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SnO2-polyaniline composites for the desensitization of Al/SnO2 thermite composites.

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SnO₂-polyaniline composites for the desensitization of Al/SnO₂ thermite composites.

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Abstract

Nanothermites consisting of a reducing metal and a metal oxide nanopowder represent a new generation of energetic materials in pyrotechnics due to their impressive reactive properties. However, their extreme sensitivity regarding electrostatic discharge appears to be detrimental to their future practical applications. Herein, the mitigation of the sensitivity thresholds of the aluminium/tin (IV) oxide energetic nanocomposite is successfully achieved by using a conducting polymer, polyaniline (PAni). PAni was introduced within the thermite by the chemical polymerization of an oxidizer/PAni hybrid matrix. The SnO₂-PAni composites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, electrical conductivity measurements and transmission electron microscopy. The derived Al/SnO₂-PAni thermites were investigated in term of sensitivities and reactivity. Results revealed gradual desensitization of the Al/SnO₂ thermite as a function of the concentration of PAni for both the electrostatic discharge (0.14 mJ to 1212 mJ) and friction (216 N to 360 N) tests while maintaining reactive energetic composites. This work presents a way for the preparation of insensitive and reactive energetic formulations.

Keywords: Nanothermites; Tin (IV) oxide; Electrostatic discharge; Conducting polymer; Reactive properties.

1. Introduction

Energetic composites or thermites are physical mixtures made of fuel and oxidizer powders having an exothermic redox reaction characterized by impressive heat release and high temperature. Fischer et al. have established a list of possible energetic mixtures, by varying the chemical nature of the reactants, accompanied by their thermochemical data.¹ When downsized, thermites called nanothermites or metastable intermolecular composites (MICs) have attracted a growing interest for both civil and military applications due to their many advantages compared to their micron-scale counterparts. For example, nanothermites show higher combustion velocities, lower ignition delay times and reduced ignition temperatures.^{2,3}

However, nanothermites can present some drawbacks such as sensitivity toward diverse forms of stresses leading to unwanted burning during the preparation, handling and transportation steps.

The stresses, which can cause such unexpected effects/reactions, are essentially of mechanical and electrostatic nature. For example, most of the thermite compositions are extremely sensitive to electrostatic discharge ($< 1.5 \text{ mJ}$)⁴ widely below what that the human body can generate (8.33–20 mJ)^{5,6}, and in more isolated cases, they are sensitive to the friction phenomenon which can develop between moving particles. The high mechanical and electrostatic discharge sensitivities may limit the use of such energetic nanocomposites in numerous potential applications. The desensitization of thermite energetic nanocomposites may enable important applications.

In the literature, the mitigation of the sensitivity of the nanothermites is addressed either by acting on the fuel (especially when aluminium is used), modifying the particle size and changing the alumina/aluminium ratio constituting the fuel particles^{7,8}, or inserting a third compound (desensitizer) within the conventional binary fuel/oxidizer energetic mixture.⁹⁻¹⁹ With regards to the use of an additive, different kinds of carbonaceous compounds (carbon black, graphite, nanotubes, nanofibers, graphene and nanodiamonds), polymers (polytetrafluoroethylene and polyaniline) and inorganic species (molybdenum sulphide) have been tested, and many of them have a positive effect on the electrostatic discharge (spark) desensitization as well as a lesser

effect toward mechanical stress such as friction. While the conducting properties of desensitizers are exploited when the energetic composite is submitted to the spark test, their lubricant properties are solicited during the friction phenomena. The different compounds were added either as “isolated/individual” nanoparticles^{9-14,16-18} within the fuel/oxidizer energetic composite or through the synthesis of a desensitizer/oxidizer or a desensitizer/fuel composite^{15,19,20} before it was mixed with the fuel or the metal oxide to form the final energetic mixture. The use of polyaniline conducting polymer (PAni) as an additive is particularly interesting and promising, as reported by Gibot et al.¹³ For example, when added to an Al/WO₃ nanothermite, the PAni additive allowed the considerable mitigation of the electrostatic sensitivity (with the friction threshold increasing) while preserving an acceptable reactivity for the energetic mixture considered.¹³ In this work, the conducting polyaniline nanofibers were separately synthesized before they were added to the fuel/oxidizer nanocomposite.

Herein, the addition of the intrinsic conducting polyaniline polymer (PAni) in an aluminium/tin (IV) oxide energetic mixture was examined. This time, the polymer was introduced within the thermite from the preparation of an inorganic/organic hybrid material such as tin (IV) oxide/polyaniline material (SnO₂-PAni). The hybrid material was prepared by the chemical polymerization of aniline in an aqueous dispersion of SnO₂ nanoparticles. The as-prepared SnO₂-PAni composites have been characterized by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, electrical conductivity measurements and transmission electron microscopy. The sensitivity properties and combustion ability of the Al/SnO₂-PAni thermites were investigated as a function of the concentration of PAni additive.

2. Experimental section

Tin (IV) oxide material (SnO₂, < 10 µm, 99%) and aniline (C₆H₅NH₂, 99.5%) were purchased from Sigma Aldrich. Aluminium nanopowder Al-50P (Al, 50 nm, 99%) and potassium dichromate (K₂Cr₂O₇) were obtained from Nanotechnologies Inc. and Merck, respectively.

