



## Microstructure, Mechanical and Detonation Properties of Elastomeric Micro/Ultrafine-rubber Modified TNT-based Molten Energetic Composites

Qing MA<sup>1,2</sup>, Ping-sheng WANG<sup>2</sup>, Guan LUO<sup>2</sup>, Mao-ping WEN<sup>2</sup>,  
Da-yuan GAO<sup>2</sup>, Bao-hui ZHENG<sup>2,\*</sup>, Yuan-jie SHU<sup>3,\*\*</sup>

<sup>1</sup> *School of Chemical Engineering,  
Nanjing University of Science & Technology,  
210094, Nanjing, P.R. China*

<sup>2</sup> *Institute of Chemical Materials,  
China Academy of Engineering Physics,  
621900, Mianyang, P.R. China*

<sup>3</sup> *Xi'an Modern Chemistry Research Institute,  
Xi'an, 710065, P.R. China*

*E-mails: \*zhengbaohui305@163.com; \*\*syjfree@sohu.com*

**Abstract:** Elastomeric micro- and ultrafine-rubber are first considered as binders in melt-cast explosives for improving the mechanical properties. Acrylonitrile-butadiene rubber (NBR), in ultrafine fully vulcanized form (UF-NBR), carboxylated acrylonitrile-butadiene rubber (CNBR), in ultrafine fully vulcanized form (UF-CNBR), styrene-butadiene rubber (SBR), in ultrafine fully vulcanized form (UF-SBR), carboxylated styrene-butadiene rubber (CSBR), in ultrafine fully vulcanized form (UF-CSBR), acrylic rubber (ACM), in ultrafine fully vulcanized form (UF-ACM), room temperature vulcanized silicone rubber (RTV), in ultrafine fully vulcanized form (UF-RTV) and polytetrafluoroethene (PTFE) in micro-rubber form (PTFE-M) were utilized for modifying 2,4,6-trinitrotoluene (TNT) based melt-cast explosives. Based on their dispersity in TNT and RDX slurry, only UF-NBR, UF-CNBR and PTFE-M can be used. In the modification experiment, their influence on the mechanical and detonation performance of the matrixes were studied, as well as the impact sensitivity. Compared with PTFE-M and UF-CNBR, UF-NBR improved the tensile and compressive strength of the original formulation CYCLOTOL-65/35. The toughening mechanism was also explained through interfacial interactions and fracture energy analysis. The predicted detonation properties of the modified formulations (detonation pressure variations from 26

to 28 GPa, detonation velocity variations from 7900 to 8100 m/s) are at the same energy level as CYCLOTOL-65/35. In addition, the drop hammer impact testing results confirm that the formulation containing UF-NBR is more sensitive than the one with UF-CNBR, with the same amount of additive.

**Keywords:** micro and ultrafine rubber, 2,4,6-trinitrotoluene, molten energetic composites, mechanical property, detonation performance

## 1 Introduction

2,4,6-Trinitrotoluene (TNT), with its excellent thermal stability makes it suitable as a carrier for melt-loading more powerful explosives, such as 3-nitro-1,2,4-triazol-5-one (NTO), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), cis-1,3,4,6-tetranitrooctahydroimidazo[4,5d]imidazole (BCHMX) and hexanitrohexaazaisowurtzitane (CL-20) [1-2]. Despite other candidates having been developed, such as 2,4-dinitroanisole (DNAN), 1,3,3-trinitroazetidine (TNAZ), 3,4-dinitrofurazanfuroxan (DNTF), 1-methyl-2,4,5-trinitroimidazole (MTNI), and 3(5)-nitropyrazoles (DNP) [3-7], TNT is still used widely in military munitions because of its mature process and low manufacturing cost. However, as a carrier TNT has its own problems. Composition B (RDX/TNT = 60:40 [wt.%]) exhibits poor mechanical properties, and shows undesirable defects such as cracks, exudation, voids, irreversible growth and brittleness, which have negative effects on the ballistic performance and impact sensitivity [8, 9].

Like the conventional binders used in polymer bonded explosives (PBXs), incorporation of di-isocyanate and 1,4-butyleneoxide polyglycol [10], cellulosic resin [11], polyurethane elastomer [12-14], thermoplastic elastomer [15-17] into melt-cast formulations were employed to avoid the issues of oily exudation and voids, including lowering the sensitivity. Additionally, 2,2',4,4',6,6'-hexanitrostilbene (HNS) was developed for toughening molten TNT [18-20]. Another method to control the crystal morphology in TNT casting is to use 5-nitrobarbituric acid or its trihydrate at 0.5-2 wt.% [21]. The cost was reduced and the required amount was less compared to HNS. However, the above procedures have issues which limit their applications, such as complicated procedures, high casting temperatures and expensive manufacturing costs.

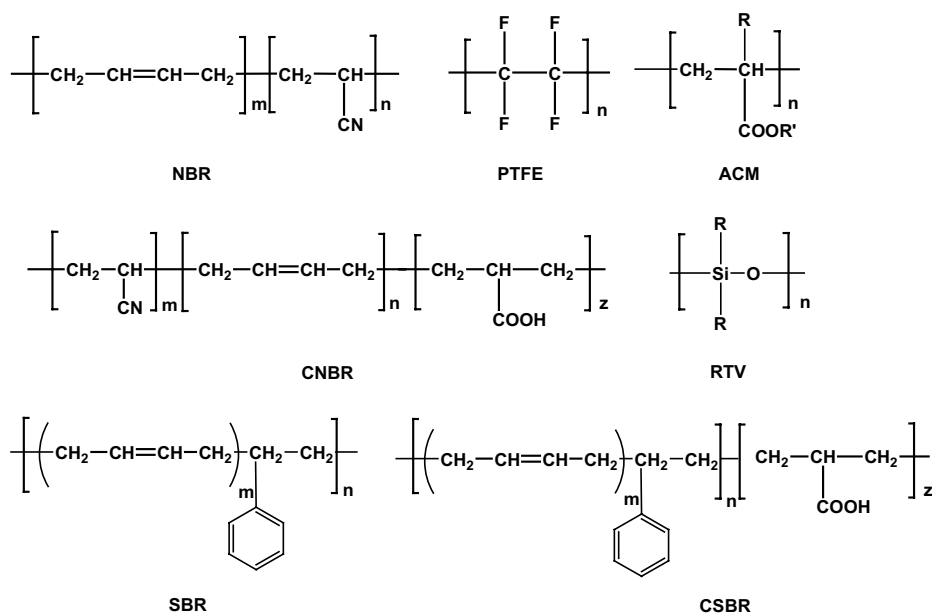
It is well-known that polymer bonded explosives (PBXs) contain approximately 5-10 wt.% polymeric binder, which is usually an amorphous polymer. However, in melt-cast explosives only 2 wt.% binders are required to

be used, since as a carrier TNT is fusible and can bind most of the other solid explosives. Recently, elastomeric nanoparticles were developed [22] and used in applications that require oil resistance, toughness and high abrasion resistance [23, 24]. The unique characteristics of elastomeric micro or ultrafine rubber have drawn much attention from other composite research areas. In energetic materials, only ultrafine metal particles have been used for improving the burning rate [25], whilst elastomeric micro or ultrafine rubber have not been investigated as fillers in energetic composites, as far as we are aware. In the present work, seven types of elastomeric rubber were chosen and incorporated into melt-cast energetic composites based on formulation CYCLOTOL-65/35 (RDX:TNT = 65:35 [wt.%]). Scanning electron microscopy (SEM) was used to understand the interfacial interactions. Tensile, compressive and shear tests were employed to characterize the mechanical properties, and the toughening mechanism was analyzed through SEM and the mechanical testing results. Finally, detonation and sensitivity performance are also discussed.

