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Polypyrrole material for the electrostatic discharge sensitivity mitigation of Al/SnO₂ energetic composites

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Abstract

Nanothermites are composite energetic materials made of fuel and oxidizer nanoparticles characterized by impressive exothermic reactions (highly flame temperatures and impressive heat combustion releases). However, nanothermites suffer from their high electrostatic discharge (ESD) sensitivity that may be at the origin of accidental ignitions during handling. The present study deals with the use of doped-polypyrrole conducting polymer in aluminium/tin (IV) oxide energetic formulation (Al/SnO₂). X-ray diffraction, Fourier transforms infrared spectroscopy, scanning electron microscopy, conductivity measurements, sensitivities and combustion tests were implemented to characterize the polypyrrole-doped Al/SnO₂ energetic composite. The results revealed a significant gradual ESD desensitization of the nanothermite (< 0.14 mJ to 246.40 mJ) as a function of the doped-polypyrrole amount (0 to 15 wt. %). The reactive properties of the polypyrrole-enriched Al/SnO₂ nanothermite were verified and an acceptable reactive behaviour was claimed. The successful adding of doped-polypyrrole conducting polymer within energetic nanocomposites is reported for the first time.

1. Introduction

Explosives are a waste materials class that can be divided into two categories; military and civil explosives. In the former, three main categories were identified depending of nature of explosives or ingredients; explosives, propellants (low explosives), and pyrotechnics.¹ Formulations based on fuel and oxidizer, called thermites or Metastable Intermolecular Composites (MICs), integrate the latter.² Stressed by various stimuli as heat, friction and electrostatic discharge (spark), an oxidation-reduction chemical reaction occurs (oxygen transfer from metal oxide to reducing metal) releasing high amount of heat accompanied by elevated temperatures and sometimes by production of gas. A listing of fuel/oxidizer reacting couples, completed by some characteristics as density, adiabatic flame temperature, state of products, gas production and heat of reaction, has been offered by Fischer et al.³ Applications for thermite mixtures may concern welding, airbag gas generator materials, torches for operations of cutting/perforation in severe environment (underwater).

At the beginning of 2000s, research topics on thermites were concentrated on the use of fuel and oxidizers nanopowders. The downsizing of ingredients led to improve homogeneity and contact between fuel and oxidizer evolving a decrease matter transport limitations. The reactivity of the mixture was thus enhanced and the combustion rate was greatly increased up to 3 orders of magnitude.⁴ Since the past decade, the research effort has been directed towards the shaping of three-dimensional (3D) objects at diverse scales as well as the development of desensitized thermite energetic nanocomposites. Concerning the latter aspect, nanothermites systematically exhibit extreme sensitivity to electrostatic discharge, sometimes accompanied by mechanical sensitivity, particularly in friction testing.^{5,6} The sensitivity to electrostatic discharge (ESD) is such that the minimal energy for triggering the combustion reaction requires less than one millijoule, which is widely below the human being discharge capacity estimated around 8.33 – 20 mJ.^{7,8} Consequently, accidental risks cannot be totally excluded during the formulation and handling stages of these energetic mixtures, unless the operator is grounded. One way to by-pass this intrinsic hazard is to add a third ingredient to the nanothermites. This ingredient must meet two main criteria, namely to have conductive properties and to be in sufficient concentration to create a 3D conductive network in the nanothermite (percolation threshold). Its role will be to evacuate

the electrostatic charges on the surface of the particles, thus avoiding high surface charge densities that can lead to local heating (hot spots) and ignition of the energy mixture.⁹