Hydrochloric acid (HCl, 37%) and acetonitrile (CH₃CN, 99%) were obtained from Prolabo. All chemicals were used without any further purification.

2.1. Elaboration of the SnO₂-polyaniline composites

The SnO₂-PAni composites were synthesized according to a method reported by Chen et al.²¹ Typically, 300 mg of SnO₂ powder was vigorously dispersed in 50 mL of demineralized water before acidification of the solution to 1 mol/L by means of hydrochloric acid. While stirring, 0.1 g of K₂Cr₂O₇ was added, followed by 0.2 mL of aniline monomer. The resulting solution was stirred for 10 min., ultrasonicated for 30 min. and stirred again for 6 hours. The solution stood for at least 24 hours at room temperature for chemical polymerization of aniline. The suspension was centrifuged, and the collected solid phase was washed (x 3) with demineralized water and ethanol and then it was dried at 60 °C for 6 hours. Finally, the as-obtained green material was ground in a mortar. Different SnO₂-PAni composites were thus prepared by fixing the concentration of PAni at 3.7, 7.5, 11.2 and 14.7 wt. %. It should be noted that the values will correspond to concentrations of PAni of 2.5, 5, 7.5 and 10 wt. %, respectively in the Al/SnO₂-PAni thermites. The aniline/potassium dichromate weight ratio was kept constant for all of the syntheses. The different samples were denoted SnO₂-PAni-X, where X is the theoretical weight percent of polyaniline polymer within the composite considered.

2.2. Preparation of the Al/SnO₂-polyaniline thermites

The SnO₂-PAni composites were mixed with the aluminium nanopowder Al-50P to form the energetic mixtures whose combustion reaction is given in (1):

According to the stoichiometry, the fuel/oxidizer weight ratio or equivalence ratio (Φ) is equal to 0.239 for the energetic formulation investigated. The equivalence ratio is calculated from the formula reported in (2):

$$\Phi = (\text{F/O})_{\text{exp.}}/(\text{F/O})_{\text{st.}} \quad (2)$$

where F and O are the concentrations of fuel (reactive Al) and oxidizer (SnO_2), respectively, and the subscripts exp. and st. are the experimental and stoichiometric values, respectively. It should be noted that aluminium nanoparticles exhibit a core/shell structure with a native alumina layer (Al_2O_3) surrounding a pure aluminium core representing 52.2 wt. % of the sample (determined by means of thermogravimetric analysis).

The Al/ SnO_2 -PAni energetic mixtures were prepared as follows: the passivated-Al powder and the SnO_2 -PAni-X composite were mixed in a round-bottomed flask with 100 mL of acetonitrile according to an excess of aluminium fuel of 1.2 (Φ). The dispersion was stirred (1 hour) and sonicated (3 x 5 min.) to break up agglomerates and obtain a homogeneous solid-phase mixture. The removal of the solvent was achieved by means of a rotary evaporator (100 rpm, 80 °C and 200 mbars). The resulting mixture was placed in an oven at 80 °C for 4 hours. The process was repeated with each SnO_2 -PAni-X composite while keeping the same experimental parameters. The as-prepared energetic formulations were denoted as Al/ SnO_2 -PAni-X. An Al/ SnO_2 nanothermite without PAni additive was formulated as a reference.

2.3. Characterization techniques

2.3.1. Characterization of the SnO_2 -PAni composites

The structures of the SnO_2 -PAni nanocomposites were examined by X-ray diffraction analysis performed on a D8 Advance diffractometer (XRD, Cu $K\alpha$ radiation, $\lambda = 0.154026$ nm, Bruker) operating at 40 kV and 40 mA. The concentration of polyaniline (PAni) in the different SnO_2 -PAni composites was determined by thermogravimetric analysis (TGA) performed on a SDT Q600 device (TA Instrument). The composites were heating between 25–1000 °C under air (100 mL/min.) with a 5 °C/min heating rate. The Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical compositions of the SnO_2 -PAni composites. The analyses were performed on a Tensor 27 spectrophotometer (Bruker) using the transmission mode (KBr pellets). The samples were dried in a desiccator overnight. Spectra were recorded between wavenumbers

ranging from 450 to 4000 cm⁻¹ and with a resolution limit of 4 cm⁻¹. The microstructures of the composites were determined by transmission electron microscopy (TEM) using an ARM-200F microscope (JEOL, Japan) operating at 200 kV. Samples were dispersed in ethanol, and one drop was supported on a carbon-coated copper grid. For the electrical conductivity measurements a two point probing set up ~~similar to~~ was used.¹⁰ A high resistance low conductance meter (HRLC 2, Alpha Lab Inc., USA) was used to measure the electrical resistance (in Ohms) with an accuracy of 2%. The sample (± 50 mg) was located in an insulating hollow cylindrical matrix (inner diameter: 4 mm) to prevent interference from the external sources. Two copper electrodes, connected to the HRLC device, were inserted to each either end of the matrix till being in contact with the sample. Prior recording the electrical resistance, the sample was pressed at 2.5 MPa for 60 s. The electrical conductivity (σ in Siemens per meter, S/m) was determined by using the equation given below:

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

with R the electrical resistance (Ω), e the thickness (m) and S the section surface (m²), respectively, of the sample through which the current passes.