## 2 Experimental Section

### 2.1 Materials

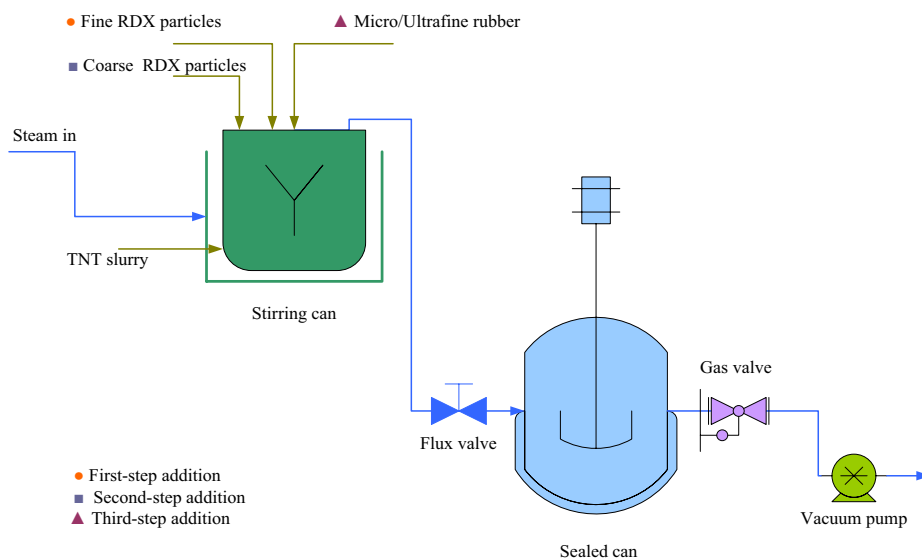
TNT (purity 99%, slabs) was provided by Liaoning Qingyang Chemical Industry Co., Ltd. RDX (purity 99%, fine crystals with particle size 20-45  $\mu\text{m}$ , and coarse crystals with particle size 245-350  $\mu\text{m}$ ) was supplied by Gansu Yinguang Chemical Industry Co., Ltd. UF-NBR, UF-CNBR, UF-SBR, UF-CSBR, UF-ACM, UF-RTV, all having a median particle size of approximately 100-200 nm, were manufactured by Beijing BHY Chemical Industry New Technology Co., China. PTFE-M, having an average particle size of approximately 5  $\mu\text{m}$ , was provided by Beijing Academy of Chemical Engineering. The molecular formulas of the binders are listed in Figure 1.



**Figure 1.** Molecular formulas of NBR, CNBR, SBR, CSBR, ACM, RTV and PTFE.

## 2.2 Specimen preparation

As shown in Figure 2, the TNT raw materials were first melted at 90-100 °C with steam in a jacketed vessel. Subsequently, RDX with fine and coarse particle sizes was consecutively added to the TNT slurry in two steps, and finally different types of elastomeric micro/ultrafine rubber were added. Maintaining the temperature at 90-100 °C, the mixtures were stirred until the RDX and elastomeric rubber had dispersed homogeneously in the molten TNT. The blends were subsequently subjected to vacuum (approximately 0.5 MPa) to remove air bubbles, and then poured into pre-heated moulds for curing at ambient temperature (1 h).



**Figure 2.** A schematic diagram of the process of specimen preparation.

### 2.3 Methods

The morphologies of the tensile fracture surface of the samples were examined by scanning electron microscopy (SEM; TM-1000, Hitachi, Japan) at an accelerating voltage of 12 kV. The prepared surfaces were coated with platinum/palladium in order to prevent charge build up on the specimen surfaces.  $T_g$  (glass-transition temperature) values were obtained from the Q200 DSC instrument at a heating rate of 5 K/min in flowing high purity nitrogen (99.99%, flow rate 50 mL/min), in the range of  $-200$  to  $200$  °C.

Tensile, compressive and shear tests were conducted at room temperature using a Universal Testing Machine (Instron® 5582, UK) following the Chinese Military Standard GJB772A-97 method [26]. The compression strength was determined at a crosshead speed of 0.50 mm/min with sample dimensions  $50 \times 50 \times 50$  mm ( $W \times L \times T$ ). The tensile strength, elongation at break, and tensile modulus of the samples were measured at a crosshead speed of 10 mm/min. The samples were hot moulded and shaped with a dumbbell-shaped cutter. The thickness and width of the specimens were 0.5 and 4 mm, respectively. The shear strength test was undertaken at a crosshead velocity of 10-11 mm/min with sample dimensions  $\Phi 20 \times 30$  mm. The loading direction was in accordance with the principal axis of the testing machine, and orthogonal with the medial axis of the sample.

Impact sensitivity was characterized by the drop hammer impact test, with

a hammer weight of 20 kg and a maximum height of 12 m. The sample was processed into the dimensions  $\Phi 20 \times 10$  mm. In the experiment, the drop hammer is located at the release set, which is elevated to the setting-up height. Then the hammer is released and hits the sample. Through the high-speed camera and the overtaking pressure characterization, the interval zone and probability of explosion can be recorded and analyzed, which can be further used for the test of sensitivity and safety. This method is appropriate for the safety characterization of melt-cast explosives and also other PBXs.

### 3 Results and Discussion

#### 3.1 Dispersion of elastomeric micro and ultrafine rubber in a melt-cast matrix

To choose proper elastomeric rubber for the modification experiments, particle size, glass transition temperature and dispersive ability were investigated. Seven types of polymer, including UF-NBR, UF-CNBR, PTFE-M, UF-SBR, UF-CSBR, UF-ACM and UF-RTV, were selected for dispersion experiments. In melt-cast explosives, there are several factors that need to be considered, such as viscosity and dispersive properties, which directly influence the physical properties.

