



*Cent. Eur. J. Energ. Mater.* 2018, 15(3): 468-484; DOI: 10.22211/cejem/92444  
*Research paper*

## **Influence of Polytetrafluorethylene on the Mechanical and Safety Properties of a Composite Modified Double Base Propellant**

**Shixiong Sun, Tianfu Zhang, Benbo Zhao, Guangpu Zhang, Xiaoyu Li, Yunjun Luo\***

*Beijing Institute of Technology, 5 South Zhongguancun St.,  
Haidian District, Beijing 100081, China*

*\*E-mail: yjluo@bit.edu.cn*

**Abstract:** A novel Composite Modified Double Base (CMDB) propellant, formed by mechanically mixing aluminium/polytetrafluorethylene (Al/PTFE) powders, was prepared through a rolling process. A variety of tests, such as tensile properties, particle size analysis *etc.*, were carried out to study the influence of PTFE on the CMDB propellant properties. The PTFE deformed from particles to fibres under a uniform shear force, forming a fibre network which greatly improved the propellant's mechanical properties. Compared to that of the CMDB propellant without PTFE, the elongation of the propellant containing 6% PTFE was increased by 26 times, and moreover, the impact strength was enhanced by 326% at  $-40^{\circ}\text{C}$ . Significantly, the propellant friction and impact sensitivities were reduced by 75.8% and 35.6%, respectively. In addition, the presence of PTFE in the propellant resulted in fluorination of the Al. The gaseous combustion product  $\text{AlF}_3$  reduced the propellant combustion agglomeration. Consequently, PTFE significantly promoted the propellant's mechanical performance, decreased the shock (friction, impact) sensitivity and reduced combustion agglomeration.

**Keywords:** PTFE fibres, CMDB propellant, mechanical properties, mechanical sensitivity, combustion

**Supporting information (SI) available at:**

<http://www.wydawnictwa.ipowaw.pl/CEJEM/contents/2018/vol-15-no-3.html>

## 1 Introduction

Double base propellants have been widely applied to solid rocket motors due to their various advantages, such as smokeless products, adjustable energy, abundant sources of raw materials, mature technology and so on. They are especially suitable for free standing rocket motor grains due to their high strength and elastic-modulus [1]. However, double-base propellants have the drawbacks of low-temperature embrittlement, largely caused by the semi-rigid nitrocellulose (NC) macromolecules, and limited energy, due to the limited concentration of oxidizer fragments [2, 3]. Al and nitramines like hexogen (RDX) [4], octogen (HMX) [3, 5, 6], hexanitrohexaazaisowurtzitane (HNIW or CL-20) [2, 5, 7], *etc.* are incorporated in propellant compositions to achieve higher performance. Increases in specific impulse ( $I_{sp}$ ) were achieved [2] as was expected. However, the presence of some high energy materials and liquid nitrate esters in CMDB propellants make these systems extremely hazardous and sensitive [2, 5, 8, 9]. What is more, the low temperature mechanical performance becomes worse. In view of both the potential structural failure caused by various mechanical stimuli during processing, handling, and transportation, and the increasing demands on performance, reliability and cost, it was hoped that its mechanical and safety performance, as well as retaining a high energy density for CMDB propellants, could be improved in a facile way.

Mechanical properties, energy density and shock sensitivities of double-base propellants are highly dependent on the mixture ratio of NC, nitroglycerin (NG), stabilizers and so on [2, 10]. However it is difficult to reach perfection in every respect, without a sacrifice in certain performance criteria, by varying the NG mass fraction and the inclusion of other chemicals such as diethyl phthalate (DEP) and dibutyl phthalate (DBP) [2]. To reconcile the divergence and improve the comprehensive performance, many chemicals are incorporated in propellant compositions. Other nitrate esters, such as diethyleneglycol dinitrate (DEGDN), triethyleneglycol dinitrate (TEGDN) and trimethylolethane trinitrate (TMETN), with lower sensitivity can be mixed with NC to achieve insensitive propellants. However, these nitrate esters are less energetic than NG. Although the desensitizer mass fraction used in propellant formulations can be reduced, compared to NG containing propellants, leading to no energy reduction [2], there is no significant improvement in mechanical performance. The addition of crosslinkers and binders into traditional double base propellant slurries for cross-linked double-base propellants (XLDB) is a feasible way to promote low temperature elongation and energy density of propellants. However, the low temperature strength is poor, which means that it may not satisfy the demands for cryogenic launch, although its elongation may be greatly enhanced [11-14]. In addition, the

processing method is not suitable for free standing rocket grains [1]. Coating is a common and useful method to stabilize sensitive nitramine oxides [4, 15-19]. Suitable coating may not only desensitize the nitramine particles but may also contribute to the mechanical performance of the propellant [4]. However, the energy density may be decreased due to the introduction of a non-energetic cell. Although in some cases an energetic component such as NC [4] has been used as a coating layer, the complex process may increase the cost and the scale-up processes need to be explored further [20]. Thus, a facile strategy which could improve a CMDB propellant's comprehensive performance, including excellent safety, high energy density, especially low temperature mechanical properties, is still desirable, though many meaningful attempts have been made.