Among tested additives for ESD sensitivity mitigation of nanothermites, carbon material has been most intensively investigated. For example, electrically conducting carbon nanotubes (CNT) were inserted into an aluminium/copper (II) oxide energetic system. An ESD sensitivity threshold > 100 mJ was recorded with an addition of 3.8% by volume of CNT (compared to 0.14 mJ for an Al/CuO mixture without additive) with a reactive behaviour of this NT-doped system (no self-propagated combustion without CNT additive).¹⁰ For a same energetic mixture but prepared from nanopowders, 13% by volume of nanotubes were required to observe a drastic increase in the electrical conductivity (9×10^{-6} S/cm to 0.07 S/cm) coupled to a no ignition (ESD > 100 mJ) of the nanothermite. However, below 2 vol. %, no self-propagated combustion was noted¹¹. Graphite oxide platelets (rGO) additions were also examined with an aluminium/iron (II) oxide energetic mixture. With 9.6 wt. % of additive, the ESD threshold raised to 24.5 mJ (vs. < 2 mJ for binary Al/Fe₂O₃ system) without that the reactive behaviour was checked¹². Nanoparticles of nanodiamonds (NDs) were also introduced into an aluminium/bismuth (III) oxide energetic mixture. With only a concentration of approximately 2.7 weight %, the ESD sensitivity threshold was enhanced up to be > 20 mJ (< 0.14 mJ for Al/Bi₂O₃ system). At the same time, the combustion velocity was decreased by a factor 5 to be inferior to 100 m/s. The authors advanced the formation of the aluminium carbide ceramic (Al₄C₃) acting as a thermal barrier.¹³ Finally, the use of carbon nanofibres (Pyrograph-III) was tested in an aluminium/manganese (IV) oxide energetic nanosystem.¹⁴ Depending on the way the nanofibres were introduced, either as a reactor where the manganese (IV) oxide nanoparticles were crystallized inside or as a third chemical element, 37.16 weight % of fibrous carbon additive raised the ESD sensitivity threshold to 35 mJ and 1800 mJ, respectively (1 mJ for the binary system). Nevertheless, a quasi-extinction of the reactive properties was recorded. The high concentration of nanofibres combined with the formation of Al₄C₃ was suggested by the authors to explain this behaviour.

The second type of desensitizing additives used to mitigate the ESD threshold of nanothermites is polymer use. A first example is the work of Foley et al. for whom the coating of Viton A® (10 weight %) on the surface of copper (II) oxide nanoparticles increased the ESD sensitivity threshold of the

Al/CuO nanothermite to 21.22 mJ¹⁵. More recently, Gibot and co-workers have demonstrated the efficiency and ability of the polyaniline conductive polymer (PAni) to desensitize Al/WO₃ and Al/SnO₂ energetic formulations to electrostatic discharges.^{16,17} Two polymer morphologies were addressed, such as nanofibres and a matrix in which oxidizer particles were incorporated. With PAni nanofibres, 5% by weight was sufficient to increase ESD sensitivity to 120 mJ and 7.7% by weight of PAni matrix was required to increase the ESD threshold to 96.5 mJ (compared to <0.14 mJ for both energetic composites formulated without additives). Both energy systems showed encouraging reactive properties (ignition, combustion rate) in unconfined and confined configurations, especially in the case of the Al/WO₃ nanothermite where about 70% out of combustion rate was preserved despite the adding of PAni fibres.¹⁶ For us, this approach seems to be a viable way to design thermite energetic composites with acceptable reactivity doubled of enhanced safety.

Herein, the polypyrrole conducting polymer (PPy) was introduced within an aluminium/tin (IV) oxide energetic mixture. A marketed available doped-polypyrrole powder was selected and introduced in a controlled manner and in well-defined concentrations into the considered energetic mixture. The as-formulated Al/SnO₂/doped-polypyrrole nanothermites were characterized through a comprehensive examination involving the characterisation of the conducting polymer and the PPy-enriched Al/SnO₂ nanocomposites, in particular by electrical conductivity measurements, electrostatic discharge sensitivity determination and evaluation of the reactive behaviour.

2. Experimental section

2.1. Materials

Polypyrrole (doped-PPy, (C₄H₂NH₂⁺)_n, σ = 10-50 S/cm (pressed pellet)), and acetonitrile (CH₃CN, 99%) were supplied from Sigma-Aldrich. Tin (IV) oxide (SnO₂, < 10 μ m powder, 99.9%) was purchased from Alfa Aesar. Aluminium nanopowder (Al, specific surface area (SSA) = 27 m².g⁻¹, 99%) was provided by QNA Intrinsic Materials Inc.

2.2. Preparation of the Al/SnO₂/doped-polypyrrole energetic composites

The exothermal reaction of the Al/SnO₂ energetic composite material is given below:

In the present study, aluminium was mixed with tin (IV) oxide in a 29.6/70.4 weight percent that is corresponds to a fuel rich equivalence ratio of 1.2, considering the active aluminium content in the commercial powder (68 wt. %, determined from a thermo-gravimetric analysis carried out on the Al powder exposed to an argon/oxygen flow). The equivalence ratio (Φ), widely used in pyrotechnics and specifically for nanothermites preparation, is described by Eq. (2):