It has to be noted from Table 1, only UF-NBR, UF-CNBR and PTFE-M are well dispersed in the RDX/TNT slurry. When the filler content was increased to 2 wt.%, the viscosity became slightly high, which indicates that they can be used for experiments without exceeding 2 wt.%. In addition, the low glass transition temperature ( $T_g$ ) of a binder is required in energetic composites because cooling below  $T_g$  would change the modulus of the energetic composites, and  $T_g$  is also related to the storage performance of explosives. According to this principle, UF-ACM cannot be selected since its  $T_g$  is close to ambient temperature. Table 1 also reveals that particle size does not influence the viscosity of a melt-cast slurry directly, which can be explained by the differences in molecular structure of the elastomeric rubber and the interfacial interaction between the explosives and the elastomeric rubber. Considering the dispersion and  $T_g$  of the binders, UF-NBR, UF-CNBR, and PTFE-M were chosen for further modification experiments.

**Table 1.** Characteristics and dispersion of different micro and ultrafine rubber in the RDX/TNT slurry

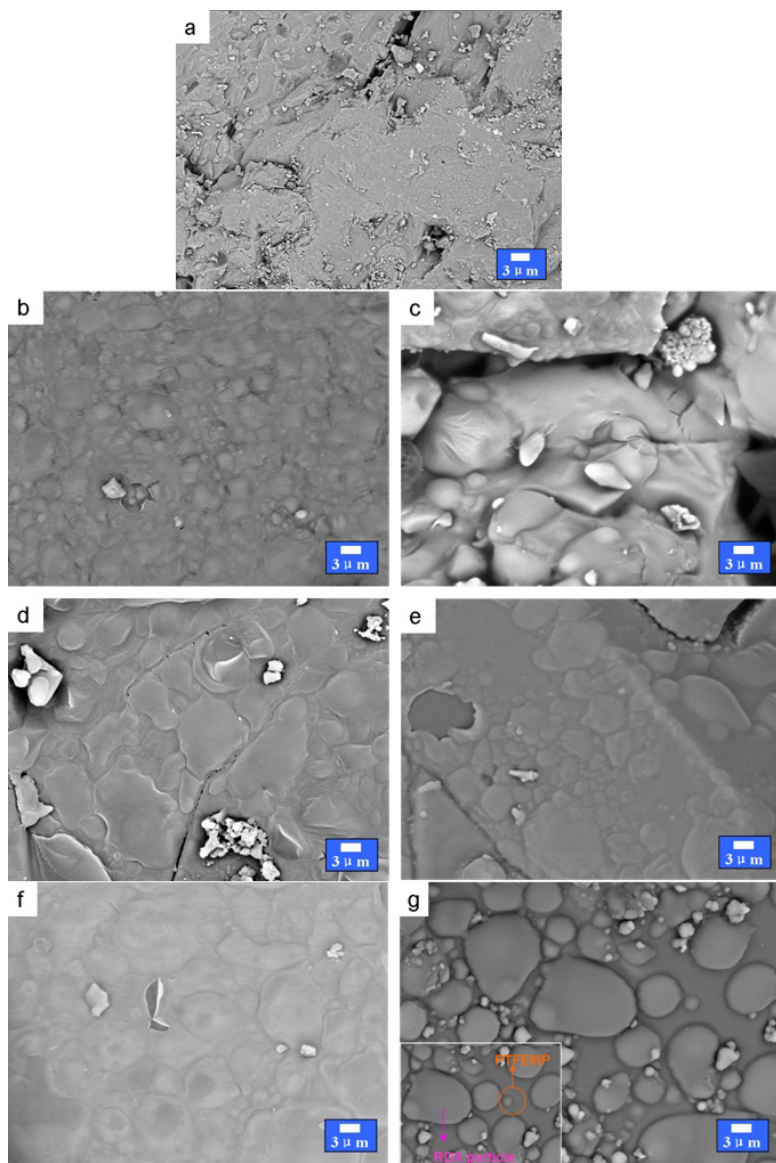
Type	T <sub>g</sub> [°C]	Average grain size [nm]	Filler content [%]	Phenomenon	
				Viscosity variation	Dispersion effect
UF-SBR	-25.37	100	0.6	obviously increased	agglomerating
UF-CSBR	-21.89	170	0.6	obviously increased	agglomerating
UF-ACM	22.42	130	0.6	obviously increased	agglomerating
UF-NBR	-33.00	170	0.6	not increased	homogeneous when curing
			2	slightly increased	
UF-CNBR	-25.99	90	0.6	not increased	homogeneous when curing
			2	slightly increased	
UF-RTV	-120.0	100	0.6	obviously increased	agglomerating
PTFE-M	-113.0	<5 μm	0.6	not increased	homogeneous when curing
			2	slightly increased	

### 3.2 Microstructure of the fractured surface of the unmodified and modified matrixes

To determine the toughening effect of elastomeric rubber in melt-cast explosives, SEM was employed to observe the fracture surface of the cast samples. Figure 3 shows the fractured surfaces of neat RDX/TNT, RDX/TNT/UF-NBR, RDX/TNT/UF-CNBR and RDX/TNT/PTFE-M. In the next part of this paper the following symbols and abbreviations are applied:

**CYCLTOTL-65/35:** 65/35 RDX/TNT; **CYCL-1:** 65/34/1 RDX/TNT/UF-NBR; **CYCL-2:** 65/33/2 RDX/TNT/UF-NBR; **CYCL-3:** 65/34/1 RDX/TNT/UF-CNBR; **CYCL-4:** 65/33/2 RDX/TNT/UF-CNBR; **CYCL-5:** 65/34/1 RDX/TNT/PTFE-M; **CYCL-6:** 65/33/2 RDX/TNT/PTFE-M.

It can be seen that neat RDX/TNT samples contain a lot of voids and cracks [27], which disappear after toughening with the elastomeric rubber. When filled with 2 wt.% PTFE-M, it was found that there are so many explosive crystals exposed that the explosive and polymer are clearly distinguishable. The SEM images also show that the ultrafine rubber disperses better than micro rubber. When micro rubber are introduced, there are some agglomerates, but the dispersion still remains homogeneous.



**Figure 3.** SEM photographs ( $\times 3000$ ) of the RDX/TNT fractured surface filled with various amounts of elastomeric micro/ultrafine rubber: (a) CYCLOTOL-65/35, (b) CYCL-1, (c) CYCL-2, (d) CYCL-3, (e) CYCL-4, (f) CYCL-5, (g) CYCL-6.



### 3.3 Compression and tension properties

Compression and tension properties are vital for blended explosives, determining whether they have the ability to resist external forces under the conditions of impact and distortion. In addition, enhancing the mechanical strength can prohibit the easy formation of stress concentrations under external forces. This may be related to safety performance in ammunitions, such as “hot spot” forming or accidental detonation [8].