Polytetrafluoroethylene (PTFE) has been utilized to reinforce the mechanical performance of fluororubbers and silicon rubbers since the middle of the last century [21], by the deformation of PTFE from particles to fibres under a uniform shear force. Therefore, the potential application of PTFE in propellants and pyrotechnics has been proposed, based on its notable reinforcing effect. In addition, Al/PTFE composites have attracted much attention due to the altered ignition and reaction characteristics [22-25], and the remarkable theoretical reaction enthalpy of up to 21 GJ/m<sup>3</sup> [26, 27]. Studies [22-25] have shown that gaseous AlF<sub>3</sub> production in a propellant flame could facilitate oxidation of Al and reduce the two-phase flow losses in rocket motors. These possibilities may potentially increase a propellant's  $I_{sp}$  [25, 28]. In the present work, PTFE stirred with Al was introduced into a CMDB system and a possible mechanism for the reinforcing effect of Al/PTFE on the propellant's mechanical performance, as well as its safety properties, are discussed. As a consequence, PTFE significantly enhanced the propellant's mechanical properties and decreased its shock sensitivity, while reducing combustion agglomeration. Thus, it promises that PTFE may expand the field of application of CMDB propellants.

## 2 Experimental

### 2.1 Materials

NC and NG were obtained from Shanxi Northern Xing An Chemical Industry Co. Ltd., China. The N content was 12 wt.%. PTFE (particles of 25  $\mu$ m) was obtained from Ji'nan Jinhui Chemical Co. Ltd., China. Spherical Al of 3  $\mu$ m was obtained from Changyuan Mingyu Aluminium Industry Co. Ltd., China. RDX of 72  $\mu$ m (specified by supplier) was obtained from Gansu Yinguang Chemical Industry Group Co. Ltd., China.

## 2.2 Preparation of PTFE-CMDB propellant

Six kinds of powders were obtained by varying the Al/PTFE mass ratio (6:1, 6:2, 6:3, 6:4, 6:5, 6:6) by stir mixing in hexane for 3 h followed by vacuum drying for 2 h. The CMDB propellants with PTFE inclusions (PTFE-CMDB) were then prepared through a rolling process. After preliminary dehydration of the propellant slurry, it was transferred to a calender to be sheared. During this process, the slurry could dehydrate further and become plasticized. A primary CMDB propellant tablet could then be obtained. (These repeated shear processes are often called rolling processes). The detailed chemical ingredients are shown in Table 1. The additives were organic lead-salts, organic copper-salts and carbon black, vaseline and N,N'-dimethylcarbanilide.

**Table 1.** Composition of PTFE modified CMDB propellants [wt.%]

Sample	NC	NG	PTFE	Al	RDX	Additives
A	24.2	23.3	0	6	42.5	4
P-1	24.2	23.3	1	6	41.5	4
P-2	24.2	23.3	2	6	40.5	4
P-3	24.2	23.3	3	6	39.5	4
P-4	24.2	23.3	4	6	38.5	4
P-5	24.2	23.3	5	6	37.5	4
P-6	24.2	23.3	6	6	36.5	4

## 2.3 Measurements

A propellant's tensile performance was determined using an AGS-J Electromechanical Universal Testing Machine according to the China Military Standard GJB770B-2005 413.1. The conditions were: temperature  $-40\text{ }^{\circ}\text{C}$ ,  $20\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$ ; tensile rate 10 mm/min. The impact strength of a propellant was determined with a TCJ-25 simply-supported impact testing machine according to the China Military Standard GJB770B-2005 417.1 at  $-40\text{ }^{\circ}\text{C}$ ,  $20\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$ . The friction sensitivity was determined according to the China Military Standard GJB770B-2005 601.2, using a pendulum friction apparatus. The conditions were: pendulum weight 1.5 kg; swaying angle 66 deg; pressure 2.45 MPa; sample mass  $20 \pm 1$  mg. Initiation probability P was obtained from 50 trials. Impact sensitivity was determined according to the China Military Standard GJB770B-2005 602.1, on a drop-hammer apparatus using an up-and-down method. The conditions were: sample mass 30 mg; hammer weight 2 kg. Based on 25 go/no-go trials, the height for 50% probability of explosion ( $H_{50}$ ) can be calculated. Calorimetric analysis of Al/PTFE was carried out with a Parr 6200 Calorimeter. The morphological characteristics of the CMDB propellant was examined using a S4800 cold field

scanning electron microscope (SEM). Energy dispersive spectrometry (EDS) measurements were also conducted. The size distribution of the collected slags were determined *via* a HELOS (H3185) instrument, with alcohol as the medium.

