Research paper

Determination of the Mechanical and Thermal Properties, and Impact Sensitivity of Pressed HMX-based PBX

Yuxiang Li, Peng Wu, Cheng Hua, Jun Wang, **Bing Huang**, **Jin Chen, Zhiqiang Qiao, Guangcheng Yang***

Institute of Chemical Materials, China Academy of Engineering Physics, 64 Mianshan Road, *Mianyang, Sichuan, P. R. China*
*E-mail: ygcheng@caep.ac.cn

Abstract: Submicron- and nano-explosives have attracted growing attention, while the mechanism of how particle size influences the impact sensitivity is not completely understood. In the present work, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) based PBXs (plastic bonded explosives) of three particle size distributions (1-2 and 10-20 μm, and 100-300 nm) and two pressed densities (91%TMD and 79%TMD) were characterized and tested with a range of techniques to determine their mechanical and thermal properties and impact sensitivities. The results demonstrated that with decreased particle size, the mechanical strength as well as the thermal conductivity were dramatically improved, and the impact sensitivity was significant decreased. The structure of impacted samples suggested that the ignition mechanism is dependant on the particle size. Samples with higher density were more sensitive to impact, as the impact force acting on these samples was higher. The correlation between particle size and impact sensitivity is discussed in detail.

Keywords: nano-explosives, impact sensitivity, particle size, hot-spot

Nomenclature:
TMD Theoretical maximum density
Φ   Diameter [mm]

1   Introduction

There are increasing demands for reducing the sensitivity of explosives in order to minimize the risk of accidental detonation caused by unintentional impact or shock. The common method for desensitizing high explosives (*e.g.* RDX, HMX and CL-20) is by coating them with additives such as wax, graphite or polymer, which will, however, lower the energy density. So a real challenge is to reduce the sensitivity meanwhile maintaining or enhancing the explosive performance.

Submicron- and nano-explosives have attracted growing attention over the past decade due to their improved sensitivity, combustion and detonation performances [1-3]. Considerable efforts have been made worldwide on reducing the particle size of common explosives and a number of studies have found that submicron- and nano-explosives have much lower impact sensitivity when compared with conventional explosives [4-9]. However, some studies have presented opposing results, showing that reducing the particle size increases the impact sensitivity [10-14]. The uncertainty in the bulk density of loose powder samples used in the standard impact sensitivity test was assumed to account for this inconsistency [15]. Without a fixed bulk density, the micro-structure as well as the physical properties of the tested samples might vary over a wide range and lead to inaccuracies in the test results.

In previous publications, the effect of reducing the particle size on the impact sensitivity was generally explained to be a consequence of the smaller void size among the explosive particles. According to hot-spot theory [16], ignition of explosives under impact stimuli is substantially a mechanical-thermal-chemical process [17]. Through interaction between the stress wave and inhomogeneities in the explosives such as voids and cracks, mechanical work done on explosives converges at localized regions and is converted to thermal energy, which produces hot-spots with high temperatures and leads to decomposition, deflagration, and detonation. However, these physical-chemical properties associated with impact sensitivity might change significantly when the particle size is reduced down to the nano-scale, and has not been systematically studied yet.

The aim of the presented work was to determine any correlation of particle size with mechanical and thermal properties as well as impact sensitivity, and thus obtain a deeper understanding of how particle size influences impact sensitivity. In this work, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) based PBXs (plastic bonded explosives) of three particle size distributions and two pressed densities were characterized and tested *via* a variety of techniques, including SEM (scanning electron microscopy), quasi-static compression tests, thermal conductivity measurements, DSC (differential scanning calorimetry), and