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

with F and O the masses of pure fuel (Al) and oxidizer (SnO_2) reactants, and the subscripts exp. and st. the experimental and stoichiometric conditions. This equivalence ratio value of 1.2 was demonstrated to be an optimal composition for achieving the highest combustion velocity.¹⁸ Doped-polypyrrole conducting polymer was added following different amounts (1, 5, 10, 15, and 20 wt. %) to the previous reactive mixture. The ternary mixtures (500 mg) were dispersed in acetonitrile (100 mL), stirred (1 hour) and sonicated (3 x 5 min.) to break up agglomerates and ensure homogeneous mixtures. The removal of the liquid phase was achieved using a rotating evaporator (80 °C, 200 mbars). The doped-PPy-enriched Al/ SnO_2 energetic composites were dried at 80 °C (4 hours) and placed in safety boxes. The mixtures were labelled as Al/ SnO_2 /PPy-X where X corresponds to the wt. % of the conducting polymer additive within the nanothermite. X was fixed at 5, 10, 12.2, 15, 30 and 50 wt. % corresponding to 14.6, 26.4, 31, 37.8, 58.8 and 76.4 volume percent. An Al/ SnO_2 nanothermite without doped-PPy additive was formulated as a reference and labelled Al/ SnO_2 .

2.3. Characterization techniques

Fourier-transform infrared spectroscopy (FTIR) was used to characterize the functional groups consisting the conducting polypyrrole polymers. The analyses were conducted on a Tensor 27 spectrometer (Bruker, Billerica, MA, USA) in transmission mode and by superposing 16 scans recorded within the 4000 – 520 cm^{-1} range with a definition of 4 cm^{-1} . The sample/potassium bromide (KBr) disks (200 mg) used for FTIR were pressed at 10 tons during 1 min. The microstructure and morphology of the different samples (PPy, SnO_2 , and Al) were imaged by means of a Nova Nano-SEM 450

microscope (FEI, Tokyo, Japan) working with a 10 kV current. A D8Advance X-ray diffractometer (XRD, Bruker, Billerica, MA, USA), equipped with a copper radiation, a Lynxeye detector and working at 40 kV – 40 mA, was used to record the structure of the materials. The X-ray diffraction patterns were collected at 2θ from 20 to 80° with a step size of 0.02° . The electrical conductivity measurements of the materials were achieved using a Model 2010 low noise multimeter (Keithley, Solon, Oh., USA). For that, the powdered sample (approximately 50 mg) was placed inside an insulating tube (inner diameter = 4 mm), between two copper electrodes, and pressed at 2.5 MPa (1 min.). The electrical conductivity (σ in Siemens per centimeter, S/cm) was determined by using the equation:

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

with R the measured electrical resistance (Ω , averaged value on 5 measurements taken all 1 min. during 5 min.), e the thickness of the sample (cm) and S the section surface (cm^2) of the pelletized materials.

The energetic performances of both Al/SnO₂ nanothermites (w/o doped-polypyrrole) were investigated through the sensitivities thresholds determination, the thermal behaviours investigation and the determination of the front reaction propagation velocities. Concerning the sensitivity properties of the energetic nanocomposites, three main tests were implemented namely the electrostatic discharge (ESD), the friction and the impact tests. The tests were performed on an ESD 2008 testing device (OZM Research s.r.o., Hrochuv Tynec, Czech Republic), a BAM friction and a Julius Peters BAM fallhammer apparatuses, respectively, in compliance with the NATO standard.¹⁹⁻²¹ Comprehensive descriptions of the principles were given in the literature.¹⁷ The threshold sensitivity values determined on the loose powders (expressed in joules (J) for ESD and impact stresses and in newtons (N) for friction stimulus) correspond to the highest values for which six successive reaction tests resulting in no reaction (no combustion, clapping sound, colour change etc.). Regarding the combustion speeds measurements of the different Al/SnO₂ nanothermites; i.e. w/o doped-polypyrrole conducting polymer, the set-up used was described in the literature¹⁷. Briefly, nanothermite powders were ignited by means of an optical flash igniter and a Photron FASTCAM high-speed camera (1×10^4 frames/s) placed in front of the device was used to record the combustion reactions.

3. Results and Discussion

Characterizations of the doped-polypyrrole polymer additive

The doped-polypyrrole polymer was investigated by using two main techniques as the Fourier transform infrared spectroscopy (FTIR) and the scanning electron microscopy (SEM) to characterize the chemical bonds constituting it and its microstructure (morphology and dimensions), respectively.

Figure 1 shows the FTIR spectrum of the polypyrrole material. An active domain is observed between 500 and 1800 cm^{-1} that is consistent with the infrared bands characteristic of the conducting form of the polypyrrole as reported in the literature.²²⁻²⁴

Figure 1: FTIR spectrum of the doped-polypyrrole conducting polymer.