### 3 Results and Discussion

#### 3.1 Tensile properties of the CMDB propellants

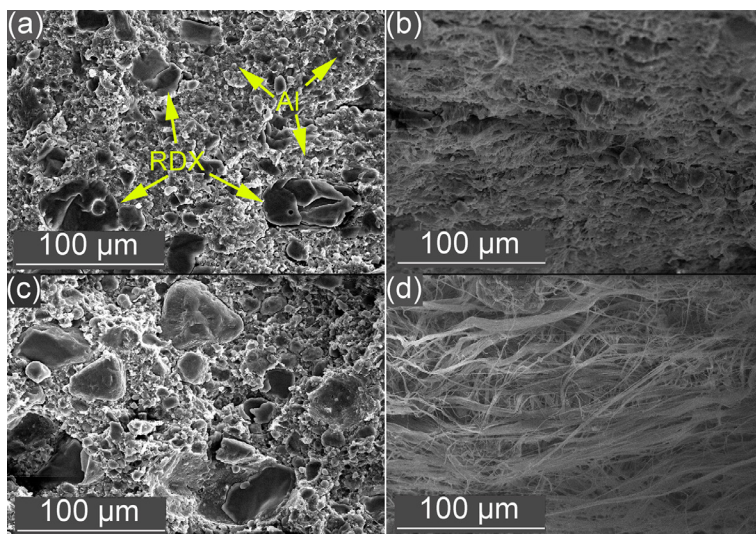
Table 2 lists the tensile properties of the propellants. The propellant tensile strength was reduced and the elongation remained unchanged with increasing PTFE content in the region of low PTFE concentrations (below 2%), and then both tensile strength and elongation were increased with further increases in PTFE content. Generally, the elongation of the CMDB propellants at  $-40^{\circ}\text{C}$  was limited to 10% [1]. This may be reduced to 3% when a large amount of nitramine is incorporated in the formulation [4, 29, 30]. In the present work, elongation at maximum strength of blank CMDB propellant at  $-40^{\circ}\text{C}$  was only 0.88%. This is mainly caused by the high RDX concentration above 40% [1, 8]. In addition, industrial grade RDX was used here, whose unregular shape is shown in Figure S1 (the S Figures are in SI), and may also lead to a reduction in tensile properties. However it was increased significantly for PTFE-CMDB propellants at  $-40^{\circ}\text{C}$ . Enhancement of the tensile strength was also obtained at  $50^{\circ}\text{C}$ . For example, 6 wt.% PTFE (P-6) increased the elongation dramatically, up to 23.8% at  $-40^{\circ}\text{C}$ . This means that elongation of P-6 has increased by a factor of 26 and exceeded almost all CMDB propellants with a high solid content. Instead of being accompanied by loss of strength, as with XLDB propellant, the tensile strength for P-6 propellant was increased by 69% compared to propellant A.

**Table 2.** Propellant tensile properties

Sample	20 °C		50 °C		−40 °C	
	$\sigma^a$ [MPa]	$\varepsilon^b$ [%]	$\sigma^a$ [MPa]	$\varepsilon^b$ [%]	$\sigma^a$ [MPa]	$\varepsilon^b$ [%]
A	4.99	1.52	3.04	2.31	26.3	0.88
P-1	3.98	2.80	2.88	4.45	24.2	1.17
P-2	3.98	7.95	2.62	8.19	29.4	2.28
P-3	4.69	18.3	2.74	19.2	32.8	7.15
P-4	5.11	31.3	3.11	27.2	33.6	15.7
P-5	5.76	38.1	3.82	34.4	41.2	21.7
P-6	7.14	42.5	4.72	38.7	44.5	23.8

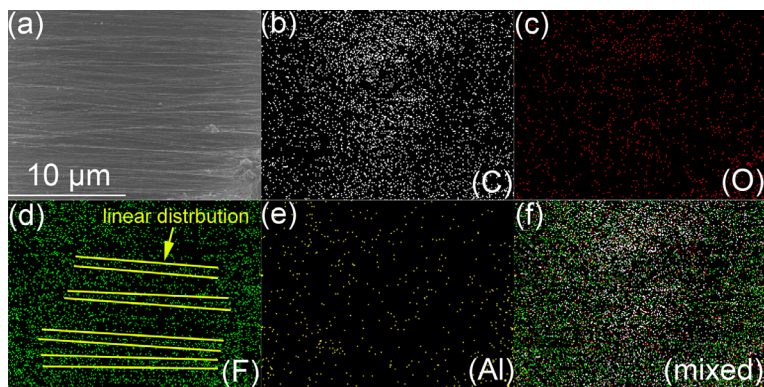
<sup>a</sup>  $\sigma$ : tensile strength; <sup>b</sup>  $\varepsilon$ : elongation at maximum tensile strength

SEM was used to obtain an insight into the structure of the propellants, to help to understand the mechanism of this enhancement. The morphological characteristics of propellant A and a typical PTFE-CMDB propellant (P-5) cross section are shown in Figure 1.



**Figure 1.** SEM images of propellant fracture surfaces: (a) propellant A snapped after being frozen in liquid nitrogen, (b) propellant P-5 snapped after being frozen in liquid nitrogen, (c) propellant A snapped at room temperature, (d) propellant P-5 snapped at room temperature

It may be seen from Figure 1 that the cross section of frozen propellant A is flat and contains a large amount of RDX and Al particles. The snapped fracture surface at 20 °C was similar. The appearance of the SEM images of P-5 propellant is quite different. The cross sections of both frozen propellant P-5 and propellant snapped at room temperature consisted of an abundance of fine fibres, which were uneven. This morphological distinction indicates that PTFE can increase propellant toughness at low temperatures. It also means that PTFE can improve the critical defects of CMDB propellant. To verify that these fibres are PTFE, an EDS analysis was applied on the brake surface, as shown in Figure 2.



**Figure 2.** SEM image and elemental maps of propellant P-5 fracturing position: (a) SEM image, (b) C, (c) O, (d) F, (e) Al, (f) mixed

The fluorine map shows a linear distribution in accordance with fibres in the propellant breaking position. Thus, the fibres in the fracture surface of the PTFE-CMDB propellant are PTFE. It may also be inferred that PTFE evolves into fibres under the uniform shear forces in the preparation of the propellant.

The relationship between the tensile properties of the propellant and the PTFE content was drawn (see Figure S2 in SI) for clarity from the relationship between PTFE and the propellant's tensile properties. The tensile strength was reduced as the concentration of PTFE was increased in the region of low PTFE concentrations, below 2%. Then a minimum value for the tensile strength appeared followed by increasing tensile strength and elongation with increasing PTFE content. Studies [31, 32] have shown that nanofibres can form a network structure when their concentration reaches a critical value, and then results in enhanced mechanical performance. Thus, the reinforcement in our work on the PTFE-CMDB propellants may result from the formation of a PTFE fibre network [21, 33].