fall hammer tests. The force acting on the samples during impact was recorded by a piezoelectric force sensor in a self-designed apparatus. The relationship between particle size and mechanical-thermal properties, and their influences on the impact sensitivity are discussed in detail.
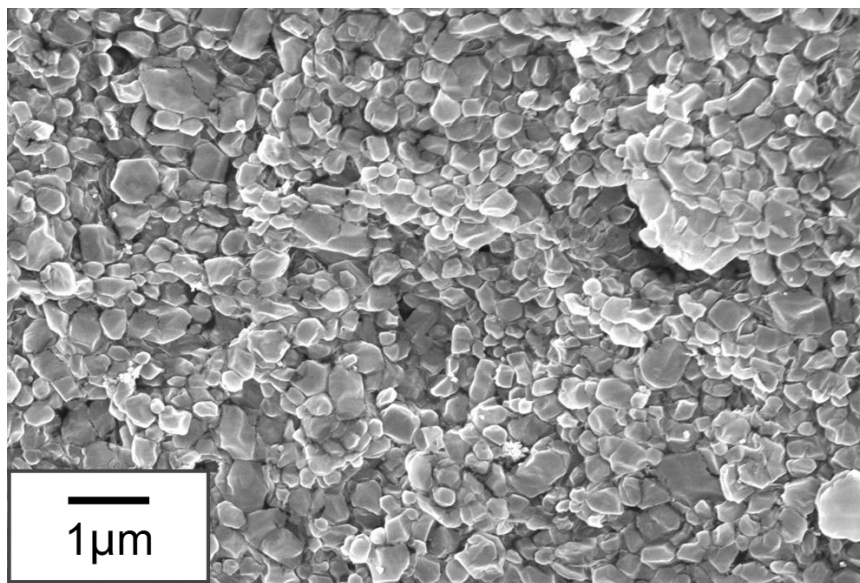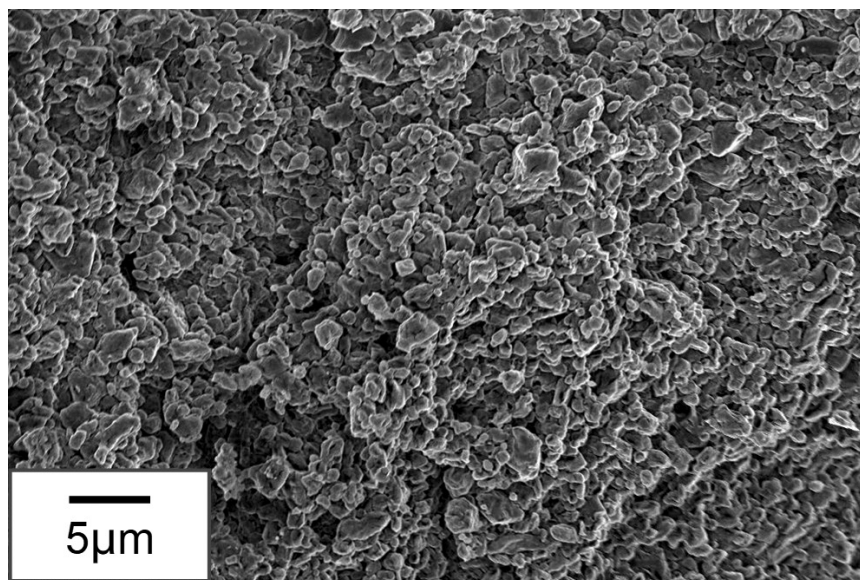
2 Materials and Methods

2.1 Sample preparation

The HMX based PBXs used in this work were all from the Institute of Chemical Materials, Mianyang, China. All PBXs consisted of 97.5 wt.% β-HMX and 2.5 wt.% F_{2311} binder (copolymer from vinylidenedifluoride and chlorotrifluoroethylene in a molar ratios of 1:1), and were entitled by particle size as PBX-1 (100-300 nm), PBX-2 (1-2 μm) and PBX-3 (10-20 μm), respectively. The PBX powders were pressed by a hydraulic machine at room temperature into cylindrical charges with precisely controlled dimension and pressed density. The pressed densities chosen in this work were 1.74 and 1.50 g·cm⁻³, with relative densities of 91%TMD and 79%TMD. The parameters of the pressed PBX samples are listed in Table 1. The morphology of the raw samples is shown in Figure 1. All PBXs had narrow size distributions and nearly spherically shaped with a smooth surface.