For example, the infrared peaks located at 1446 and 1556 cm^{-1} were assigned to the C-C and C=C stretching vibrations of the polypyrrole ring. The stretching vibration of the C-N and -C=N bonds in the ring were observed at 1319 and 1178 cm^{-1} , respectively. The N-H wagging vibrations were located at 751 and 1031 cm^{-1} .²² The peak at 782 cm^{-1} may be assigned to =C-H in-plane vibration.²³ Finally, regarding the PPy compound, the peaks at 3120, 1284 and 914 cm^{-1} were attributed to the aromatic C-H stretching and N-H out-of plane vibrations, respectively.^{22,24} Other infrared bands visible on the spectrum were attributed to the doping agent identified as 2,4 hydroxybenzophenone reactant (not

discussed here).²⁵ For example, the IR bands at 3170 cm^{-1} and 1627 cm^{-1} were attributed to the stretching and the in-plane bending vibrations of the O–H bond and the weak band at 3064 cm^{-1} was assigned to the aromatic =C–H vibration. Between 2800 cm^{-1} and 2950 cm^{-1} , the C–H stretching vibrations in CH_x group were observed. The peak at 1595 cm^{-1} was attributed to the C=C stretching vibration of benzene structure. IR peaks observed at 1490 and 1508 cm^{-1} were defined as the non-symmetrical bending vibrations of the C–H bonds. At 1164 cm^{-1} , the C–O stretching vibration was identified accompanied by the C–H out-of-plane (ring) deformation vibrations in the $850\text{--}860$ region.^{25,26} The bands at 626 cm^{-1} and 700 cm^{-1} were also characteristic of the (mono and meta substituted) sp^2 C–H bending region of phenyl ring.²⁶

Representative scanning electron microscopy pictures of the doped-polypyrrole are presented in Figure 2. The low magnified image (Figure 2A) indicates that the sample is made of two populations of particles. Small thread-like particles, which appear to be highly agglomerated, overlay larger highly faceted particles. The smallest particles seem to exhibit a size widely under the micrometre while the biggest ones can reach a size of several micrometres. These latter particles were identified as the doping agent. The wired-shape of the smallest particles was evidenced by high magnified pictures as shown in Figure 2B and 2C. The particles were strongly entangled with each other and exhibit submicron or even micrometric dimensions. For example, the diameter of the wires appears to be around $200\text{--}250\text{ nm}$ and the length around the micrometre (Figure 2B). In spite of this entanglement, the aggregates formed by these particles were highly airy suggesting a possible deagglomeration of the threads by agitation/sonication steps in a liquid medium. The Figure 2C shows that the threads of polypyrrole polymer were in fact made of quasi-spherical particles sintered between themselves to give this anisotropic form. The average particles size was determined close to 200 nm corresponding to the diameter of the threads.

Figure 2: SEM images of the polypyrrole conducting polymer.

The polypyrrole polymer was then mixed with Al and SnO₂ powders to formulate the corresponding thermite energetic materials. Characterizations, such as FTIR and XRD analyses, were performed on the different Al/SnO₂/PPy composite materials prepared (PPy content ranging from 5 to 50% by weight). The results have been compiled in Supporting Information (Figure S1 and S2, respectively).

Properties of the Al/SnO₂/PPy-X energetic composites

Electrical conductivity of the doped-PPy-enriched Al/SnO₂ energetic composites

The electrical conductivity values of the diverse pressed pellet Al/SnO₂/PPy-X energetic nanocomposites, determined by means of a two points method, were reported in Table 1.

For the binary Al/SnO₂ nanothermite (X = 0), the conductivity value characterizes an insulating behaviour of the mixture with a value of 6.158×10^{-7} S/cm. This behaviour is close of the insulating character of the SnO₂ material (49 vol. % in the Al/SnO₂ energetic system) whose electrical conductivity (σ) was determined equal to 3.62×10^{-7} S/cm. The electrical conductivity of the Al powder was measured as low as 10^{-8} S/cm due to an insulating alumina coating surrounding the Al core. Then, when doped-polypyrrole additive ($\sigma = 1.26$ S/cm) was added to the energetic medium an improvement of the conductivity of the Al/SnO₂ nanothermite was obviously observed up to reach a value as high as 4.053×10^{-1} S/cm with a concentration of 50 wt. % of polypyrrole polymer, corresponding to a gain of about 6 orders of magnitude. In addition, as expected, the conductivity of the doped-PPy-enriched Al/SnO₂ nanothermites was depending of the conducting polymer concentration since the electrical conductivity gradually increased with the increase of the doped-PPy concentration.