2.3.2. Characterization of the Al/SnO₂-PAni energetic composites

The sensitivities of the thermites toward the mechanical (impact and friction) and electrostatic discharge stresses were determined according to the standard characterization techniques defined by the NATO organization.²²⁻²⁴ Photographs of the different devices are given in the Supporting Information (Figure S1). Regarding the impact and friction sensitivities, a fall-hammer apparatus and a Julius Peter BAM device (Suceska 1992) were used, respectively. The impact sensitivity threshold (expressed in joules) is determined by submitting 40 mm³ of energetic mixture to the drop of a 5 kg weight from a variable height, thus adjusting the stress intensity. The friction sensitivity threshold (expressed in newtons) is defined by scrubbing 10 mm³ of energetic formulation between a ceramic stick against a ceramic plate. The friction intensity of the stick is

a function of the position of weights hung on a lever. Regarding the electrostatic discharge test, an ESD 2008 electrostatic spark sensitivity device from OZM Research s.r.o. was used. A low concentration of matter placed between two electrodes 1 mm away is submitted to a spark whose energy (in joules) is calculated from the voltage and capacitance implemented. The sensitivity threshold values for the different Al/SnO₂-PAni-X thermites correspond to the value of six consecutive “no-go”, i.e., without a combustion reaction.

Figure S1: Photographs of the (A) impact, (B) friction and (C) electrostatic discharge apparatus, respectively, used for the determination of the sensitivities of the energetic thermite composites.

Combustion tests of the thermites in an unconfined configuration were performed by means of an optical flash igniter equipped with a Xenon lamp.²⁵ The powdered mixtures were placed on a glass substrate placed on the optical flash igniter. A metal washer (thickness of 1 mm, inner diameter of 4 mm) interlaced between the igniter and the glass holder was used to delimit the optical flash and avoid luminous disturbance during the recording. Under these conditions the powders were submitted to an energy density of 0.11 J/cm². The combustion phenomena were recorded by using a Photron FASTCAM high-speed camera (1×10⁴ frames/s) placed in front of the igniter.

3. Results and Discussion

3.1. Characterizations of the SnO₂-PAni composites

The different as-prepared SnO₂-PAni-X composites were characterized by X-ray diffraction (XRD). The corresponding X-ray patterns, which are all similar, are shown in Figure 1 (B to E). The diffraction peaks can be attributed to a tetragonal structure with a P42/mnm space group, which describes a rutile structure as adopted by the SnO₂ Cassiterite phase described in the JCPDS card No. 041-1445 (Figure 1A). The diffraction peaks of the composites were not subjected to any significant position modifications compared to the international card, suggesting that the

experimental protocol involved for the preparation of the SnO₂-PAni composites does not modify the structure of the SnO₂ oxide ceramic. The polyaniline component probably exhibits an amorphous or a poorly crystallized structure since no other peaks were observed in the diffractograms.²¹

Figure 1: XRD patterns of the (A) SnO₂ Cassiterite phase (JCPDS card No. 041-1445) and the SnO₂-PAni-X hybrid nanocomposites with the PAni concentration X equal to (B) 3.8, (C) 7.5, (D) 11.2 and (E) 14.7 wt. %, respectively. For clarity's sake, the XRD pattern of the commercial SnO₂ material used in this work is reported in the Supporting Information (S2).

Figure S2: XRD patterns of the commercial SnO₂ material used in this work and the corresponding JCPDS card.

To verify the presence of polyaniline conducting polymer in the inorganic/organic composites, Fourier transform infrared analyses (FTIR) were performed on the different SnO₂-PAni-X samples. The corresponding FTIR spectra are shown in Figure 2 and compared to the pure PAni and SnO₂ phases spectra. Two main domains were observed for wave numbers near 800 cm⁻¹. Below this limit, the wide vibration band located between 500-700 cm⁻¹ is characteristic of tin-oxygen bonds.²⁶ The three peaks observed at 535 cm⁻¹, 604 cm⁻¹ and 673 cm⁻¹ can be assigned to the stretching modes of Sn-O bonds (terminal and bridged) in the SnO₂ tin (IV) oxide phase. Regarding the peaks above 800 cm⁻¹, they are in good agreement with the vibration bands characteristic of the pure PAni phase (Figure 2E). Moreover, a small shift to higher wavenumbers was observed that can be originated to SnO₂-PAni chemical interactions. Based on the literature²⁷, the vibration bands at 1560 cm⁻¹ and at 1488 cm⁻¹ can be assigned to the C=C stretching and bending vibrations of the quinoïd (Q) and the benzenoid (B) rings, respectively, in PAni polymer exhibiting the emeraldine salt phase. The peak at 823 cm⁻¹ describes the out-of-plane bending vibration of the C-H bond in a meta-substituted aromatic cycle, while the band at approximately 1300 cm⁻¹ is characteristic of the C-N stretching vibration of the amine group with an aromatic ring. The IR bands observed at 1245 cm⁻¹ and 1146 cm⁻¹ correspond to the C-N⁺ stretching

vibration in the polaron lattice and the vibration mode of the $-\text{NH}^+$ in the $\text{Q}=\text{NH}^+-\text{B}$ or $\text{B}-\text{NH}^+-\text{B}$ groups. Their presence translates to a high degree of electron delocalization. Finally, the two vibration bands observed at 1640 cm^{-1} and around $3200 - 3400\text{ cm}^{-1}$ on the SnO_2 spectrum (Figure 2F) were attributed to the vibration modes of physisorbed water molecules at the surface of the material.