Table 1. Pressed density, particle size, mechanical properties, thermal conductivity properties and impact sensitivity of pressed PBX samples
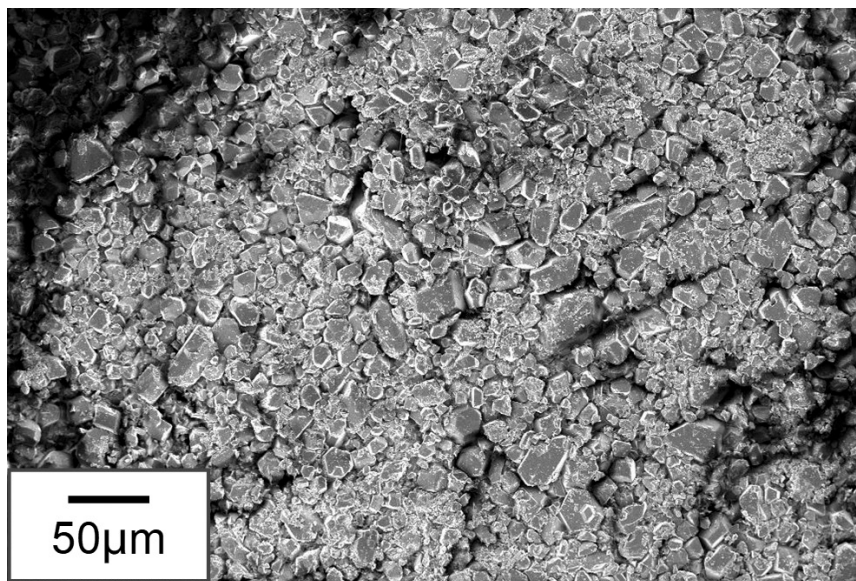
Sample	Particle size [μm]	Pressed density [%TMD]	Compressive strength [MPa]	Compressive modulus [GPa]	Thermal conductivity [W·(m·K)⁻¹]	Thermal diffusivity. [mm²·s⁻¹]	Impact sensitivity [J]
PBX-1-H	0.1-0.3	91	43.76	1.75	0.406	0.202	18.5
PBX-1-L		79	14.89	0.69	0.247	0.195	19.1
PBX-2-H	1-2	91	37.67	1.17	0.321	0.149	12.3
PBX-2-L		79	11.45	0.41	0.230	0.167	15.3
PBX-3-H	10-20	91	14.55	0.69	0.244	0.158	9.4
PBX-3-L		79	2.51	0.11	0.190	0.134	10.8

(a)

(b)

(c)

Figure 1. SEM images of raw tablets: (a) PBX-1-H, (b) PBX-2-H and (c) PBX-3-H

2.2 Characterization and test

The morphology of the raw and impacted samples was observed by a field emission-scanning electron microscope (FE-SEM, Zeiss ΣIGMA HD, Germany) with an accelerating potential of 4-5 kV. The quasi-static compression tests were carried out on a universal testing machine (INSTRON 5582) at 25 °C. The device crosshead moves at constant displacement rate of 0.5 mm/min to compress the samples. The dimension of the tested sample was Φ 10.0 mm × 10.0 mm (diameter × thickness). The thermal conductivity measurements were conducted by the laser flash method [18] *via* a laser thermal conductivity apparatus (LFA 447 Nanoflash) at 25 °C. The dimensions of the tested samples were Φ 12.9 mm × 2.0 mm. A graphite layer was coated onto the samples before testing.

Differential scanning calorimetry (DSC) tests were recorded on a TGA/ DSC 1 instrument (Mettler Toledo) under a nitrogen atmosphere (flow rate: 75 mL/min). Approximately 1 mg samples in aluminum crucible were heated from 40 °C to 350 °C at a heating rate of 5 °C/min.