Compressive and tensile strengths were measured based on Equation (1):

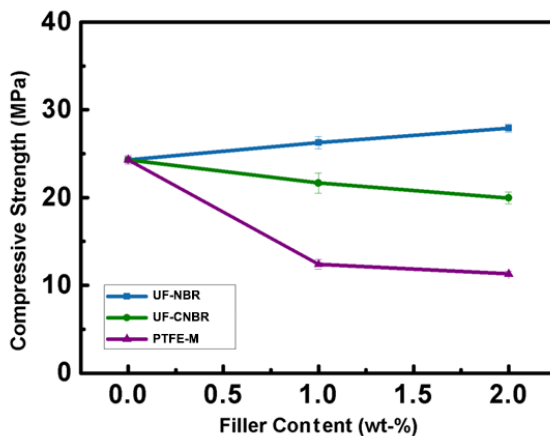
$$\sigma = \frac{F}{\frac{\pi}{4}d^2} \quad (1)$$

where  $\sigma$ ,  $F$ , and  $d$  represent the measured values of strength (Pa), maximum load applied (N), and diameter of initial cross section (m), respectively.

Standard deviation was determined as follows:

$$S = \sqrt{\frac{\sum_{i=1}^n (\sigma_i - \bar{\sigma})^2}{n-1}} \quad (2)$$

where  $S$  and  $n$  is the standard deviation and specimen number, respectively.



**Figure 4.** Effect of filler content on compressive strength. Error bars indicate the standard deviations of the mean values.

The relations between compressive strength and the filler content are shown in Figure 4, and the effects of the elastomeric rubber on the compressive properties are summarized in Table 2. The formulation filled with UF-NBR shows higher strength than those with added UF-CNBR or PTFE-M. The compressive strength of CYCL-1 and CYCL-2 are 26.26 and 27.90 GPa respectively, which are 8-15% higher than the original formulation CYCLOTOL-65/35. This result can be explained by the interfacial interaction between UF-NBR and the explosive particles being stronger than with the other two additives. However, the addition of PTFE-M leads to a reduction of both in compressive strength. These unexpected results may be attributed to PTFE-M aggregation occurring in the melt-cast process because of its relatively large grain size. That is to say, with smaller grain sizes, elastomeric rubber may enhance the toughening effect in the modification of melt-cast explosives.

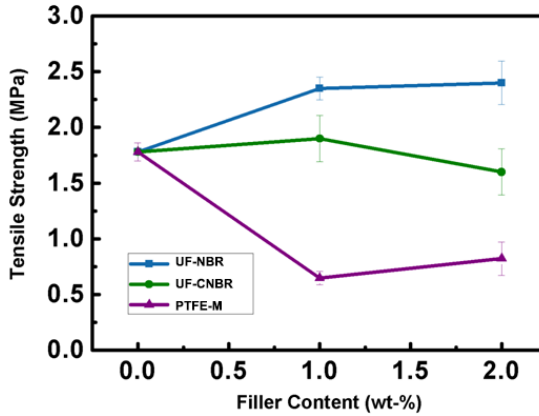
The highest enhancement in compressive strength with CYCL-2 was obtained with the addition of UF-NBR at 2.0 wt.%. However, the three types of elastomeric rubber do not contribute to an increase in compressive modulus, which means that their Young's modulus is much lower than that of RDX and TNT explosives, since most polymers usually exhibit a low modulus. The grain size and molecular structure of the elastomeric rubber have a massive effect on the mechanical properties. The modification results from the three types of elastomeric rubber indicate that large grain size may decrease the mechanical properties.

**Table 2.** Mean values of mechanical properties for unmodified and modified melt-cast formulations under compressive testing

Samples	$\sigma_c$ , [MPa]	$E_c$ , [GPa]	$\epsilon_c$ , [%]	$W_c$ , [J]
CYCLOTOL-65/35	24.31	9.795	0.346	0.2464
CYCL-1	26.26	9.770	0.360	0.2621
CYCL-2	27.90	9.464	0.354	0.2649
CYCL-3	21.66	9.449	0.385	0.2558
CYCL-4	19.96	8.379	0.348	0.1944
CYCL-5	12.39	6.033	0.303	0.1082
CYCL-6	11.30	6.161	0.278	0.1048

Figure 5 shows the relationships between filler content and the tensile mechanical properties, and Table 3 summarizes the effects of elastomeric rubber on the tensile strength ( $\sigma_t$ ) together with elongation at break ( $\Delta L/L$ ) and tensile modulus ( $E_t$ ). It can be seen that CYCL-1 and CYCL-2, toughened with UF-NBR, have higher tensile strengths. The toughness occurs in the order: UF-

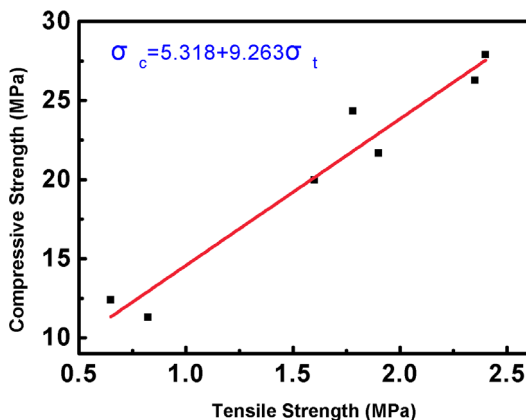
NBR > UF-CNBR > PTFE-M. The pattern in tensile properties is consistent with compressive strength.



**Figure 5.** Effect of filler content on tensile strength. Error bars indicate the standard deviations of the mean values.

**Table 3.** Mean values of mechanical properties for unmodified and modified melt-cast formulations under tensile testing

Samples	$\sigma_t$ , [MPa]	$\Delta L/L$ , [%]	$W_t$ , [mJ]	$E_t$ , [GPa]
CYCLTOL-65/35	1.78	0.0300	0.8060	6.86
CYCL-1	2.35	0.0359	1.2140	6.94
CYCL-2	2.53	0.0360	1.0920	7.39
CYCL-3	1.90	0.0251	0.6992	7.77
CYCL-4	1.60	0.0242	0.5670	6.74
CYCL-5	0.649	0.0330	0.4214	5.04
CYCL-6	0.823	0.0227	0.3190	5.83



**Figure 6.** Correlations between  $\sigma_t$  and  $\sigma_c$  mechanical parameters for melt-cast energetic composites.

In addition, Figure 6 reveals that an elevated linear correlation exists between compressive and tensile strength for the modified formulations. This relation is represented by the following equation:

$$\sigma_c = 5.318 + 9.263\sigma_t \quad (3)$$

where  $\sigma_t$  and  $\sigma_c$  stand for compressive and tensile strength, respectively. The results also indicate that melt-cast explosives toughened by elastomeric rubber may have good compressive strength whilst simultaneously exhibiting high tensile strength.

### 3.4 Shear strength

For melt-cast blended explosives, the shear strength is a significant parameter for designing the dimensions and manufacture of the ammunitions, and determines the characteristics of facile shaping and moulding, so as to satisfy different designs for missiles and munitions.

