authors. The polymer matrix containing tin (IV) oxide particles was able to desensitize Al/SnO₂ system by requiring an amount of PANi of 7.7 wt. % (Figure 8, orange-star). The authors observed that some part of polyaniline was not linked to the oxide, which probably explains why a larger amount of polyaniline was needed to significantly desensitize the investigated mixture. In the present investigation, the optimization of the oxide-polymer structuring was achieved via specific experimental conditions: the use of ammonium persulfate as the oxidizing agent, which exhibits a higher solubility in aqueous solution than potassium dichromate [18] and the decrease of the polymerization reaction temperature which improves the reaction yield (5°C vs. room temperature [18]). These synthesis conditions allowed to obtain a more controlled and defined conducting polymer coating on SnO₂ nanoparticles leading to a considerably reduction of ESD sensitivity with a percolation threshold around of 2 wt. % (7.7 wt. % for [18]). Furthermore, this work is carried out on SnO₂ nanoparticles which have a higher specific surface area (SSA) than the micrometric oxidizer used in [18]. SSA increases by a factor of 4 with this work (27 m²/g vs. 7 m²/g). Therefore, the surface area of SnO₂ to be protected with the polymer coating of direct contacts with the Al fuel is higher. This challenge was not only met, but with a much lower amount of polymer desensitizer (2 wt. % vs. 7.7 wt. %) than in the previous studies. This is the first time that such ESD desensitization effect is achieved with such a low percolation threshold for the conducting additive. This result is in fact twofold interesting because, with a small amount of additive, the confined combustion reaction was successful and the determination of the propagation velocity determined (which was not possible in [15,14,18]). Undeniably, the present work represents a significant improvement compared to the recent literature

[17-18]. To explain such results, a mechanism of electrostatic discharges dissipation by the polymer additive can be advanced. First, as a reminder, the ignition of energetic mixtures by electrostatic discharges can be explained by the accumulation of electrostatic charges on the surface of the particles - constituting the energetic mixture - which can lead to a local heating by Joule effect. By increasing the temperature at the interphase of the particles, hot spots are generated. These hot spots can cause ignition of the energetic materials. Thus, it can be speculated that the synthesis of conductive polymer-oxide composites, where the polymer is able to dissipate charges into the volume of the energetic mixture, avoids this increase in electrostatic charge density on the surface of the nanoparticles and therefore mitigates the temperature increase. The ignition of the energetic mixture will therefore require a higher electrostatic energy - compared to a mixture without polymer - to take place (**Figure 8, pink-diamond**).

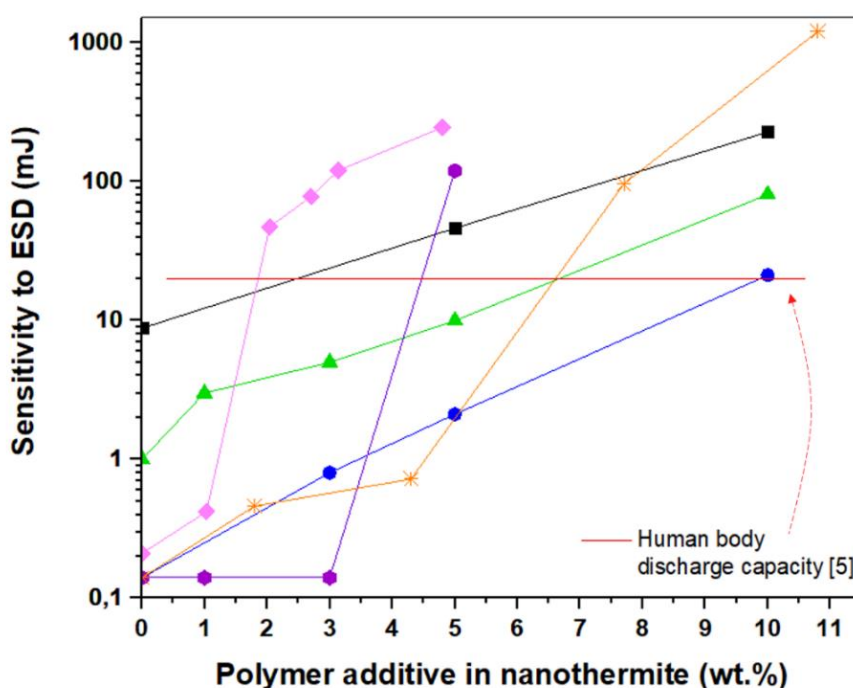


Figure 8 : ESD sensitivity as a function of the different polymer additives (literature and present work). Black-square: CTBN (Al/CuO/CTBN [44]), Blue-sphere: VitonA (Al/CuO/VitonA [15]), Green-triangle: Nitrocellulose (Al/Bi₂O₃@NC [14]), Purple-hexagon: PAni fibres (Al/WO₃/PAni [17]), Orange-star: PAni-matrix (Al/SnO₂-PAni [18]), Pink-diamond: the desensitized composition Al/SnO₂-PAni-X presented in this study.

Conclusion

In this study, the use of a conductive polymer, polyaniline polymer (PAni) for desensitizing Al/SnO₂ energetic compositions (thermites) to electrostatic discharge (ESD) was investigated. Two ways of introducing the polymer were followed: adding PAni in powdered form and elaborating a SnO₂-PAni hybrid composite. The addition of powdered PAni material did not raise the ESD threshold, but the preparation of the SnO₂-PAni composite resulted in a high desensitization with a spark sensitivity threshold of 47 mJ using only 2 wt. % of PAni (0.42 mJ for the binary energy system Al/SnO₂). This threshold is twice what a human body can generate according to the literature (8.33 - 20 mJ). In addition, the reactivity of the PAni-rich Al/SnO₂ energetic system was deemed acceptable – its combustion rate, in confined mode, is about 60 % of the Al/SnO₂ binary energetic system. Another result is the low intensity of the light signature emitted during the combustion of the PAni-enriched energetic composition. Indeed, although this result may be synonymous with a reduced adiabatic flame temperature and lower heat of reaction, this kind of composition could be a real asset for discrete and cover-up applications. Finally, the introduction of the polymer using an additive-oxide structure opens up new paths for the development of advanced nanothermites. The nanothermite composition with polyaniline-tin oxide hybrid composite has a low-light signature, acceptable reactivity and can be handled safely.

Looking ahead, other polymer structuring approaches (fibrous architectures) could be investigated for the development of safer and more reactive nanothermites.

Acknowledgments

The authors gratefully acknowledge the French Defence Innovation Agency (DGA/AID, Paris, France) French-German Institute of Saint Louis (ISL, Saint Louis, France) for the operational sponsorship and the financial support of the Ph.D. project.

The authors thank Mr Boehrer (ISL, Saint-Louis, France), Mr Schnell (NS3E, Saint-Louis, France) and Mr Vidal (IS2M, Mulhouse, France) for the combustion video recordings, the scanning electron microscopy and the transmission electron microscopy analyses respectively.

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