The impact sensitivity tests were performed on a KAST fall hammer machine with a 2 kg weight. A tablet sample with precisely controlled

dimensions (Φ 9.4 mm $\times$ 0.7 mm) was sandwiched between two rollers (Φ 10.0 mm $\times$ 10.0 mm) and the whole was confined with a collar (Φ 10.2 mm). The impact sensitivity was determined by the up-and-down method [19] and was expressed as the drop energy E_d, *versus* the percentage of initiation. Only a 50% probability of initiation was used in this article.

The impact force acting on the samples in the fall hammer test was measured by the apparatus illustrated in Figure 2. A piezoelectric force transducer (Kistler 9331B, Switzerland) was mounted under the lower roller to record the force history during the fall hammer impact. The drop weight was 2 kg, and to ensure explosion did not occur, the drop height was fixed at 12 cm (drop energy is 2.4 J). The mass of the powder sample was 79 mg, the same as the mass of a 79%TMD tablet.
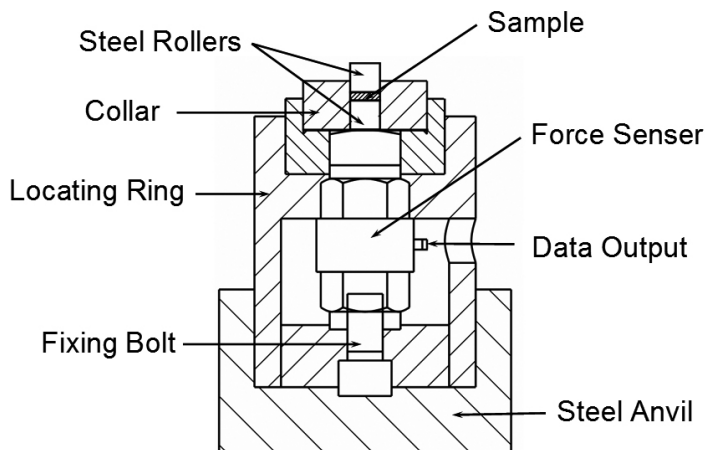

Figure 2.   Schematic profile of apparatus for determining impact force

3   Results and Discussion

3.1 Mechanical properties

It has been observed that, PBX samples with different particle size exhibit different pressed density under the same pressure. To determine the appropriate pressing conditions, PBX molding powder with mass 0.35 g was subjected to various pressures in the same mould (Φ 12.9 mm) for 1 min pressing time. The dependence of the pressed density on pressing pressure is illustrated in Figure 3. It may be observed that, a PBX with larger particle size exhibits

a higher pressed density. In other words, to obtain identical pressed density, a PBX with a smaller particle size needs to be pressed at a higher pressure.
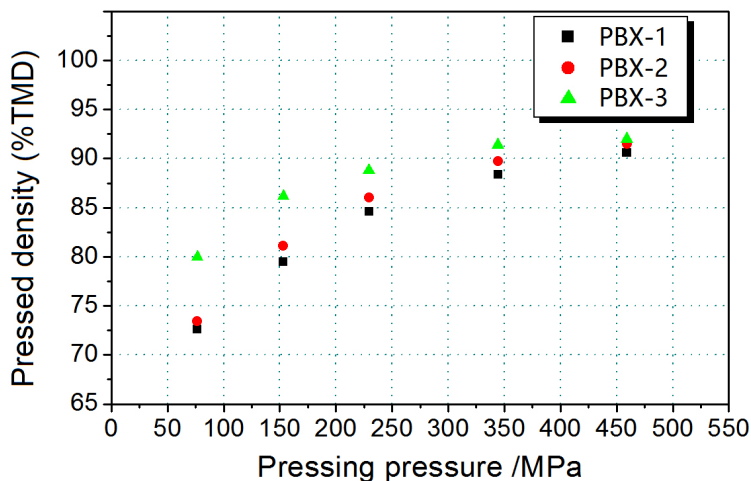