PPy wt.% (X)	0	5	10	12.2	15	30	50
σ ($\times 10^{-6}$ S/cm)	0.616	0.281	11.167	387.33	1338.4	28904	405270

Table 1: Electrical conductivity data of the Al/SnO₂/PPy-X energetic composites depending on the PPy concentration (X).

By scrutinizing the evolution of the conductivity value as a function of doped-polypyrrole loading (Figure 3), a jump is clearly observed around 10 – 15 wt. % of polypyrrole polymer within the nanothermite (X). This may correspond to the percolation threshold of PPy in the energetic mixture that means the creation of a conducting continuous phase within the Al/SnO₂ energetic formulation. At higher loadings, conductivity increases further but not dramatically with values of 2.89×10^{-2} S/cm and 4.053×10^{-1} S/cm for additions of 30 and 50 % by weight, respectively (i.e. close to the value obtained for 15 % by weight).

Figure 3: Conductivity of Al/SnO₂/PPy-X energetic composites as a function of the doped-PPy concentration (X).

Sensitivities of the PPy-enriched Al/SnO₂ energetic composites

Electrostatic discharges sensitivity thresholds for the series of Al/SnO₂ nanothermites enriched at various doped-polypyrrole (PPy) concentration are gathered in Table 2. Based on the previous results, only the samples containing up to 15 wt. % of PPy were tested. Overall, a trend emerges from these results, i.e. that the more PPy concentration increases within the nanothermite, the higher the ESD sensitivity threshold is. For example, without PPy polymer additive, the Al/SnO₂ nanothermite shows an extremely low ESD value of < 0.14 mJ, whereas for a maximum tested concentration of 15% of conducting polymer, the sensitivity threshold reaches the value of 246.40 mJ. As a reminder, the

discharge capacity of the human body has been estimated to be around of 8.33 – 20 mJ.^{7,8} While the Al/SnO₂ energetic system can be considered of being highly sensitive and therefore dangerous to handle, the nanothermite enriched with 15 wt. % of polymer can be ranked as totally insensitive, offering a maximum safety for the operator. As seen in Table 2, the minimal concentration of doping PPy agent need to obtain a sensitivity just above the human body capacity was determined at 10 wt. % with an ESD value of 20.36 mJ. This result is of the same order of magnitude than this mentioned by Foley and al.¹⁵ where Viton polymer was introduced within an Al/CuO energetic system (ESD sensitivity of 21.22 mJ with 10 wt. % of C₂F₄). By using polyaniline polymer (PAni), Gibot et al.^{16,17} have desensitized Al/WO₃ nanothermites with 5 and 7.7 wt. % of PAni nanofibres and matrix, respectively with ESD sensitivity thresholds of 96.5 and 120 mJ, respectively. Nevertheless, a direct comparison is complex because of the conducting properties and the morphology of polymers are different.

By scrutinizing the different ESD values determined with the increase of the polypyrrole polymer within Al/SnO₂ energetic nanocomposite, the value of doped-PPy concentration leading to the ESD sensitivity value of about 56.56 mJ that means widely exceeding the human body discharge capacity (20 mJ); that means more than two times, was obtained for an additive concentration likely around 12 – 13 wt. %. Finally, this mitigated ESD sensitivity threshold is consistent with the evolution of the electrical conductivity of Al/SnO₂/PPy-X nanocomposites, carried out in the previous section, where a percentage of 10 – 15% by weight of PPy seemed necessary to reach the percolation threshold of the conducting phase within the Al/SnO₂ insulating nanocomposite to ensure the passage of the current. Current voltage that could be at the origin to an accidental initiation of the Al/SnO₂ energy formulation by the increase of the surface energy density located at the surface of the fuel and oxidizers nanoparticles might leading to the formation of hot spots, triggers of the Al/SnO₂ combustion reaction.⁹

PPy wt.% (X)	0	5	10	12.2	15
ESD (mJ)	< 0.14	2.89	20.36	56.56	246.40

Table 2: Electrostatic discharge sensitivity values of Al/SnO₂/PPy-X energetic composites as a function of the PPy concentration (X).

Additional sensitivity properties were determined on the different Al/SnO₂/PPy-X energetic materials (X = 0 to 15 wt. %). In particular, mechanical stimuli were studied with shock and friction sensitivities. Generally speaking, the results demonstrate an insensitivity to impact and friction for Al/SnO₂/PPy formulations regardless of the concentration of the PPy polymer since they exhibit impact and friction sensitivity threshold values at least equal to 40 J and greater than 360 N, respectively^{20,21}. Thus, the as-formulated energetic composite materials are safe for handling. However, an increase of the impact sensitivity (> 100 J to 40 J) was observed as a function of an increase of the PPy wt. % (0 to 15 wt. %, except with 12.2 wt. %) in the nanothermite. To explain this trend, it can be assumed that the energy generated by the impact leads to the decomposition of the polymer and/or the doping element which generates a local heating in the thermite and that when the temperature is sufficiently high, the ignition of the Al/SnO₂ energetic domains occurs. Therefore, the higher the amount of doped-PPy, the higher the probability of hot spots and ignition of the material.