To confirm the presence of a PTFE network, propellants P-1, P-2 and P-5 were dissolved in acetone for 5 h and then analyzed by SEM (see Figure S3 in SI). Propellant P-2 was chosen as resulting in minimum tensile strength. Propellant P-1 and P-5 are the ones with lower/higher PTFE content than that of propellant P-2. It is clear that few fibres can be found in the images of propellant P-1. For propellant P-2, however, PTFE fibres formed an elementary entanglement structure. A much tighter entanglement network appeared when the PTFE concentration reached 5 wt.%.

Based on the above information, some conclusions may be drawn: 1) PTFE evolved into fibres during the repeated shear process in the propellant preparation;

2) PTFE fibres formed an elementary network structure when its concentration reached 2 wt.%; 3) the entanglement of the PTFE network enhanced the propellant's low temperature mechanical properties. It is worth noting that the propellant tensile strength for propellant P-1 is lower than that of the blank propellant. This may be mainly caused by two factors. On the one hand, PTFE fibres did not form a network; on the other hand, interfacial adhesion between PTFE and the double base components is lower than that between the solid particles of the double base components, and thus it may weaken the propellant. In addition, it may be observed that enhancement of the propellant tensile properties is reduced with an increase in temperature. This may be caused by the elementary PTFE network. When the PTFE concentration was increased to 2 wt.%, the fibre network structure was elementary. However, elongation of this network is limited to some extent due to an insufficient fibre concentration. At  $-40\text{ }^{\circ}\text{C}$ , the elongation of the double base matrix (with solid particles) in this paper was only 0.88%. In this range of deformation, the PTFE network did not break. Thus, it enhanced the propellant tensile strength. When the temperature was increased to  $20\text{ }^{\circ}\text{C}$ , however, the elongation of the matrix increased to 1.52%. This range might exceed the deformation limitation of the PTFE network, which means that the network might have been broken after the propellant had been deformed 1.52%. Thus, 2 wt.% PTFE may result in little enhancement in propellant tensile strength at  $20\text{ }^{\circ}\text{C}$ , while the small enhancement is eliminated by the increased interface for propellant P-2 compared to P-1. Thus, P-2 had a similar tensile strength to P-1. This network may barely result in enhancement at  $50\text{ }^{\circ}\text{C}$ , and thus, propellant P-2 was found to be weaker than P-1 at  $50\text{ }^{\circ}\text{C}$ . In addition, PTFE undergoes transitions at  $19\text{ }^{\circ}\text{C}$  and  $30\text{ }^{\circ}\text{C}$  [34-36]. The transition at  $19\text{ }^{\circ}\text{C}$  is considered important because it significantly affects the product's behaviour. Around  $19\text{ }^{\circ}\text{C}$ , a slight untwisting of the molecule occurs, from a  $180^{\circ}$  twist per 13  $\text{CF}_2$  groups to a  $180^{\circ}$  twist per 15  $\text{CF}_2$  groups. At the  $30\text{ }^{\circ}\text{C}$  transition, the hexagonal unit cell disappears and the rod-like hexagonal packing of the chains in the lateral direction is retained [35, 36]. Below  $19\text{ }^{\circ}\text{C}$  there is an almost perfect three-dimensional order; between  $19\text{ }^{\circ}\text{C}$  and  $30\text{ }^{\circ}\text{C}$  the chain segments are disordered; and above  $30\text{ }^{\circ}\text{C}$ , the preferred crystallographic direction is lost and the molecular segments oscillate around their long axes with a random angular orientation in the lattice [35, 36]. These transitions are accompanied with a break in the modulus of PTFE. Thus, transitions of PTFE may also contribute to the reduction in the enhancement of the propellant's mechanical performance with increasing temperature.

### 3.2 Impact performance

Table 3 shows the impact strength of the CMDB propellants. The impact strength of propellant A was found to be only 2.31 MPa. This is mainly caused by the crystallinity of the adhesive molecule [37]. By contrast, the impact strength of the PTFE-CMDB propellants were greatly increased by the PTFE. For example, the impact strength for P-6 propellant had increased by 326%, from 2.31 MPa to 9.84 MPa at  $-40\text{ }^{\circ}\text{C}$ . Furthermore, some specimens for propellant P-6 were not broken into two pieces at  $20\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$ . As with the tensile properties examination, this enhancement could also be attributed to the formation of a PTFE network structure. The reinforcement effect was enhanced with PTFE enrichment, with a more tight and tough network. It is worth noting that the impact strength of P-1 was even increased by 30.7% at  $-40\text{ }^{\circ}\text{C}$ . This is contrary to the propellant tensile property test results. The increased enhancement effect may be mainly caused by the changed loading mode and the loading rate of stress. A double base propellant is a significant strain-rate-dependent material. It exhibits ductile behaviour at low strain rates while it exhibits impact brittleness at high strain rates. PTFE could improve the CMDB propellant brittleness as shown by the tensile property test results. Thus, it enhanced the propellant impact strength. During deformation, internal friction between the PTFE fibres and the double base matrix may occur, resulting in loss of impact energy. This frictional loss increases with increasing temperature due to larger deformation. Thus, unlike the tensile property test results, enhancement in impact strength at higher temperature occurred. The impact strength for propellant P-1 in which the PTFE fibres did not form a network structure was even increased for the same reason.