The shear strength was measured by using Equation (4):

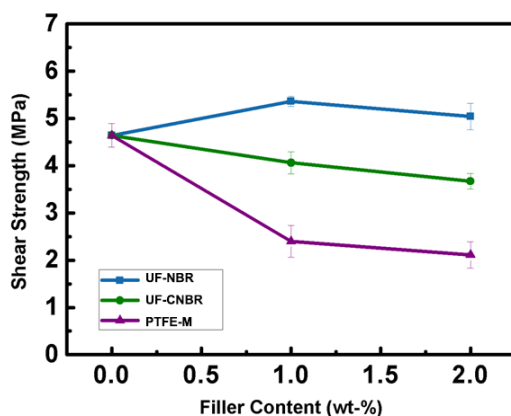
$$\tau = \frac{F_{\max}}{2A_0} \times 10^{-6} \quad (4)$$

where  $\tau$  (MPa) is the measured value of the shear strength,  $F_{\max}$  (N) is the maximum shear load applied when the sample fractures and fails,  $A_0$  (m<sup>2</sup>) is the cross section.

The standard deviation was determined as follows:

$$S = \sqrt{\frac{\sum_{i=1}^n (\tau_i - \bar{\tau})^2}{n-1}} \quad (5)$$

where  $S$  and  $n$  represents the standard deviation and specimen number, respectively.



**Figure 7.** Effect of filler content on shear strength. Error bars indicate the standard deviations of the mean values.

Figure 7 depicts the trend of shear strength with different binders and their amount. It is clear that CYCL-1 with 1 wt.% UF-NBR has the higher shear strength, and CYCL-2 with 2 wt.% UF-NBR is also better than the unmodified formulation.

### 3.5 Toughening mechanism

To gain insight into the toughening mechanism of TNT-based melt-cast explosives, the morphologies and mechanics analysis were employed to understand the experimental phenomena. SEM photographs of fractured surfaces revealed that the voids caused by the TNT shrinking effect gradually decrease after incorporating the elastomeric rubber, with RDX and TNT explosive particles closely integrated. This result can be attributed to stronger interfacial interactions, because the large contact-area of elastomeric micro or ultrafine rubber enhances the intermolecular interaction with fine crystalline RDX and TNT. Due to the complex interactions between each of the constituents and explosive molecules,

the interfacial adhesion between the matrix and multi-scale elastomeric rubber is enhanced by the ultrafine rubber, especially UF-NBR, thereby resulting in the observation of the surrounding ultrafine rubber combined, tightly and homogeneously, in fracture surfaces. Owing to the improved interactions, enhancements in modulus and strength are also observed in composites containing UF-NBR, due to their robust mechanical properties allowing for improved stress transfer between load-bearing ultrafine rubber. Tensile and impressive strength in the composites are enhanced without reducing the strain to failure, and the shear strength is increased by 20-35% on addition of UF-NBR.

Fracture toughness ( $K_{IC}$ ) can be used for determining the toughness of materials. For energetic composites, it is difficult to machine a three-point bending specimen since brittle materials such as melt-cast explosives have low strength. Kuruppu and Chond [28, 29] first demonstrated that fracture toughness of brittle materials could be tested by using semi-circular bend (SCB) specimens. Chen *et al.* [30] used an SCB method to determine the fracture toughness ( $K_{IC}$ ) of mixed explosives, which required that the tested samples should be critically processed to certain dimensions. Recently, we found that fracture energy had a good correlation with fracture toughness through testing results on blended explosives, which may simplify the determination of toughness. Meanwhile, testing and analyzing the fracture energy was also revealed to be an easy and effective way to obtain the micromechanical properties of high energy explosives [31] and even to estimate the fracture toughness of energetic composites, especially for energetic composites with lower strength such as melt-cast explosives. Fracture energy ( $W$ ) is an integral calculated from the proportion between the highest value of stress and its corresponding strain surrounding the curves, which is defined as:

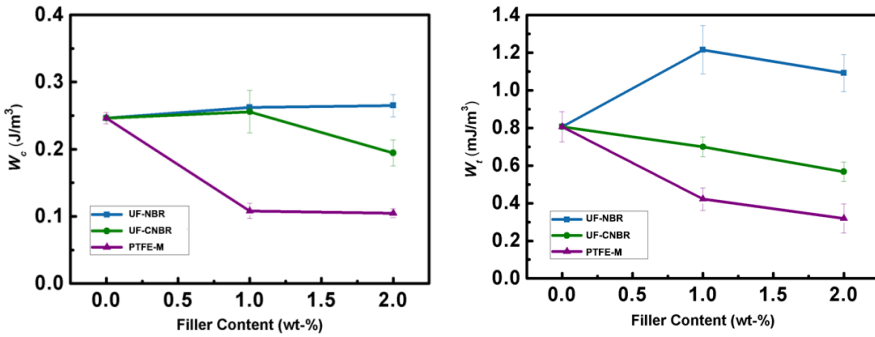
$$W_t = \int_0^{\varepsilon_b} \sigma_t(\varepsilon) d\varepsilon \quad (6)$$

$$W_c = \int_0^{\varepsilon_b} \sigma_c(\varepsilon) d\varepsilon \quad (7)$$

where  $W_t$  and  $W_c$  are the fracture energies under the tension and compression tests, respectively.  $\varepsilon$ ,  $\sigma_t$ ,  $\sigma_c$  separately represent the values of strain, stress under tension and compression.

Here, we intend to use the fracture energy ( $W$ ) to predict the toughness of melt-cast explosives. Fracture energy curves from compression and tension tests are shown in Figure 8. It may be noted that UF-NBR has a better effect on improving the toughness of the melt-cast explosives, but formulations filled with

the other two types of elastomeric rubber are worse. Meanwhile, with 1 wt.% UF-NBR filler content, the toughness of composites can be increased by 50%, indicating that the elastomeric ultrafine rubber can enhance their intermolecular interaction with explosives. The fracture energy of melt-cast composite explosives determines the characteristic of toughness. According to Figure 9,  $W_c$  and  $W_t$  of UF-NBR are not only higher than is the case for UF-CNBR and PTFE-M, but also exceed the unmodified melt-cast explosives.



**Figure 8.** Fracture energy of unmodified/modified melt-cast formulations under compressive and tensile testing, respectively. Error bars indicate the standard deviations of the mean values.