Figure 3.   The relationship between pressing pressure and pressed density

To obtain data on compressive strength and modulus, uni-axial quasi-static compression tests were performed with a strain rate of 0.05 min^{-1} (8.3·10^{-4} s^{-1}). The stress-strain curves of PBX samples at 91%TMD and 79%TMD are shown in Figure 4 and Figure 5, respectively.
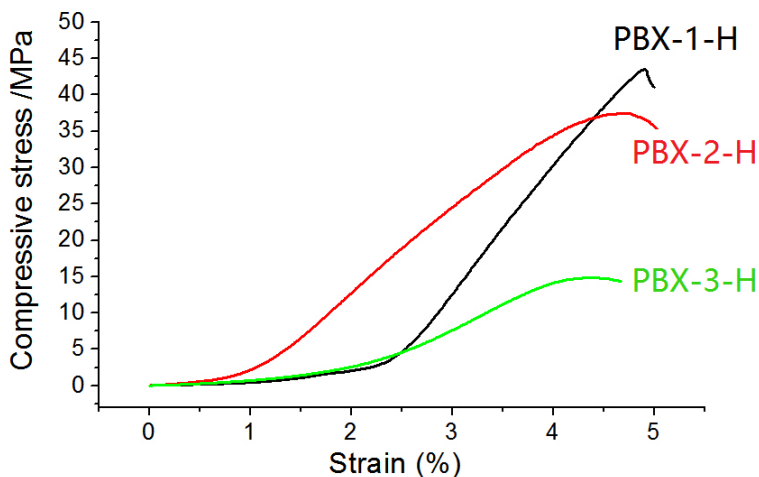

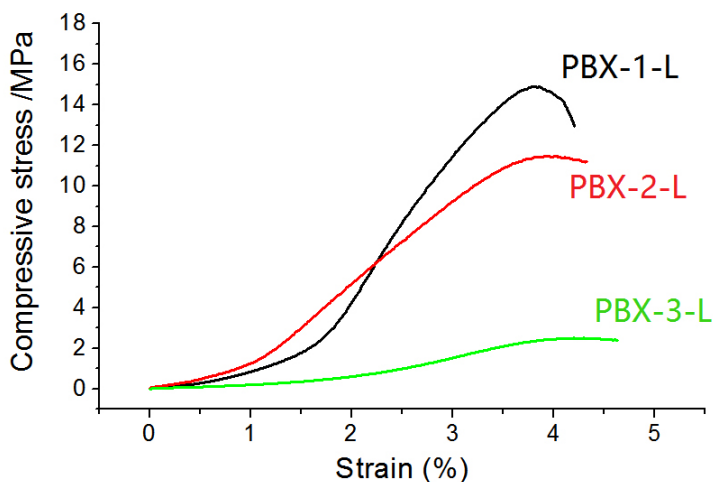**Figure 4.**   The compressive stress-strain curve of PBXs at 91%TMD

Figure 5.   The compressive stress-strain curve of PBXs at 79%TMD

All of the above compressive stress-strain curves above consist of four parts. Firstly, the sample is slightly deformed by stress, but the slope is quite uncertain in repeated tests. This may be caused the upper and lower faces of the cylinder not being parallel. After the initial unstable compression, the stress-strain curve increases into a linear region and the slope of this portion is the compressive modulus. This linear region terminates at what is known as the yield point, and the stress at the yield point is the compressive strength [20]. After the yield point, the stress begins to decrease. The compressive strength and compressive modulus data obtained from stress-strain curve are summarized in Table 1. Each value is an average of six parallel tests.

The results clearly revealed that, at same pressed density, the compressive strength and compressive modulus increased dramatically with a decrease in the particle size. Compared with PBX-3-H, the PBX-1-H exhibited an increase of about 200% in compressive strength and about 150% in compressive modulus. This relationship between particle size and mechanical strength is the result of grain-boundary strengthening. A decrease in particle size leads to an increase in grain boundary area in the same volume. As crystalline materials deform through the movement of dislocation and grain boundaries that would impede dislocation movement, a small particle size would result in higher yield strength.