**Table 3.** Impact strength of the PTFE-CMDB propellants

Sample	Impact strength [MPa]		
	$-40\text{ }^{\circ}\text{C}$	$20\text{ }^{\circ}\text{C}$	$50\text{ }^{\circ}\text{C}$
A	2.31	3.87	5.38
P-1	3.02	5.08	9.11
P-2	4.14	9.22	16.0
P-3	4.70	15.3	22.9
P-4	5.64	22.1	--
P-5	7.42	34.3	--
P-6	9.84	--	--

-- means broken, but not into two pieces

### 3.3 Mechanical sensitivity

The propellant shock sensitivity test was conducted to measure the influence of PTFE on the propellant safety performance. The results are shown in Table 4. Friction and impact sensitivity ( $H_{50}$ ) for propellant A was found to be 66% and 21.5 cm, respectively. This means that propellant A is more sensitive to mechanical stimuli [1, 4, 8, 9]. Some factors may contribute to the increased sensitivity of the propellant in this work. First of all, NG was used as an energetic plasticizer in this work, and no other plasticizers, such as DEP or DBP, were incorporated in the composition. NG is much more sensitive than other plasticizers. In addition, industrial grade RDX, with irregularly shaped crystals, was used in this work. Studies have shown that RDX particles with smooth surfaces are less sensitive [38-40]. Thus, the CMDB propellant in this work is more sensitive than some others. Comparable results can be found in the literature in which the formula and materials are similar to those in this work [41]. The shock sensitivity for the PTFE-CMDB propellants, however, was significantly reduced. For example, incorporation 1 wt.% PTFE reduced the propellant friction sensitivity by 54.5%, from 66% to 30%, and the impact sensitivity by 24.4%, from 21.50 cm to 26.75 cm. The propellant sensitivity was reduced further with increasing PTFE content. The friction and impact sensitivity of propellant P-6 were reduced by 75.8% and 35.6%, respectively.

**Table 4.** Sensitivity of the CMDB propellants

Sample	Friction sensitivity [%]	Impact sensitivity, $H_{50}$ [cm]
A	66	21.5
P-1	30	26.7
P-2	26	27.4
P-3	20	27.9
P-4	24	28.0
P-5	18	29.1
P-6	16	29.3

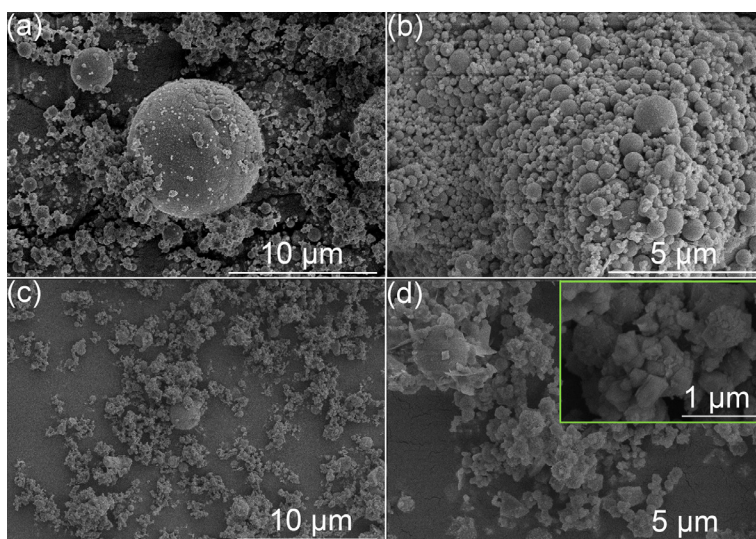
Some of the clearer SEM images (shown in Figure S4 in SI) taken from the fracture surfaces of propellants A and P-5 are shown to clarify the mechanism of desensitization caused by PTFE. Many RDX particles can be found in the cross-section of propellant A, while only a few can be seen in the image of propellant P-5. Based on these observations, RDX particles may be preserved in the abundant PTFE fibres, similar to a coating. Coating has been proved

to be a useful way of reducing sensitivity [4, 19, 20]. Thus, both impact and friction sensitivity were decreased for the PTFE-CMDB propellants. In addition, the enhancement of the mechanical performance changed the propellant's deformation behaviour, which relates to the dissipation of impact energy [42, 43] and ignition during the flow caused by impact [44, 45]. The brittle propellant A produced a jagged or cracked surface, which may lead to hot spot formation [44]. The PTFE network in the propellant, however, greatly enhanced the propellant's ductility. This enhancement delays the appearance of flaws. This changed deformation behaviour is also a key factor contributing to the propellant's insensitivity. Finally, PTFE additives can reduce the composite's friction coefficient [46] due to its lubricating action. Lubrication between particles could reduce energy absorption during viscoelastic/plastic deformation [47]. In this regard, the probability of hot spot formation can be further reduced. According to the factors mentioned above, friction and impact sensitivity are greatly reduced for PTFE-CMDB propellants.

### 3.4 Combustion characteristic

Studies [23, 25] have shown facilitation for aluminum ignition in activated Al/PTFE composites. This composite can reduce Al agglomeration in the propellant. To investigate whether mechanically stirred Al/PTFE could promote Al ignition, calorimetric analyses *via* an oxygen bomb were carried out (see Table S2 in SI).