### 3.6 Detonation properties

Density ( $\rho$ ), the heat of explosion ( $Q$ ), detonation velocity ( $D$ ), and detonation pressure ( $P$ ) are very important factors used to evaluate the performance of energetic materials. Many theoretical methods have been used to predict the detonation properties, such as the Kamlet-Jacobs equations [32] and the  $\omega$ - $\Gamma$  method [33]. In this work, the  $\omega$ - $\Gamma$  method was chosen for the calculations since it is more suitable for both mono and blended explosives, which were also compared with the results determined by EXPLO5 [34]. The heat of explosion ( $Q$ , J/g), detonation velocity ( $D$ , m/s), and detonation pressure ( $P$ , GPa) are defined as follows:

$$Q = \frac{\Delta H_f - \sum n_i \Delta H_i}{M} \quad (8)$$

$$D = 33.05Q^{1/2} + 243.2\omega\rho \quad (9)$$

$$P = \frac{\rho D^2 \times 10^{-6}}{\Gamma + 1} \quad (10)$$

where  $\Delta H_f$ ,  $n_i$ ,  $\Delta H_i$  and  $M$  represent the heat of formation (J/mol) of the explosive, the quantity of the  $i$ th detonation product (mol) and the heat of formation of the  $i$ th detonation product, and the molecular weight of the explosive (g/mol), respectively;  $\omega$ ,  $\rho$  and  $\Gamma$  are individually the potential energy factor, the density of the explosive (g/cm<sup>3</sup>), and the adiabatic exponent. Based on the simplification of the C-J (Chapman-Jouguet) theory of detonation waves and  $D$  derived from Equation (9), the detonation pressure ( $P$ , GPa) can be simplified as follows:

$$P = \frac{1}{4} \rho D^2 \times 10^{-6} \quad (11)$$

**Table 4.** Predicted detonation performances of unmodified and modified energetic composites

Name	Composition <sup>a</sup>	$\rho$ , [g/cm <sup>3</sup> ] <sup>b</sup>	P, [GPa]	Q, [J/g]	D, [m/s]
CYCLO-TOL-65/35	C <sub>1.96</sub> H <sub>2.53</sub> N <sub>2.22</sub> O <sub>2.68</sub>	1.72 <sup>c</sup> (1.74) <sup>d</sup>	27.73 <sup>c</sup> (29.10) <sup>d</sup>	5262.8 <sup>c</sup> (5563.0) <sup>d</sup>	8031 <sup>c</sup> (8241) <sup>d</sup>
CYCL-1	C <sub>1.99</sub> H <sub>2.59</sub> N <sub>2.22</sub> O <sub>2.66</sub>	1.71 <sup>c</sup> (1.72) <sup>d</sup>	27.38 <sup>c</sup> (28.41) <sup>d</sup>	5231.4 <sup>c</sup> (5550.8) <sup>d</sup>	8003 <sup>c</sup> (8187) <sup>d</sup>
CYCL-2	C <sub>2.03</sub> H <sub>2.65</sub> N <sub>2.21</sub> O <sub>2.63</sub>	1.69 <sup>c</sup> (1.71) <sup>d</sup>	26.65 <sup>c</sup> (27.83) <sup>d</sup>	5200.0 <sup>c</sup> (5538.7) <sup>d</sup>	7942 <sup>c</sup> (8133) <sup>d</sup>
CYCL-3	C <sub>1.98</sub> H <sub>2.58</sub> N <sub>2.21</sub> O <sub>2.67</sub>	1.71 <sup>c</sup> (1.72) <sup>d</sup>	27.26 <sup>c</sup> (28.44) <sup>d</sup>	5202.7 <sup>c</sup> (5563.2) <sup>d</sup>	7986 <sup>c</sup> (8192) <sup>d</sup>
CYCL-4	C <sub>2.01</sub> H <sub>2.63</sub> N <sub>2.20</sub> O <sub>2.65</sub>	1.69 <sup>c</sup> (1.71) <sup>d</sup>	26.43 <sup>c</sup> (27.93) <sup>d</sup>	5142.5 <sup>c</sup> (5563.8) <sup>d</sup>	7909 <sup>c</sup> (8147) <sup>d</sup>
CYCL-5	C <sub>1.95</sub> H <sub>2.51</sub> N <sub>2.21</sub> O <sub>2.66</sub> F <sub>0.04</sub>	1.73 <sup>c</sup> (1.74) <sup>d</sup>	27.97 <sup>c</sup> (29.48) <sup>d</sup>	5240.8 <sup>c</sup> (5524.3) <sup>d</sup>	8042 <sup>c</sup> (8255) <sup>d</sup>
CYCL-6	C <sub>1.94</sub> H <sub>2.48</sub> N <sub>2.19</sub> O <sub>2.63</sub> F <sub>0.08</sub>	1.73 <sup>c</sup> (1.74) <sup>d</sup>	27.82 <sup>c</sup> (29.89) <sup>d</sup>	5218.9 <sup>c</sup> (5481.6) <sup>d</sup>	8020 <sup>c</sup> (8258) <sup>d</sup>

Note: <sup>a</sup> Glossary of compounds for composite explosives based on 100 g for mixtures of different compounds; <sup>b</sup> Theoretical Maximum Density (TMD); <sup>c</sup> Values were calculated using  $\omega$ - $\Gamma$  method; <sup>d</sup> Values were calculated using the software EXPLO5 (v.6.01) [34].

Table 4 shows the predicted detonation properties of unmodified and modified energetic composites. It may be noted that the detonation velocity ( $D$ ) and detonation pressure ( $P$ ) are mainly determined by the density ( $\rho$ ), heat of explosion ( $Q$ ) and the factor of thermal energy ( $\omega$ ) of the explosives. The theoretical densities of UF-NBR, UF-CNBR and PTFE-M are 0.92, 0.90 and 2.15 g/cm<sup>3</sup>, respectively. Since the modifiers do not contain energetic units in their structures, this means that with W% increasing, the  $Q$  and  $\omega$  of the modified composites will decrease. Compared with the experimental values for CYCLOTOL-65/35 ( $\rho = 1.714$  g/cm<sup>3</sup>,  $D = 7967$  m/s,  $P = 28.6$  GPa [35]), the theoretical results from the  $\omega$ - $\Gamma$  method are closer to the experimental data. The results determined by EXPLO5.0 are slightly higher than the values from the  $\omega$ - $\Gamma$  method, except that the detonation pressure calculated from EXPLO5.0 is closer to the test results than that from the

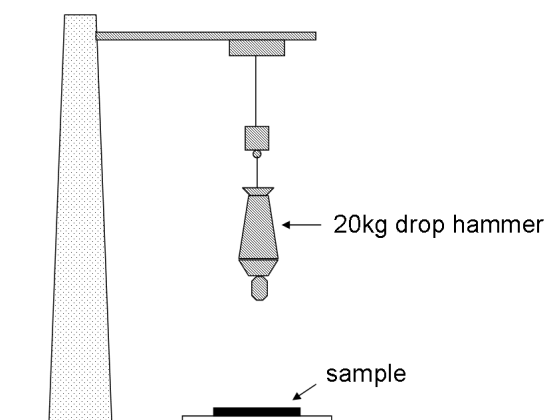


$\omega$ - $\Gamma$  method. EXPLO5.0 is based on the Becker-Kistiakowsky-Wilson (BKW) equation, which is more suitable for monoexplosives than blended explosives.