Figure 2: FTIR spectra of the SnO_2 -PAni-X nanocomposites with the PAni concentration X equal to (A) 3.8, (B) 7.5, (C) 11.2 and (D) 14.7 wt. %, respectively. The spectra of the pure PAni and SnO_2 phases are reported as (E) and (F), respectively. For clarity's sake, the vibrational assignments were only reported in the main text.

Thermogravimetric analyses (TGA) were performed to determine the mass percentages of organic and inorganic matter in the different as-synthesized SnO_2 -PAni hybrid materials (Figure 3). All of the thermogravimetric curves were similar and presented three mass losses in the temperature domain investigated. From room temperature to $200\text{ }^\circ\text{C}$, the mass loss was attributed to desorption of water molecules on the composite surface. The second phenomenon, recorded between $200-350\text{ }^\circ\text{C}$, may correspond to the removal of the by-products formed during the polymerization of aniline (visible on the TGA curve of pure PAni, not shown here). Finally from 350 to $550\text{ }^\circ\text{C}$, the degradation of the organic phase takes place. The different concentrations of organic phase within the SnO_2 -PAni-X nanocomposites, whose theoretical X values were 3.8, 7.5, 11.2 and 14.7 wt. %, were thus experimentally determined (from the TGA analysis) to be equal to 2.8, 6.4, 11.6 and 16 wt. %, respectively.

Figure 3: Thermogravimetric curves (under air) of the SnO_2 -PAni-X nanocomposites with the PAni concentration X equal to (A) 3.8, (B) 7.5, (C) 11.2 and (D) 14.7 wt. %, respectively.

The electrical conductivity values of the different SnO_2 /PAni-X composites are presented in Table 1. The conductivity of the pure PAni phase, synthesized according to the same experimental procedure except without the addition of SnO_2 particles, is given for comparison.

Table 1: Electrical conductivity values of the different SnO₂/PAni-X composites as a function of the PAni concentration (X).

First, compare to the pure conducting PAni phase, the electrical conductivities of the SnO₂-PAni-X composites are lower that can be explain itself by the low electrical conductivity of the SnO₂ material (3×10^{-7} S/m) major component of the composites. Then, taken into account only the different SnO₂-PAni-X materials, the electrical conductivity increases approximately from 0.2 to 2.4 S/m with the PAni conducting polymer concentration (X) ranging from 2.8 to 16 weight percent within the composite. Based on the plot of the conductivity as a function of the PAni wt. %, presented in the Supporting Information (Figure S3), a significant increase of the conductivity is recorded for a PAni concentration higher than 6% followed by a pseudo-plateaus below 12 wt. %. This trend suggests that the percolation threshold of the conducting phase is probably around 8 – 10 wt. %. To remember, the percolation threshold is the value for which a minority phase in a composite forms a homogeneous and continue network in all the considered composite. In the current case, the network is conducting and allows the flow of current through all the matter without interference.

Figure S3: Electrical conductivity of the SnO₂/PAni-X composites as a function of the PAni weight % (X).

Further characterization was carried out by TEM to observe the microstructures of the SnO₂-PAni-X nanocomposites. Figure 4 shows the SnO₂-PAni composite prepared with a PAni concentration of 11.6 wt. % (value determined by TGA). As seen in the image at low magnification, the composite is constituted of agglomerates of SnO₂ nanoparticles (dark areas) embedded in a PAni matrix (light areas). The insert in Figure 4 (higher magnification) shows obvious evidence supporting this result. No isolated SnO₂ primary particles covered by the polymer were visible, but in contrast, in some places of the view, elongated alone PAni particles were observed. From meticulous observation, uncoated SnO₂ agglomerates were also observed.

Accordingly, based on these microstructural observations, it may be concluded that the SnO₂-PAni-11.6 composite does not seem homogeneous even if the SnO₂-PAni multimaterials represent the majority of the composite.

Figure 4: Transmission electron microscopy views of the SnO₂-PAni-X hybrid nanocomposite (X = 11.6 wt. % of PAni).

Finally, based on these analyses, the synthesis of SnO₂-PAni nanocomposites with the oxide component embedded in a conducting polymer matrix was demonstrated.