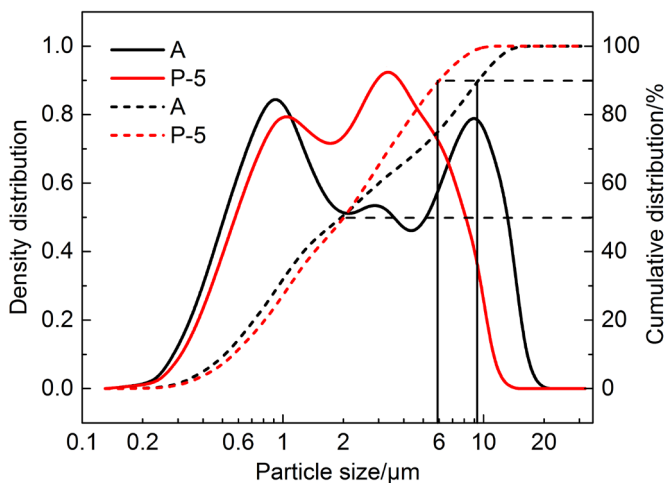
Surprisingly, the gravimetric reaction enthalpies of Al/PTFE were found to be very close to the estimated theoretical reaction enthalpy. This means that PTFE in stir-mixed Al/PTFE powders has reacted completely with the Al, and may be caused by the high reactivity of fluoride free radicals produced by the PTFE. Thus, stir-mixed Al/PTFE may facilitate Al ignition and reduce agglomeration in propellants.



**Figure 3.** SEM images of collected slag: (a) slag from propellant A, (b) smoke products from propellant A, (c) slag from propellant P-5, (d) particles in slag from propellant P-5

To investigate whether the shear-forced PTFE could influence the combustion of Al in CMDB propellants, slags were collected in a similar manner to Gaurav's work [28] and analyzed by SEM, EDS and Mastersizer. SEM images of the collected slags for propellant A and a typical PTFE-CMDB propellant (P-5) are shown in Figure 3.

It is obvious that the residue from propellant A consists of spheres only. They are Al and  $\text{Al}_2\text{O}_3$  (verified by elemental mapping images and XRD analysis in Figures S5 and S6, respectively, in SI). However the slag from propellant P-5 contains not only spheres but also lots of angular particles. This infers that the PTFE has reacted with Al in the CMDB propellant. Thus, agglomeration may be reduced by fluorination of Al. However, although an obvious distinction can be found in the morphology of the two residues, it is not easy to say which one is smaller in size. The particle size distributions were measured using a HELOS (H3185) instrument with alcohol as the medium, as shown in Figure 4.



**Figure 4.** Particle size distributions of collected slags from propellant A and propellant P-5

Interestingly, the  $D_{50}$  of the two collected products were the same although the size distributions were apparently different. To be specific, the density was slightly larger for propellant A, for particles  $<1\ \mu\text{m}$ . Except for these smoke products, more particles of about  $3.5\ \mu\text{m}$  were present for the slag from propellant P-5. However, products of  $9.2\ \mu\text{m}$  occupy the largest proportion in slag from propellant A. The  $D_{90}$  for slag from propellant P-5 exhibited a decrease of 37%, from  $9.31\ \mu\text{m}$  to  $5.87\ \mu\text{m}$ , compared to that from propellant A. This means that PTFE has reduced the percentage of large agglomerates, and may be caused by the consumption of aluminum and formation of gaseous  $\text{AlF}_3$  when the Al melt-reacts with fluorine [24]. The agglomerate diameter had decreased by 66% for HTPB propellant with mechanically activated Al/PTFE in the work by Sippel *et al.* [25]. The relatively low effect of agglomeration reduction in the present work may be mainly caused by poor dispersion or combination between Al and PTFE. In addition, the collection method, Al size, Al concentration and adhesion system used here are different to those of Sippel *et al.*, which may generate a different agglomeration trend and influence the reduction effect of PTFE. Nonetheless, in view of the observed results mentioned above, it could be inferred that mechanically mixed Al/PTFE powder decreased the large agglomerates, which usually result in two-phase flow loss. Thus, it can potentially improve the  $I_{\text{sp}}$  performance.

To confirm the production of  $\text{AlF}_3$  in the agglomerates, X-Ray diffraction (XRD) tests with Cu  $K\alpha$  radiation were carried out on the collected products

and the results are shown in SI (Figure S6). Slag from propellant A was also examined as a control. The two XRD patterns were similar to the diffraction peaks of Al and  $\text{Al}_2\text{O}_3$ . However, the intensity of the peaks of Al and  $\text{Al}_2\text{O}_3$ , which is directly proportional to the concentration of the component producing it [48], was reduced for the slag from propellant P-5. The obvious  $\text{AlF}_3$  diffraction peaks, located at  $25.2^\circ$ ,  $25.9^\circ$ ,  $26.2^\circ$  and  $51.8^\circ$  [23, 28] show up in the XRD pattern of products from propellant P-5.

## 4 Conclusions

In summary, mechanically mixed Al/PTFE was introduced into a CMDB propellant, and resulted in improvements in the propellant's mechanical and safety performance. PTFE evolved into fibres through the rolling process, forming an entanglement network structure and finally reinforcing the CMDB propellant. It is especially significant that the propellant elongation and impact strength at low temperature were enhanced. Additionally, the abundance of PTFE fibres offered protection for the RDX particles, as with coating. This protection could buffer mechanical stimuli and decrease the possibility of shock induced ignition. The greatly enhanced ductility could reduce the jagged surface and cracks when subjected to impact. Thus, enhancement of the propellant's mechanical performance could also contribute to its insensitivity. The lubricating action of PTFE, which may reduce the energy absorbed during deformation could also reduce the probability of hot spot formation. Finally, PTFE in mechanically mixed Al/PTFE participated in Al fluorination and decreased the size of large agglomerates. This reduction, which may result in a decrease of two-phase flow loss as well as the gaseous  $\text{AlF}_3$  combustion product in the flame from the CMDB propellant, may potentially improve the specific impulse performance. This work has shown that Al/PTFE inclusion can significantly enhance the mechanical and safety performance of a CMDB propellant and reduce propellant agglomeration.

Current and future efforts are focused on what and how Al/PTFE would influence the burning rate pressure dependence and combustion wave structure.