PPy wt. %	Impact (J)	Friction (N)
0	> 100	> 360
5	85	> 360
10	45	> 360
12.2	80	> 360
15	40	> 360

Table 3: Mechanical sensitivity thresholds of the Al/SnO₂/PPy-X energetic composites as a function of the PPy concentration (X).

Reactive properties of the PPy-enriched Al/SnO₂ energetic composites

Taking into account the ESD sensitivity results presented in the section discussed-above, the reactive properties determination (initiation and combustion velocity) of the Al/SnO₂/PPy-X energetic composites were specifically carried out on the one constituted of 12.2 wt. % of doped-PPy since it exhibits a ESD sensitivity sufficiently far away of the human body discharge capacity (56.56 mJ vs 20 mJ) with the minimal concentration of additive. For comparison purpose, the Al/SnO₂ nanothermite, i.e. without PPy additive, was also investigated. The combustion video image sequences of the two selected

Al/SnO₂ energetic formulations, prepared w/o polypyrrole conducting polymer as a desensitising agent, are shown in Figure 4.

Concerning the Al/SnO₂ energetic composite (Figure 4A), just after the optical flash is ignited, the combustion reaction is extremely violent and complete because of no traces of residue were observed on the glass substrate at the end of the test. The reaction was characterized by the emission of a clapping sound^{18,27,28} combined with an intense and very bright spray of incandescent particles which quickly disappears to give way to a cloud of purple smokes. Based on the time scale, the duration of the combustion reaction seems to be of about 3 – 4 ms since the last visible white/orange/yellow zones (incandescent zones) were observed in frame 5 of Figure 4A.

For the doped-polypyrrole-enriched Al/SnO₂ energetic composite (Figure 4B), the reactive behaviour is different but still with a total consumption of the reactants (no residue on the glass substrate after the burnt experiment).

Firstly, the combustion reaction is much longer than the Al/SnO₂ system taken as a reference (Figure 4A) since 26 to 27 images were necessary to visualise the reaction in its integrity. Beyond that, no incandescent domain was observed on the corresponding frames. Considering the time elapsed between the images, the duration of the reaction was determined to be close to 26 – 27 ms. Taking into account this time scale and assuming an equivalent bulk density close to 10% of the theoretical maximum density for the two energy composites, as is generally the case for powder samples²⁹, and a similar amount of burnt material, the combustion rate of the doped-PPy-enriched system was therefore assumed to be lower than that of its un-doped counterpart.

Secondly, the visual aspect of the combustion reaction of the PPy-enriched Al/SnO₂ formulation is different. The combustion phenomenon is characterized by the progressive growth of a sheaf of incandescent particles whose shape seems to be more controlled and spatially defined than for its PPy-free counterpart above-discussed. This behaviour can be seen on the first pictures; i.e. ranging from 2 to 9/10 of Figure 4B, and then evolves towards something more diffuse where dark orange fumes were observed. Subsequently, the combustion phenomena of the Al/SnO₂/PPy-12.2 nanocomposite is rather characterized by successive ignition points in various and numerous areas of the sheaf. The ignition points were represented by the lightest zones (white luminous signal) embedded in a huge dark red

cloud. This behaviour extends to picture 24 (Figure 4B, last image in line 4) before a progressive cooling of the reaction is observed (Figure 4B, last line). To corroborate the fact that the reaction of the Al/SnO₂/PPy-12.2 took place on a much longer time (less violent reaction), it can be noted that the sound heard during the burn experiment was quieter meaning that the gases produced by the energetic system are released less suddenly. As a result, the pressure peak generated during the reaction was lower than for the un-enriched Al/SnO₂ nanocomposite.

A final point that differs between the two energetic nanocomposites is the luminous intensity of the incandescent zones. In the case of the Al/SnO₂ nanothermite (Figure 4A), these zones are intensely white (saturated signal), whereas for the PPy-enriched Al/SnO₂ nanothermite (Figure 4B), the white colour seems less pronounced, suggesting a lower adiabatic flame temperature in the latter case.