3.2 Thermal conductivity and diffusivity
The thermal conductivity and diffusivity of the pressed PBXs were measured by the laser flash method and the results are listed in Table 1. It may be observed

that, as with the mechanical properties, the thermal conductive properties also increase greatly with a decrease in particle size and an increase in pressed density. At a pressed density of 91%TMD, the thermal conductivity of PBX-1-H is nearly twice that ofPBX-3-H. The thermal diffusivity, which is defined as the ratio of thermal conductivity to density and specific heat capacity, followed a similar trend.

The high thermal conductivity of nano-sized PBX-1 was assumed to be due to a larger specific surface area and a more homogeneous micro-structure. With a decrease in particle size, the thickness of the interface between particles decreases, lowering the resistance to heat transfer, and, since there are more contact points between particles, providing more pathways in the heat transfer network. Wang [21] analyzed the ETC (effective thermal conductivity) of multi-phase granular porous media using mesoscopic statistics based numerical methods, and the results indicated that, with decreasing particle size at same porosity, the thermal conduction model in porous media changes gradually from a series conduction model to a parallel conduction model which results in a higher ETC. Furthermore, the incremental increase in ETC with increasing pressed density in a certain range is consistent with the results from our experiments.

3.3 Thermal stability

The thermal stability of samples was evaluated by the DSC test at a heating rate of 5°C/min. As the pressed density was assumed to have little effect on the chemical reactivity, tests were performed on the molding powders of the three PBXs, instead of pressed tablets. Figure 6 shows the endothermic peaks (phase transformation of β-HMX to δ-HMX) at around 200 °C. The peak temperature of the three samples varies between 197 and 211 °C but shows no dependence on particle size. Figure 7 shows the exothermic peaks (thermal decomposition of HMX) at around 280 °C. The peak temperatures for PBX-1, PBX-2 and PBX-3 were 282.38, 282.51 and 282.86 °C respectively, indicating that the influence of particle size on thermal decomposition is negligible.
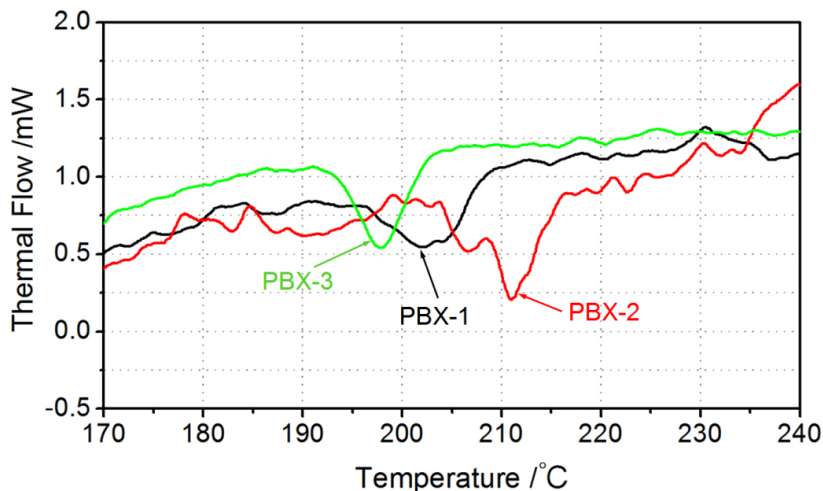
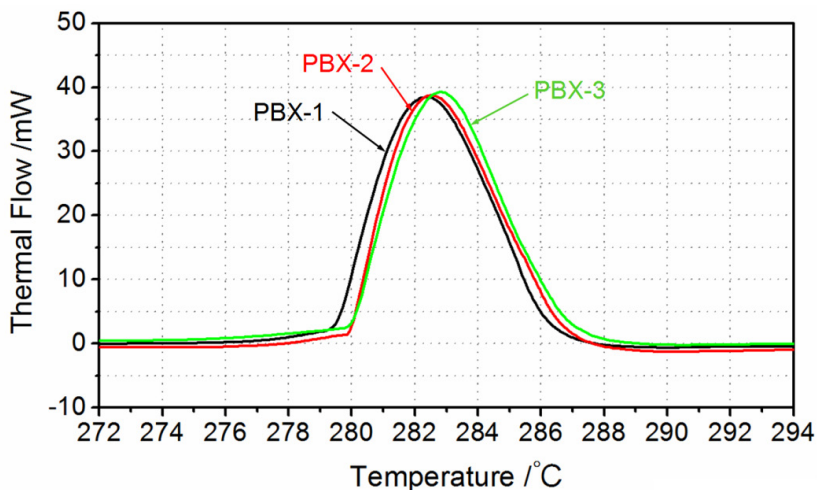**Figure 6.**   Endothermic peaks of samples measured by DSC