## References

- [1] Tan, H. M. *The Chemistry and Technology of Solid Rocket Propellant*, Beijing Institute of Technology Press, Beijing, **2015**, pp. 114-420.
- [2] Kubota, N. *Propellants and Explosives*. Wiley-VCH, Weinheim **2006**, pp. 69-112;

ISBN 9783527314249.

- [3] Kubota, N. Energetics of HMX-Based Composite Modified Double-Base Propellant Combustion. *J. Propul. Power* **1999**, 15(6): 759-762.
- [4] An, C. W.; Li, F. S.; Wang, J. Y.; Guo, X. D. Surface Coating of Nitroamine Explosives and Its Effects on the Performance of Composite Modified Double-Base Propellants. *J. Propul. Power* **2015**, 28(2): 444-448.
- [5] Nair, U. R.; Gore, G. M.; Sivabalan, R.; Divekar, C. N.; Asthana, S. N.; Singh, H. Studies on Advanced CL-20-based Composite Modified Double-Base Propellants. *J. Propul. Power* **1971**, 20(5): 952-955.
- [6] Yano, Y.; Kubota, N. Combustion of HMX-CMDB Propellants (II). *Propellants Explos. Pyrotech.* **2010**, 11(1): 1-5.
- [7] Asthana, S. N.; Athawale, B. K.; Singh, H. Impact, Friction, Shock Sensitivities and DDT Behaviour of Advanced CMDB Propellants. *Def. Sci. J.* **1989**, 39(1): 99-107.
- [8] Choudhari, M. K.; Dhar, S. S.; Shrotri, P. G.; Singh, H. Effect of High Energy Materials on Sensitivity of Composite Modified Double Base (CMDB) Propellant System. *Def. Sci. J.* **2013**, 42(4): 253-257.
- [9] Gautam, G. K.; Pundlik, S. M.; Joshi, A. D.; Mulage, K. S.; Singh, S. N. Study of Energetic Nitramine Extruded Double-Base Propellants. *Def. Sci. J.* **2013**, 48(2): 235-243.
- [10] Yan, Q. L.; Li, X. J.; Wang, Y.; Zhang, W. H.; Zhao, F. Q. Combustion Mechanism of Double-Base Propellant Containing Nitrogen Heterocyclic Nitroamines (I): the Effect of Heat and Mass Transfer to the Burning Characteristics. *Combust. Flame* **2009**, 156(3): 633-641.
- [11] Bhat, V. K.; Singh, H. Cross-Linked Slurry Cast Composite Modified Double Base Propellants: Mechanical Properties. *Def. Sci. J.* **1987**, 37(1): 39-44.
- [12] Robinson, A. E. *Crosslinked Double Base Propellant Binders*. Patent US 4234364, **1980**.
- [13] Elrick, D. E.; Gilbert, H. *Crosslinked Carboxyl Containing Polymer and Nitrocellulose as Solid Propellant Binder*. Patent US 4029529, **1977**.
- [14] Dehm, H. C. *Composite Modified Double-Base Propellant with Filler Bonding Agent*. Patent US 4038115, **1977**.
- [15] Manning, T. G.; Strauss, B. *Reduction of Energetic Filler Sensitivity in Propellants through Coating*. Patent US 6524706 B1, **2003**.
- [16] Smith, K. T.; Johansen, Ø. H.; Skjold, E.; Gjersoe, R. *Pressable Plastic-bound Explosive Composition*. Patent US 7857922 B2, **2010**.
- [17] Li, W.; Song, Q. C.; Wang, W. B.; Chen, Y. K. The Influence of DDT-Preventing Agents upon the Impact Sensitivity of the Polyurethane-bonded RDX. *Propellants Explos. Pyrotech.* **1996**, 21(5): 247-250.
- [18] Lu, M.; Chen, Y.; Luo, Y. J.; Tan, H. M. Preparation of Waterborne Polyurethane Latex and Study on Its Cladding of RDX. *J. Propul. Technol.* **2005**, 26(1): 89-92.
- [19] Dagley, I. J.; Ho, S. Y.; Montelli, L.; Louey, C. N. High Strain Rate Impact Ignition of RDX with Ethylene-Vinyl Acetate (EVA) Copolymers. *Combust. Flame* **1992**,