To sum up, the addition of doped-polypyrrole conducting polymer (PPy) had an impact on the reactive properties of the Al/SnO₂ thermite energetic nanocomposite. Changes in the nature of the combustion reaction (crackling phenomenon vs. continuous incandescent sheaf), a decrease in both the combustion rate (longer reaction time) and the intensity of the pressure peak (quieter experiment) were noted. All these aspects can be directly correlated to the non-energetic character of the polymer compound selected for this study, as mentioned in the literature with other types of desensitizing additives such as polymers and carbons.¹³⁻¹⁷ An attempt of explanation is offered in the following. Assuming doped-PPy polymer is homogeneously distributed in the Al/SnO₂ system and taking into account its concentration (12.2 wt. % or 31.03 vol. %), a coherent description of the Al/SnO₂/PPy-X mixture can be made in combining small domains of pure Al/SnO₂ energetic mixture separated between themselves by polypyrrole fibres constituting a 3D-network. Thereafter, the triggering of the optical flash creates a local heating of the powder which leads to the formation of hot spots, described in the literature as the triggers of the combustion reaction.⁹ When hot spots are located at the fuel/oxidizer interfacial contact, the redox reaction occurs and the combustion front propagates in all the mixture. However, with the presence of non-energetic PPy compound in the mixture, the polymer may act as a thermal barrier between neighbored reactive domains thus limiting to the propagation front travel. That can be an attempt of explanation on why the combustion phenomenon is likely seen as successive cracklings in the ternary Al/SnO₂/PPy nanocomposite and not as a continuous exothermal reaction as for the binary Al/SnO₂

nanocomposite. In addition, it can be also considered that during the combustion, a certain amount of the heat of combustion released by the highly exothermic Al/SnO₂ reaction is consumed by the decomposition/combustion of the polypyrrole ingredient. Consequently, the energy available for the combustion of the remaining Al/SnO₂ mixture is significantly reduced that results to a slowing down of the combustion velocity of the reaction.

Compared to the literature devoted to the use of conductive polymers as desensitizers of energetic nanocomposites, the current results could be considered as encouraging.^{17,18} For example, although a higher concentration of doped-PPy was required than PANi (12.2 wt. % (ESD 56.56 mJ) versus 7.7 wt. % (ESD 96.5 mJ)) to obtain a safer Al/SnO₂ nanocomposite than without polymer¹⁸, the reactive properties were superior in the present study (no residue, similar burn rate, and higher adiabatic flame temperature). It can be argued that a fibrous morphology of the polymer (present case) is preferable to a matrix form isolating SnO₂ nanoparticles from Al nanoparticles, thus considerably reducing Al/SnO₂ interfacial contacts.¹⁸ Now, when compared to the use of PANi fibres¹⁷, the current results are below expectations as only 5 wt. % of PANi fibres allowed to reach an ESD sensitivity value of 120 mJ while maintaining an acceptable burning rate in confined mode. Assuming a similar homogeneity in the Al/WO₃/PANi and Al/SnO₂/PPy energetic formulations, it can be speculate that the lowest aspect ratio of the PANi polymer fibres than PPy ones reduces the thermal barrier effect played by the polymer additive in the combustion behaviour of the nanothermite considered.

Figure 4: Sequences of the combustion pictures of (A) the Al/SnO₂ and (B) the Al/SnO₂/PPy-12.2 nanothermites both formulated with an equivalence ratio of 1.2. The elapsed time between pictures is 1 ms.

4. Conclusion

Doped-polypyrrole conducting polymer was successfully used as electrostatic discharge desensitizing agent within metal/metal oxide (Al/SnO₂) thermites energetic composites. Current results have shown that a concentration of 12.2% by weight of doped-polypyrrole-conducting polymer was required to reach a sensitivity threshold twice the discharge capacity of humans, i.e. 56.56 mJ as opposed to 20 mJ. This aspect is crucial to ensure a safety handling and transport of these advanced energetic composites. The reactive properties of the Al/SnO₂ thermite enriched with 12.2% by weight of doped-PPy were checked

and a decrease in the combustion rate was recorded compared to the PPy-free Al/SnO₂ nanocomposite. However, the combustion reaction was complete and its overall reactive behaviour of an acceptable level. This investigation, which is the pioneer in the use of PPy for these materials, represents a promising solution for solving safety problems in pyrotechnics. Moreover, the commercial availability of the polypyrrole polymer combined with the data in the literature concerning it (different morphologies, adjustable conductive properties), suggests a wide range of possibilities to improve the current results.