3.2. Pyrotechnic properties of the Al/SnO₂-PAni thermites

The SnO₂-PAni-X nanocomposites were mixed with the aluminium nanopowder according to an equivalence ratio (ϕ) of 1.2 in order to prepare the corresponding Al/SnO₂-PAni-X energetic composites (thermites). Taking into account the aluminium quantity added, the concentrations of PAni (X) within the Al/SnO₂-PAni-X energetic composites were calculated again to be equal to 1.8, 4.3, 7.7 and 10.8 wt. %, respectively. These data will be referenced in the text below. The performances of the various thermite mixtures, in term of sensitivity and reactive behaviour, were assessed and are discussed below.

Sensitivities of the Al/SnO₂-PAni thermites

The interest in adding polyaniline within the Al/SnO₂ thermite is to raise its electrostatic discharge sensitivity threshold. Since the polymer is an electrical conducting material, it should be able to channel the electrical energy through the energetic formulation forcing it to bypass the reactant powder (fuel/oxidizer).¹⁰ Thus, the energy density (energy provided by the electrostatic discharge), which could appear at the surface of the aluminium particles, will not be enough to lead to ignition of the mixture. Accordingly, no joule heating at the surface of the aluminium

component will occur, and no hot spots will be formed. Hot spots are generally considered to be the origin of the ignition phenomena of energetic materials.²⁸

The electrostatic discharge sensitivity thresholds of the Al/SnO₂ energetic composites doped or not doped with PANi are gathered in Table 2.

Table 2: Electrostatic discharge sensitivity thresholds of the Al/SnO₂-PANi thermite depending on the PANi wt. %.

A value of 0.14 mJ was determined for the Al/SnO₂ reference thermite (without the addition of PANi), which is far below the energy dissipated by the human body (8.33–20 mJ).^{5,6} At this extremely low level, the energetic composite shows a considerable hazard since an unwished or out of control decomposition reaction can occur during operator handling or transport causing injuries and damage. As expected, the use of the conducting polyaniline allows the electrostatic discharge (ESD) sensitivity of the binary Al/SnO₂ thermite to be mitigated (Table 2). For example, the ESD threshold value increases from 0.46 to 1212 mJ with a concentration of PANi ranging from 1.8 to 10.8 wt. %, respectively, which can be interpreted by the fact that with PANi, it is necessary to deliver a higher electrostatic discharge to ignite the combustion reaction of the Al/SnO₂ thermite. The efficiency of the polyaniline as a desensitizing agent to electrostatic discharge in thermites is obvious. By precisely examining the variation of the ESD sensitivity values, a drastic increase is recorded between 4.3 and 7.7 wt. % of PANi. Indeed, the ESD value surges by a factor 134 (96.5 mJ vs. 0.72 mJ), while the concentration of conducting phase only grows by a factor 1.8 (7.7% vs. 4.3%). In contrast, when the PANi concentration varies from 1.8 to 4.3 wt. % (x 2.4), the ESD sensitivity is only raised by a factor 1.6 (0.72 mJ against 0.46 mJ). Accordingly, the percolation threshold, which characterizes the minimal concentration of a chemical species to assure a continuous network, is likely in the range 4.8–7.7 wt. % of PANi added within the Al/SnO₂ thermite (15–22 vol. %). The electrical conductivity determination performed on the two Al/SnO₂-PANi-7.7 and Al/SnO₂ energetic composites confirmed a more

pronounced conducting character of the PANi-doped system with a value of 1.279×10^{-4} S/m compared to the value of 1.494×10^{-7} S/m for the second one. This gain of conductivity explains the successful desensitisation of the Al/SnO₂ energetic composite regarding the ESD test and **evidences** the efficiency of the PANi conducting polymer as a desensitisation agent. Now, again considering the threshold value of 96.5 mJ for the Al/SnO₂ energetic formulation doped with 7.7 wt. % of PANi (Al/SnO₂-PANi-7.7), with regards to the ESD test, it can be speculated that this composite exhibits a highly reduced risk for the operator during preparation and handling steps since this value is higher than what a human body can dissipate; i.e. 8.33-20 mJ.^{5,6} In parallel, Weir et al. demonstrated that the ignition of a microscale Al/MoO₃ energetic composite required 100 mJ of electrostatic energy for ignition; this value falls to 0.25 mJ for the nanoscale counterpart.²⁹ Accordingly, based on this result, if a nanothermite (as examined in this work) does not ignite close to an ESD of 100 mJ (as defined for the microscale systems), it can be ranked as potentially insensitive. However, caution should still be applied with this kind of energetic composite.

The literature data relating to the ESD desensitization of the thermites are gathered in Table 3. Basically, the present results are relatively equivalent to the other works with the advantage that the PANi polymer is low cost, easy to synthesize, chemically stable and its conductivity can be tailored (doping process). Attempting a direct comparison between the different approaches is very complex because numerous parameters are different such as the nature and equivalence ratio (ϕ) of the fuel/oxidizer couple, the implemented fuel particle size (micro- and nanosized Al), the intrinsic conductivity of the additive considered and the fact that the percolation threshold depends on the microstructure (the shape and the dimensions) of the additive.³⁰

Table 3: Literature data on the desensitization of thermite energetic composites. * L, l, t, Ø, Ø_o and Ø_i stand for the length, width, thickness, diameter, outer diameter and inner diameter of the different particles investigated, respectively.