Theoretically, the density of the binder is an important parameter for determining the detonation properties of energetic composites. Nevertheless, for melt-cast explosives this influence is weak, since the amount of additive is 2 wt.% or less. According to results calculated by the BKW equations, the detonation properties of melt-cast explosives modified by UF-NBR and UF-CNBR, with densities of 0.9-0.92 g/cm<sup>3</sup>, decrease less than with PTFE-M, which has a higher density of 2.15 g/cm<sup>3</sup>. From the results calculated by the  $\omega$ - $\Gamma$  method,  $D$  has the following order: CYCL-5 > CYCLOTOL-65/35 > CYCL-6 > CYCL-1 > CYCL-3 > CYCL-2 > CYCL-4, whilst the order of  $P_{CJ}$  is: CYCL-5 > CYCL-6 > CYCLOTOL-65/35 > CYCL-1 > CYCL-3 > CYCL-2 > CYCL-4.

### 3.7. Impact sensitivity

Since the common sensitivity characterization methods for explosive particles cannot be applied for testing molten explosive cylinders, the improved drop hammer impact test was used. A schematic configuration is shown in Figure 9. Based on the modification effects and influences of the filler content on the test results, we finally selected two samples containing different types of ultrafine rubber (CYCL-2 and CYCL-4) for sensitivity characterization. As shown in Table 5, the explosion threshold interval of CYCL-2 is between 8.6 and 9.8 J (close to that of CYCLOTOL-65/35 [36] and *N*-methyl-*N*,2,4,6-tetranitroaniline (Tetryl) [37]), whilst the range for CYCL-4 is from 14.7 to 15.9 J, meaning that CYCL-2 has a higher impact sensitivity than CYCL-4.



**Figure 9.** Schematic configuration of the Drop Hammer Test for the explosive cylinder.

**Table 5.** Drop hammer impact test results

Impact sensitivity [J]*	24.5	17.2	15.9	14.7	9.8	8.6	7.4	4.9
CYCL-2	reaction	–	–	reaction (19.9)*	reaction	no	no	no
CYCL-4	reaction (24.1)**	reaction	reaction (22.9)**	no	no	–	–	–
CYCLO-TOL-65/35 [36]	–	–	–	reaction	reaction	no	no	no
Tetryl [37]	–	reaction	reaction	reaction	reaction	no	no	no

\* For 20 kg drop hammer test, the conversion of drop-height (H, in meters) into impact-energy (E, in Joules), according to equation  $E = m \cdot H \cdot g$ , where m is the mass of the drop hammer in kg and g is the gravity acceleration in  $m/s^2$ , is not suitable. In this article, we used the following expression for convenient comparison: 24.5 J=8 m, 17.2 J=7 m, 15.9 J=6.5 m, 14.7 J=6 m, 9.8 J=4 m, 8.6 J=3.5 m, 7.4 J=3 m, 4.9 J=2 m, respectively;

\*\* The data in the parenthesis are the overtaking pressure during shock wave impact, kPa.

## 4 Conclusions

Incorporating proper elastomeric materials is an effective way of modifying some important mechanical properties and impact sensitivity of molten TNT-based energetic composites. In the selection of elastomeric micro and ultrafine rubber for modification, seven types of polymer were chosen for dispersion experiment, which turned out that only UF-NBR, UF-CNBR and PTFE-M were well dispersed in the RDX and TNT slurry. This study also demonstrates that elastomeric micro and ultrafine rubber could be used as binders in melt-cast explosives, especially elastomeric ultrafine particles of UF-NBR and UF-CNBR, which have a better toughening effect. SEM images of fractured surfaces show that the elastomeric additives can fill most of the voids in RDX/TNT without producing tremendous agglomeration.

When UF-NBR was used in melt-cast energetic composites, the compressive strength was enhanced by 8-15%, and the tensile strength was increased by 32-42%. With the appropriate density and grain size distribution, the toughening effect of UF-CNBR, with its introduced carboxyl group, becomes worse than with UF-NBR. The drop hammer test indicates that with the same additive amount of 2 wt.%, the modified formulation with UF-NBR is more insensitive than that with UF-CNBR. The calculated detonation properties show that

though the additives are inert binders, the modified composites are close to the original formulations in terms of sensitivity, almost without sacrificing energy. A improved drop hammer test for explosive cylinder was used for the impact sensitivity evaluation of CYCL-2 and CYCL-4, which showed that CYCL-4 (14.7-15.9 J) was more insensitive than CYCL-2 (8.6-9.8 J).

These findings also suggest that the toughness of TNT-based melt-cast explosives have a strong dependence on their fracture energies  $W_f$  and  $W_c$ . For melt-cast explosives, the fracture energy would be the proper parameter for estimating the fracture toughness, and also helps to explain the toughening mechanism.

## Acknowledgments

This investigation received financial assistance from the Foundation of National Natural Science Foundation of China and China Academy of Engineering Physics (NSAF, Grant No.11076002), and the National Natural Science Foundation of China (NSFC, Grant Nos.51373159 and 11402237). All of the authors wish to repeat their thanks to Chuanlan He for the mechanical testing and Wen Wen for the drop hammer impact testing.

## 5 References

- [1] Elbeih A., Zeman S., Jungova M., Akstein Z., Effect of Different Polymeric Matrices on the Sensitivity and Performance of Interesting Cyclic Nitramines, *Cent. Eur. J. Energ. Mat.*, **2012**, 9(2), 131-138.
- [2] Elbeih A., Zeman S., Characteristics of Melt Cast Compositions Based on Cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5d]imidazole (BCHMX)/TNT, *Cent. Eur. J. Energ. Mat.*, **2014**, 11(4), 501-513.
- [3] Janssen J.W.A.M., Koeners H.J., Kruse C.G., Habraken C.L., Pyrazoles. XII. The Preparation of 3(5)-Nitropyrazoles by Thermal Rearrangement of *N*-Nitropyrazoles, *J. Org. Chem.*, **1978**, 38, 1777-1782.
- [4] Trzciński W.A., Cudziło S., Dyjak S., Nita M., A Comparison of the Sensitivity and Performance Characteristics of Melt-pour Explosives with TNT and DNAN Binder, *Cent. Eur. J. Energ. Mat.*, **2014**, 11(3), 443-455.
- [5] Watt D.S., Cliff M.D., *Evaluation of 1,3,3-Trinitroazetidine (TNAZ)-A High Performance Melt-castable Explosive*, DSTO-TR-1000, **2000**.
- [6] Zhao F., Chen P., Hu R., Luo Y., Zhang Z., Zhou Y., Yang X., Gao Y., Gao S., Shi Q., Thermochemical Properties and Non-isothermal Decomposition Reaction Kinetics of 3,4-Dinitrofurazanfuroxan (DNTF), *J. Hazard. Mater.*, **2004**, A113, 67-71.
- [7] Singh S., Damavarapu R., Surapaneni R., Samuel P., An Insensitive Melt-cast