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References

1. Agrawal, J. P., 2010. High Energy Materials Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
2. Pantoya, M. L., Granier, J. J. *Propellants, Explos. Pyrotech.* **2005**, 30, 53-62.
3. Fischer, S.H. and Grubelich, M.C. 1998. Theoretical energy release of thermites, intermetallics, and combustible metals. Proceedings of the 24th International Pyrotechnics Seminar, pp 231-286, July 27-31, Monterey, USA.
4. Levitas, V. I., Pantoya, M. L. and Dikici, B. *Appl. Phys. Lett.*, **2008**, 92, 011921.
5. Puszynski J. A., Bulian, C. J. and Swiatkiewicz, J. J. *J. Propul. Power.* **2007**, 23(4), 698-706.
6. Gibot, P., Comet, M., Vidal, L., Moitrier, F., Lacroix, F., Suma, Y., Schnell, F. and Spitzer, D. *Solid State Sci.* **2011**, 13, 908-914.
7. Greason, W. D. *J. Electrostat.* **2003**, 59, 285–300.
8. Talawar, M. B., Agrawal, A. P., Anniyappan, M., Wani D. S., Bansode, M. K. and Gore, G. M. *J. Hazard. Mater.* **2006**, 137, 1074–1078.
9. Field, J. E, Bourne, N. K., Palmer, S. J. P. Walley, S. M. *Philos. Trans. R. Soc., A.* **1992**, 339, 269-283.
10. Poper, K. H., Collins, E. S., Pantoya, M. L. and Daniels, M. A. *J. Electrostat.* **2014**, 72, 428-432.
11. Steelman, R., Clark, B., Pantoya, M. L. and Heaps R. J. *J. Electrostat.* **2015**, 76, 102-107.
12. Yan, N., Qin, L., Hao, H., Hui, L., Zhao, F. and Feng, H. *Appl. Surf. Sci.* **2017**, 408, 51-59.
13. Pichot, V., Comet, M., Miesch, J. and Spitzer, D. *J. Hazard. Mater.* **2015**, 300, 194-201.
14. Siegert, B., Comet, M., Muller, O. Pourroy, G., and Spitzer, D. *J. Phys. Chem. C.* **2010**, 114, 19562-19568.

15. Foley, T., Pacheco, A., Malchi, J., Yetter, R. and Higa, K. *Propellants, Explos., Pyrotech.* **2007**, 32, 431-434.
16. Gibot, P., Bach, A., Vidal, L., Schnell, F., Gadiou, R. and Spitzer, D. *J. Energ. Mater.* **2017**, 35, 136-147.
17. Gibot, P., Goetz, V. *J. Appl. Polym. Sci.* **2020**, 137, 48947
18. Gibot, P., Goetz, V. *J. Energ. Mater.* **2020**, 38 (3), 295-308
19. NATO. 2001. STANAG 4490. In: Standardization Agreement (STANAG) on Explosives, Electrostatic discharge Sensitivity Tests. NATO Standardization Agency: Brussels, Belgium.
20. NATO. 2002. STANAG 4487. In: Standardization Agreement (STANAG) on Explosives, Friction Sensitivity Tests. NATO Standardization Agency: Brussels, Belgium.
21. NATO. 1999. STANAG 4489. In: Standardization Agreement (STANAG) on Explosives, Impact Sensitivity Tests. NATO Standardization Agency: Brussels, Belgium.
22. Saville, P., Polypyrrole Formation and Use, Technical Memorandum DRDC Atlantic TM 2005-004, Defence R&D Canada, 2005.
23. Omastova, M., Pavlinec, J., Pionteck, J., Simon, F., and Kosina, S. *Polymer* **1998**, 39 (25), 6559–6566.
24. Liu, R., Li, D., Wang, C., Li, N., Li, Q., Lü, X., Spendelow, J. S. and Wu, G. *Nano Energy* **2014**, 6, 73–81.
25. Trivedi, M.K., Tallapragada, R.M., Branton, A., Trivedi, D., Nayak, G., Mishra, R., Jana, S. *Clinical Pharmacology & Biopharmaceutics* **2015**, 4(4) 1000145.
26. Trivedi, M.K., Patil, S., Shettigar H., Bairwa, K., Jana, S. *Chemical Sciences Journal* **2015**, 6(3), 100098.
27. Qin, L., Gong, T., Hao, H., Wang, K. and Feng, H. *J. Nanopart. Res.* **2013**, 15, 2150-2165.
28. Sullivan, K. and Zachariah, M.R. *J. Propul. Power.* **2010**, 26, 467-472.
29. Walters, K.C., Pesiri, D.R. and Wilson, D.E. *J. Propul. Power.* **2007**, 23, 645-650.