- 89(3-4): 271-282.
- [20] Kincaid, J. F.; Reed, R. *Bonding Agent for HMX (Cyclotetramethylenetetranitramine)*. Patent US 4350542, **1982**.
- [21] Morgan, R. A.; Stewart, C. W.; Thomas, E. W.; Stahl, W. M. Reinforcement with Fluoroplastic Additives. *Rubber World, (United States)* **1991**, 204: 2.
- [22] Osborne, D. T.; Pantoya, M. L. Effect of Al Particle Size on the Thermal Degradation of Al/Teflon Mixtures. *Combust. Sci. Technol.* **2007**, 179(8): 467-1480.
- [23] Sippel, T. R.; Son, S. F.; Groven, L. J. Altering Reactivity of Aluminum with Selective Inclusion of Polytetrafluoroethylene through Mechanical Activation. *Propellants Explos. Pyrotech.* **2013**, 38(2): 286-295.
- [24] Sippel, T. R.; Son, S. F.; Groven, L. J.; Zhang, S.; Dreizin, E. L. Exploring Mechanisms for Agglomerate Reduction in Composite Solid Propellants with Polyethylene Inclusion Modified Aluminium. *Combust. Flame* **2015**, 162(3): 846-854.
- [25] Sippel, T. R.; Son, S. F.; Groven, L. J. Aluminum Agglomeration Reduction in a Composite Propellant Using Tailored Al/PTFE Particles. *Combust. Flame* **2014**, 161(1): 311-321.
- [26] Watson, K. W.; Pantoya, M. L.; Levitas, V. I. Fast Reactions with Nano- and Micrometer Aluminum: a Study on Oxidation versus Fluorination. *Combust. Flame* **2008**, 155(4): 619-634.
- [27] Mulamba, O.; Pantoya, M. L. Exothermic Surface Chemistry on Aluminum Particles Promoting Reactivity. *Appl. Surf. Sci.* **2014**, 315(1): 90-94.
- [28] Gaurav, M.; Ramakrishna, P. A. Effect of Mechanical Activation of High Specific Surface Area Aluminium with PTFE on Composite Solid Propellant. *Combust. Flame* **2016**, 166: 203-215.
- [29] Austruy, H. *Solid Rocket Propulsion Technology*. Pergamon Press Ltd., Oxford **1993**, 369-412; ISBN 9780080409993.
- [30] Zhang, Y. H.; Liu, C. T.; Lv, Y. Y.; Zhou, Z. W.; Wang, F. J.; Shao, Z. Q.; Zuo, Y. Y.; Wei, X. L. Preparation and Characteristic of Modified Double-Base Propellant Modified with Cellulose Nanofibers. *Integr. Ferroelectr.* **2016**, 171(1): 115-123.
- [31] Meesorn, W.; Shirole, A.; Vanhecke, D.; Espinosa, L. M. D.; Weder, C. A Simple and Versatile Strategy to Improve the Mechanical Properties of Polymer Nanocomposites with Cellulose Nanocrystals. *Macromolecules* **2017**, 50(6): 2364-2374.
- [32] Grunert, M.; Winter, W. T. Nanocomposites of Cellulose Acetate Butyrate Reinforced with Cellulose Nanocrystals. *J. Polym. Environ.* **2002**, 10(1-2): 27-30.
- [33] Unal, H.; Mimaroglu, A.; Kadioglu, U.; Ekiz, H. Sliding Friction and Wear Behaviour of Polytetrafluoroethylene and Its Composites under Dry Conditions. *Mater. Des.* **2004**, 25(3): 239-245.
- [34] Koch, E.-C. *Metal-Fluorocarbon Based Energetic Materials*. Wiley-VCH, Weinheim **2012**, pp. 20-22; ISBN 9783527329205.
- [35] Clark, E. S. The Molecular Conformations of Polytetrafluoroethylene: Forms II and IV. *Polymer* **1999**, 40(16): 4659-4665.

- [36] Clark, E. S.; Muus, L. T. Partial Disorder and Crystal Transitions in Polytetrafluoroethylene. *Zeitschrift Für Kristallographie* **1962**, *117*(2-3): 119-127.
- [37] Yi, J. H.; Zhao, F. Q.; Xu, S. Y.; Zhang, L. Y.; Gao, H. X.; Hu, R. Z. Effects of Pressure and TEGDN Content on Decomposition Reaction Mechanism and Kinetics of DB Gun Propellant Containing the Mixed Ester of TEGDN and NG. *J. Hazard. Mater.* **2009**, *165*(1-3): 853-859.
- [38] van der Heijden, A. E. D. M.; Bouma, R. H. B. Crystallization and Characterization of RDX, HMX, and CL-20. *Cryst. Growth Des.* **2004**, *4*(5): 999-1007.
- [39] Kröber, H.; Teipel, U. Crystallization of Insensitive HMX. *Propellants Explos. Pyrotech.* **2010**, *33*(1): 33-36.
- [40] Ruth, M. D.; Duncan, S. W. Relationship between RDX Properties and Sensitivity. *Propellants Explos. Pyrotech.* **2010**, *33*(1): 4-13.
- [41] An, C. W.; Song, X. L.; Guo, X. D.; Wang, Y.; Yan, B.; Li, F. S. Influence of Surface Coating of RDX Fillers on Mechanical Sensitivity and Properties of CMDB Propellant. *J. Solid. Rocket. Technol.* **2007**, *30*(6): 521-524.
- [42] Ho, S. Y.; Fong, C. W. Correlation between Fracture Properties and Dynamic Mechanical Relaxations in Composite Propellants. *Polymer* **1987**, *28*(5): 739-744.
- [43] Ho, S. Y.; Fong, C. W. Relationship between Impact Ignition Sensitivity and Kinetics of the Thermal Decomposition of Solid Propellants. *Combust. Flame* **1989**, *75*(2): 139-151.
- [44] Walley, S. M. Impact Sensitivity of Propellants. *Proc. Phys. Soc. London, Sect. A* **1992**, *438*(1904): 571-583.
- [45] Field, J. E. Hot Spot Ignition Mechanisms for Explosives. *Proc. Roy. Soc. A-MATH. PHY.* **1992**, *339*(1654): 269-283.
- [46] Trabelsi, M.; Kharrat, M.; Dammak, M. Impact of Lubrication on the Tribological Behaviour of PTFE Composites for Guide Rings Application. *Bull. Mater. Sci.* **2016**, *39*(5): 1-7.
- [47] Winter, R. E.; Field, J. E. The Role of Localized Plastic Flow in the Impact Initiation of Explosives. *Proc. Phys. Soc. London, Sect. A* **1975**, *343*(1634): 99-413.
- [48] Klug, H. P.; Alexander, L. E. *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. Wiley-VCH, Weinheim **1974**, 992.

Received: January 1, 2018

Revised: June 20, 2018

Published online: September 21, 2018