Further characterizations were then performed on the promising Al/SnO₂-PAni-7.7 energetic formulation such as the impact and friction tests, and the results are reported in Table 2. Regarding the binary Al/SnO₂ thermite, taken as a reference in the context of this investigation, insensitivity and a moderate sensitivity to the impact and friction tests were established, respectively.²⁹ For example, the sensitivity thresholds were determined to be higher than 49.6 mJ and equal to 216 N for the impact and friction stresses, respectively. Additionally, these values are higher than the international regulations, set at 2 J and 80 N by the United Nations for the transport of dangerous goods on public roads.³¹ By adding 7 wt. % of PAni to the Al/SnO₂ thermite, the impact insensitivity is preserved with a sensitivity value also beyond 49.6 mJ, for which no positive reactions (combustion, coloration, spark, sound, etc.) were observed. However, as this energy level is the highest one that the apparatus can determine, it is not possible to know if the sensitivity threshold really varied between the Al/SnO₂ energetic composite prepared with or without PAni polymer. With regards to the friction test, the addition of PAni (7.7 wt. %) within the Al/SnO₂ thermite led to an increase in the insensitivity level to a value superior to 360 N, thereby ranking the Al/SnO₂-PAni-7.7 energetic composite as totally insensitive.²⁹ To explain such a trend (desensitization with PAni additive) two main reasons can be suggested without being necessary independent phenomena. First, as the tin (IV) oxide (SnO₂) material is embedded in a PAni polymer matrix, it is physically moved away from the Al fuel. The contact zones between the fuel and the oxidant are then considerably reduced, and the formation of hot spots generated by the mechanical stress at the Al/SnO₂ interface is a little more difficult. It is then necessary to provide a higher energy to crush the polymeric layer, thus bringing the fuel and the oxidizing species closer together and allowing the combustion reaction. Another explanation could be the one given in ^{13,32}. The authors, referring to the fact that polyaniline material is made of the stacking of polymeric planes, suggest a sliding of these planes with respect to each other when the polyaniline material is mechanically stressed. This can result in the absorption of a portion of the energy initially provided by the friction phenomenon, leading to a residual energy that is potentially not enough for triggering the redox reaction between the Al and the SnO₂ components. Generally

speaking, regardless of the possible purpose of the PANi additive, a physical barrier between the SnO₂ and Al reactants or the effect of its lubricating properties, the higher the concentration of PANi within the Al/SnO₂ thermite is, the higher the energy absorption is and the higher the mechanical force intensity must be for the combustion reaction to take place. Regarding, the NATO criteria for the transport of hazardous goods, the Al/SnO₂-PANi-7.7 is in good compliance with the required standards for the impact and friction since its sensitivity thresholds are widely superior to the standards (2 J and 80 N, respectively).²⁹

Combustion of the Al/SnO₂-PANi thermites

The combustion test of the Al/SnO₂ and Al/SnO₂-PANi-7.7 energetic composites were evaluated according to the protocol described in section 2.3.2 ~~contrary to the one of the conventional binary Al/SnO₂-energetic composite~~. Some selected video frames of the combustion of these two energetic composites are displayed in Figure 5A and 5B, respectively. The Al/SnO₂ thermite, selected as a reference, quickly burnt, and no residual solid matter was found on the glass substrate at the end of the experiment. A clapping sound was also heard during the combustion, supporting the hypothesis of a gaseous release previously mentioned in the dedicated literature.^{1,33,34} When observing the combustion frames of this energetic composite (Figure 5A, excluding the optical flash frame), an intense luminous signal is observed in the three first images of the sequence, followed by huge blue/purple fumes moving above the optical igniter device. Taking into account the time scale, the duration of the combustion reaction seems to not exceed 3-4 ms (Figure 5A, images 4 to 5). In contrast, the combustion reaction of the Al/SnO₂ thermite enriched with the PANi polymer, according to a weight ratio of 7.7 wt. %, ~~took in much prolonged time~~, and a very small concentration of unreactive substance was collected on the glass support at the end of the test. Moreover, the combustion reaction was quieter, which is likely due to the less powerful energetic character of this ternary composite.¹³ This lower combustion energy may be due to the fact that the PANi polymer additive absorbs a portion of the combustion energy of the Al/SnO₂ composite for its own decomposition/combustion, thereby leading to a mitigation of the global