Figure 7.   Exothermic peaks of samples measured by DSC

3.4 Tablet impact sensitivity

Instead of powder samples used in the standard test, pressed tablet samples were used in the fall hammer test to investigate the respective effect of particle size and pressed density on impact sensitivity. The results listed in Table 1 showed that, at both 91%TMD and 79%TMD, the impact sensitivity E_d increases dramatically

with a decrease in the particle size. The E_d value of PBX-1-H is nearly twice that of PBX-3-H. As factors such as particle shape, surface defects and pressed density could be excluded in this study, it could be concluded that reducing the particle size would decrease the impact sensitivity.

A quite interesting and confusing finding was that, for PBXs with the same particle size, E_d for the 91%TMD sample is a little lower than that for the 79%TMD sample, indicating that samples with high pressed density are more sensitive, which is contrary to traditional views. A possible reason for this phenomenon is that the impact force acting on high density sample is higher due to its high mechanical strength and modulus. To validate whether pressed density has any evident effect on the impact force, the mechanical response during a fall hammer impact was recorded by a piezoelectric force transducer. The histories of the impact pressure (converted from impact force) acting on PBX-1 and PBX-3 samples in various forms (91%TMD tablets, 79%TMD tablets and loose powder) are shown in Figure 8.
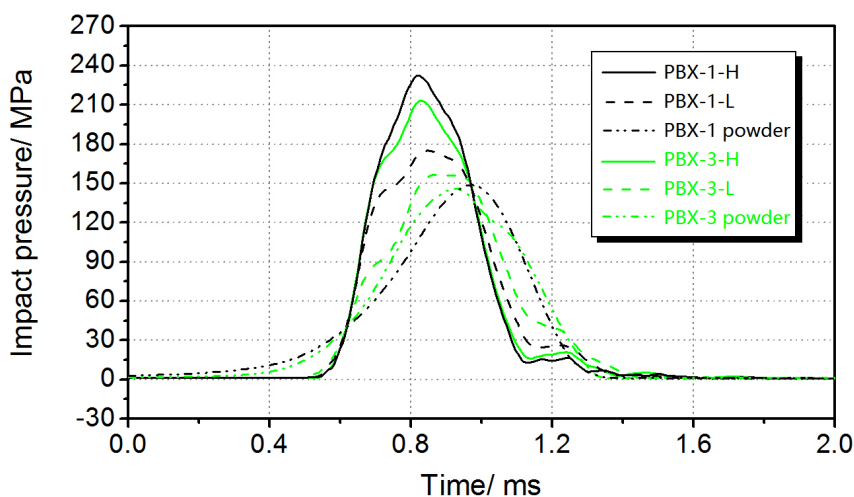

**Figure 8.**   Force-time curves during fall hammer impact

It may be seen that, for PBX with the same particle size, the effect of pressed density on the impact pressure is significant. When the pressed density increased from 79%TMD to 91%TMD, the peak pressure for PBX-1 increased from 175 to 233M Pa, and for PBX-3 increased from 156 to 213 MPa. Both exhibit about 60 MPa increments. In addition, although the mechanical data obtained from the quasi-static compression test showed a marked difference between

PBX-3 and PBX-1 at the same pressed density, the difference in the impact pressure was not obvious, being only about 20 MPa for the tablets and only 3 MPa for the powders. This difference is due to the strain rate effect, that materials' stress-strain behaviour is dependent on strain rate [22, 23]. It seems that PBXs' mechanical strength becomes less sensitive to particle size under relatively higher deformation rates.