- Energetic Material: 1-Methyl-2,4,5-trinitroimidazole: MTNI, *38th Int. Annu. Conf. ICT*, Karlsruhe, Germany, **2007**, 147.
- [8] Ma Q., Shu Y.J., Luo G., Chen L., Zheng B., Li H., Toughening and Elasticizing Route of TNT Based Melt-cast Explosives, *Chin. J. Energ. Mater.*, **2012**, 20(5), 618-629.
- [9] Ravi P., Badgajar D.M., Gore G.M., Tewari S.P., Sikder A.K., Review on Melt Cast Explosives. *Propellants Explos. Pyrotech.*, **2011**, 36, 393-403.
- [10] Voigt H.W., *Castable Explosive Containing TNT and a Reaction Product of a Diisocyanate and 1,4-Butyleneoxide Polyglycol*, US Patent 3,447,980, **2008**.
- [11] Voigt, H.W., Pell L.W., *TNT Composition Containing Cellulosic Resin which is Free from Oily Exudation upon Storage*, US Patent 3,706,609, **1972**.
- [12] Voigt H.W., Pell L.W., Picard J.P., *Cast TNT Explosive Containing Polyurethane Elastomer which is Free from Oily Exudation and Voids and Uniformly Remeltable*, US Patent 4,012,245, **1977**.
- [13] Voigt H.W., *Castable TNT Compositions Containing a Broad Spectrum Preformed Thermoplastic Polyurethane Elastomer Additive*, US Patent 4,284,442, **1981**.
- [14] Voigt H.W., Banker B.R., *Preparation of TNT-thermoplastic Polymer Granules Readily Soluble in a TNT Melt*, US Patent 4,325,759, **1982**.
- [15] Johnson N.C., Gill R.C., Leahy J.F., Gotzmer C., Fillman H.T., *Melt Cast Thermoplastic Elastomeric Plastic Bonded Explosive*, US Patent 4,978,482, **1990**.
- [16] Ampleman G., Brousseau P., Thiboutot S., Dubois C., Diaz E., *Insensitive Melt Cast Explosive Compositions Containing Energetic Thermoplastic Elastomers*, US Patent 6,562,159, **2003**.
- [17] Ampleman G., Brousseau P., Thiboutot S., Rocheleau S., Monteil-Rivera F., Radovic- Hrapovic Z., Hawari J., Sunahara G., Martel R., Coté S., Brochu S., Trudel S., Beland P., Marois A., Evaluation of GIM as Greener Insensitive Melt-cast Explosive, *Int. J. Energ. Mater. Chem. Prop.*, **2012**, 11, 59-87.
- [18] Parry M.A., Thorpe B.W., *Nucleation and Growth of TNT Containing HNS*, ADA057224, **1978**.
- [19] Parry M.A., Thorpe B.W., *The Effective Nucleant During the Grain Modification of TNT with HNS*, ADA076435, **1979**.
- [20] Trevino S.F., Portnoy S., *Effects of HNS on Cast TNT*, ADA077111, **1979**.
- [21] Portnoy S., *Production of Fine-grained Cast Charges with Unoriented Crystal Structure of TNT or Explosive Compositions Containing TNT*, US Patent 4,360,394, **1982**.
- [22] Huang F., Liu Y., Zhang X., Wei G., Gao J., Song Z., Zhang M., Qiao J., Effect of Elastomeric Nanoparticles on Toughness and Heat Resistance of Epoxy Resins, *Macromol. Rapid Commun.*, **2002**, 23, 786-790.
- [23] Saleesung T., Saeoui P., Sirisinha C., Mechanical and Thermal Properties of Thermoplastic Elastomer Based on Low Density Polyethylene and Ultra-fine Fully-vulcanized Acrylonitrile Butadiene Rubber Powder (UFNBRP), *Polym. Test.*, **2010**, 29, 977-983.
- [24] Sae-oui P., Sirisinha C., Intiya W., Thaptong P., Properties of Natural Rubber Filled

- with Ultrafine Carboxylic Acrylonitrile Butadiene Rubber Powder, *Adv. Polym. Tech.*, **2011**, 30(3), 183-190.
- [25] Ivanov Y.F., Osmonoliev M.N., Sedoi V.S., Productions of Ultra-fine Particles and their Use in High Energetic Compositions, *Propellants Explos. Pyrotech.*, **2003**, 28, 319-332.
- [26] National Military Standard of China, *Experimental Methods of Sensitivity and Safety*, GJB/772A-97, **1997**.
- [27] Lanzerotti Y.D., Sharma J., Armstrong R.W., Atomic Force Microscopy Studies of Fracture Surfaces of Composition B Energetic Materials, *Metall. Mater. Trans. A*, **2004**, 35A, 2675-2679.
- [28] Chong K.P., Kuruppu M.D., New Specimen for Fracture Toughness Determination for Rock and Other Materials, *Int. J. Fracture*, **1984**, 26, 59-62.
- [29] Kuruppu M.D., Chong K.P., Fracture Toughness Testing of Brittle Materials Using Semi-circular Bend (SCB) Specimen, *Eng. Fracture Mech.*, **2012**, 91, 133-150.
- [30] Chen P., Zhou Z., Ma S., Ma Q., Huang F., Measurement of Dynamic Fracture Toughness and Failure Behavior for Explosive Mock Materials, *Front. Mech. Eng.*, **2011**, 6, 292-295.
- [31] Hudson, R.J., Zioupos P., Gill P.P., Investigating the Mechanical Properties of RDX Crystals Using Nano-indentation, *Propellants Explos. Pyrotech.*, **2012**, 37, 191-197.
- [32] Kamlet M.J., Jacobs S.J., Chemistry of Detonations. I. Simple Method for Calculating Detonation Properties of C-H-N-O Explosives, *J. Chem. Phys.*, **1968**, 48, 23-35.
- [33] Wu X., Simple Method for Calculating Detonation Parameters of Explosives, *J. Energ. Mater.*, **1985**, 3, 263-277.
- [34] Sućeska M., EXPLO5, version 6.01, **2013**.
- [35] Hobbs M.L., Baer M.R., Calibrating the BKW-EOS with a Large Product Species Database and Measured C-J Properties, *Proc. Tenth Symp. (Int.) on Detonation*, Boston, MA, **1993**.
- [36] Liao J., Dai X., Huang Q., Wen Y., Xiang Y., Reaction Characteristic for Composition B in Drop Hammer Impact Sensitivity Test (in Chinese), *Chin. J. Explos. Propellants (Huozhayao Xuebao)*, **2013**, 36, 52-54.
- [37] Dai X., Xiang Y., Shen C., Study of Drop Hammer Impact Sensitivity for Big-pill Explosives (in Chinese), *Explosion and Shock Waves*, **2006**, 26, 381-384.