energy released by the energetic system considered. This result can be especially pronounced, as the additive is not an energetic species but rather a chemically inert substance from a pyrotechnics point of view, as is the case in the present investigation. Similar observations are mentioned in the literature, in particular with carbon particles and polymers selected as desensitizers.^{12,13} When scanning the corresponding sequence of the combustion images of the Al/SnO₂-PAni-7.7 energetic composite (Figure 5B), the combustion phenomenon is totally different from that of the binary Al/SnO₂ (Figure 5A). A sheaf of incandescent particles evolving at the surface of the energetic mixture is observed. The orange luminous sheaf grows up in a regular way, without the formation of fumes, until it reaches the maximum flame temperature symbolized by the appearance of orange/yellow incandescent particles (Figure 5B, beyond image 9). Nevertheless, it can be speculated that the reaction temperature for the Al/SnO₂-PAni-7.7 energetic composite is not as high as that for the Al/SnO₂ system since the colour of the incandescent particles is warmer in the first case (not a white luminous signal). The energy consumption by the polymer combustion, decreasing the quantity of released energy, is likely the source of such a thermal evolution. Based on the time scale, the duration of the combustion phenomenon may be estimated to be 15-20 ms (Figure 5B, images 16 to 20). Since for both energetic composites equivalent concentrations of matter were tested (see the Experimental section) and assuming that they exhibit equivalent apparent densities, close to 10 % of the theoretical maximum density (TMD) as generally attributed for powdered samples³⁵, it can be determined that the combustion velocity for the PAni-doped Al/SnO₂ thermite is lower than that of the undoped Al/SnO₂ composite. This fact may result in at least two main parameters. The first one is the one cited above relating to the fact that the polyaniline, for combustion, draws a part of the energy released by the Al/SnO₂ reactive couple during its own exothermic reaction. The second one is based on the fact that the SnO₂ oxidizer is embedded in a PAni-polymer matrix. Accordingly, the direct interfacial contacts between the SnO₂ oxidizer and the Al fuel, which facilitate the ignition and front flame propagation, are considerably reduced. Based on these attempts to explain the phenomena, the combustion speed should be dependent of the concentration of polyaniline polymer within the

Al/SnO₂ energetic composite. In other words, the larger the concentration of PANi is, the lower the combustion velocity should be.

Figure 5: Sequences of the combustion images of the (A) Al/SnO₂ and (B) Al/SnO₂-PANi-7.7 thermites. The elapsed time between images is 1 ms.

To verify that, a set of combustion tests on the different Al/SnO₂ samples enriched with polyaniline (Al/SnO₂-PANi-X with X = 1.8, 4.3, 7.7 and 10.8 wt. %, respectively) were performed. The different sequences of combustion pictures are gathered in the Supporting Information (Figure S4). In all cases, reactive formulations were observed, and some trends have been identified validating the previous observations made between the undoped and Al/SnO₂-PANi-7.7 composites. For example, the smaller the concentration of PANi is, the shorter the combustion reaction is (ascending image numbers to record the combustion phenomena for Al/SnO₂ < Al/SnO₂-PANi-1.8 < Al/SnO₂-PANi-4.3 < Al/SnO₂-PANi-7.7 < Al/SnO₂-PANi-10.8, respectively), the louder the sound is (presence of purple fumes for Al/SnO₂ and Al/SnO₂-PANi-1.8, a luminous yellow/white torch for the Al/SnO₂-PANi-4.3 and an orange luminous sheaf for the Al/SnO₂-PANi-7.7 and Al/SnO₂-PANi-10.8, respectively) and finally less residual matter remains (much more unreactive matter for the Al/SnO₂-PANi-10.8).

In summary, even if the addition of polyaniline has a prejudicial effect on the combustion behaviour of the Al/SnO₂ thermite with a significant decrease of the combustion velocity, it is important to note that for all PANi-doped Al/SnO₂ energetic composites, the self-propagation of the combustion reaction has been demonstrated regardless of the concentration of polymer used. This work provides additional evidence for the use of polyaniline polymer in the ESD desensitization of nanothermites.¹³

Figure S4: Combustion image sequences of the Al/SnO₂-PANi-X thermites with X being the PANi weight %. (A) X = 0 (i.e., the Al/SnO₂ thermite reference), (B) X = 1.8 wt. %, (C) X = 4.3 wt. %, (D) X = 7.7 wt. % and (E) X = 10.8 wt. %, respectively. The elapsed time between images is 1 ms.

4. Conclusion

This investigation showed that the polymerization synthesis of SnO₂-polyaniline (PAni) composites can be efficient to mitigate both the electrostatic discharge (ESD) and friction sensitivities of an aluminium-based energetic composite (Al/SnO₂). The addition of 7-8 wt. % of the conducting PAni within an Al/SnO₂ nanothermite allowed an ESD sensitivity threshold of ~ 100 mJ to be reached compared to < 1 mJ for the binary Al/SnO₂ energetic system. The formation of a homogenous and continuous electrostatic charge-conducting polyaniline-based pathway in the entire volume of the energetic formulation was thus suggested. As a result, no joule heating of fuel nanoparticles by the electrostatic discharges occurs, thus avoiding ignition of the energetic composition at a level comparable to what a human body can deliver. At the same time, the friction sensitivity was also mitigated to obtain a value of > 360 N (vs. 216 N for the undoped Al/SnO₂ nanothermite). The role of a physical barrier played by the polymer placed between the fuel and the oxidizer and its lubricant properties, made possible by the sliding of the polymeric planes between each other when stressed, were advanced to justify this trend. Nevertheless, this **concentration** of conducting polyaniline has a negative impact on the combustion behaviour of the Al/SnO₂ energetic composite because even if the self-propagation of the combustion reaction was checked, a significant decrease of the combustion velocity was observed. The next step of this approach could be the elaboration of SnO₂-polyaniline core/shell nanostructures, which should lead to a better optimization of the addition of PAni (better coating, lower **concentration**) within the thermite energetic composites and thereby establishing a better ratio/compromise between the sensitivities and reactivity.

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Figure captions

Figure 1: XRD patterns of the (A) SnO₂ Cassiterite phase (JCPDS card No. 041-1445) and the SnO₂-PAni-X hybrid nanocomposites with the PAni concentration X equal to (B) 3.8, (C) 7.5, (D) 11.2 and (E) 14.7 wt. %, respectively. For clarity's sake, the XRD pattern of the commercial SnO₂ material used in this work is reported in the Supporting Information (S2).

Figure 2: FTIR spectra of the SnO₂-PAni-X nanocomposites with the PAni concentration X equal to (A) 3.8, (B) 7.5, (C) 11.2 and (D) 14.7 wt. %, respectively. The spectra of the pure PAni and SnO₂ phases are reported as (E) and (F), respectively. For clarity's sake, the vibrational assignments were only reported in the main text.

Figure 1: Thermogravimetric curves (under air) of the SnO₂-PAni-X nanocomposites with X the PAni **concentration** equals to (A) 3.8, (B) 7.5, (C) 11.2 and (D) 14.7 wt. %, respectively.

Figure 4: Transmission electron microscopy views of the SnO₂-PAni-X hybrid nanocomposites (X = 11.6 wt. % of PAni).

Figure 5: Sequences of the combustion images of (A) the Al/SnO₂-PAni-7.7 and (B) the Al/SnO₂ thermites. The elapsed time between images is 1 ms.

(Figure 5: Color online only)

Figure 1

Figure 3

Figure 4

Figure 5

(A) **(B)** **(C)**

Figure S4D

[Click here to access/download;Figure;Figure S4D.tif](#)

Table captions

Table 1: Electrical conductivity values of the different SnO₂/PAni-X composites as a function of the PAni **concentration (X).**

(2-column fitting image)

Table 2: Electrostatic discharge sensitivity thresholds of the Al/SnO₂-PAni thermite depending on the PAni wt. %.

(2-column fitting image)

Table 3: Literature data on to the desensitization of the thermite energetic composites. * L, l, t, Ø, Ø_o and Ø_i for the length, the width, the thickness, the diameter, the outer diameter and the inner diameter of the different particles investigated, respectively.

(Single-column fitting image)

PA ni wt. % (X)	2.8	6.4	11.6	16	100
σ (S/m)	0.198	0.500	1.867	2.379	5.67

PAni wt. %	ESD (mJ)	Impact (J)	Friction (N)
0	0.14	> 49.6	216
1.8	0.46	n.d.	n.d.
4.3	0.72	n.d.	n.d.
7.7	96.5	> 49.6	> 360
10.8	1212	n.d.	n.d.

Energetic formulations (fuel/oxidizer)	Microstructure of the energetic components fuel/oxidizer (size)*	Desensitizer (dimensions)*	Desensitizer amount (%)		ESD threshold (mJ)	Ref.
			Vol.	Wt.		
Al/CuO	sphere (40 nm)/sphere (50 nm)	Carbon nanotubes ($\varnothing_o = 20$ nm, $\varnothing_i = 3$ nm, L = 0.1-10 μ m)	13	/	n.d.	[9]
Al/CuO	sphere (4 μ m)/sphere (50 nm)		3.8	/	> 100	[10]
Al/C ₂ F ₄	sphere (3-4.5 μ m)/particles (35 μ m)	Carbon nanotubes ($\varnothing_o = 3$ -20 nm, $\varnothing_i = 1$ -3 nm, L = 0.1-10 μ m)	> 0.2	/	> 100	[16]
		Graphene nanoplatelets (t = 8 nm, L = 0.15-3.0 μ m)	> 0.5	/	n.d.	
Al/Fe ₂ O ₃	sphere (80 nm)/coating (20 nm)	Graphite oxide (t = 1 nm, L < 1 μ m)	/	9.6	24.5	[15]
Al/Bi ₂ O ₃	sphere (100 nm)/sphere (90-200 nm)	Nanodiamonds particles ($\varnothing = 5$ nm)	/	> 2.7	> 20	[19]
Al/MnO ₂	sphere (50 nm)/rods (l = 3 nm, L = 40-80 nm)	Carbon nanofibres (Pyrograph-III) ($\varnothing_o = 100$ nm, $\varnothing_i = 20$ - 40 nm)	/	37.16	1800	[20]
Al/MnO ₂	sphere (50 nm)/particles (@carbon nanofibers)		/	37.16	35	
Al/WO ₃	sphere (50 nm)/platelets (l = 50 nm, L = 200-400 nm)	Polyaniline nanofibres ($\varnothing = 50$ nm, L = 1 – 2 μ m)	15.1	5	120	[13]
Al/CuO	sphere (80 nm)/particles (33 nm)	Viton (coating)	/	10	21.22	[11]
Al/SnO ₂	Sphere (50 nm)/particles (20-300 nm)	Polyaniline (matrix)	22	7.7	96.5	Present work