In the impact sensitivity tests, samples that were subjected to impact but did not explode, were collected and observed by SEM. The morphology of the cross-sections of these impacted tablets is shown in Figure 9. These tablets could be regarded as being at a critical condition, where the sample was heated by hot-spots, causing local melting or decomposition, but failed to lead to a sustained reaction and became sintered. In the impacted PBX-1-H (Figure 9(a)) and PBX-2-H (Figure 9(b)), melted zones could be observed of width about several microns, but the surrounding areas remained porous as in the unimpacted samples. By contrast, the morphology of the impacted PBX-3-H (Figure 9(c)) is more homogeneous; particles have merged together and inter-granular pores had basically disappeared.
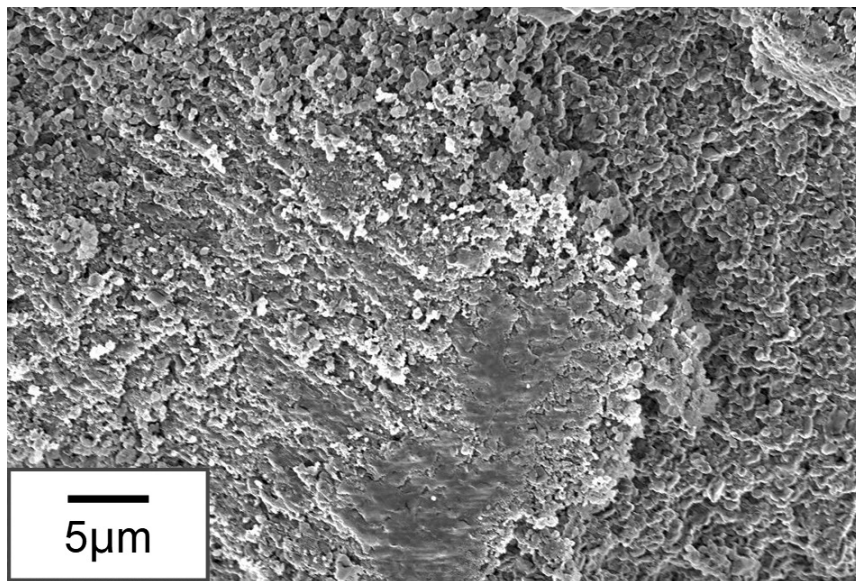
(a)
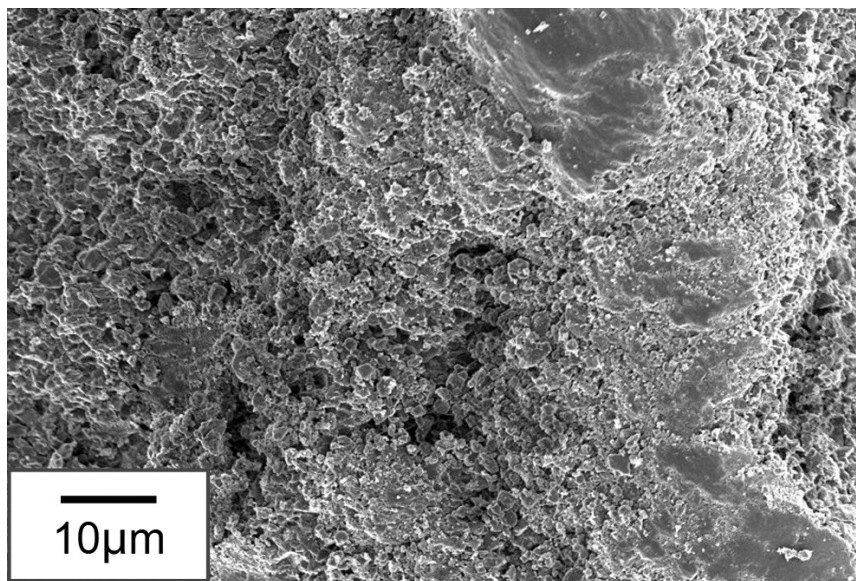
(b)
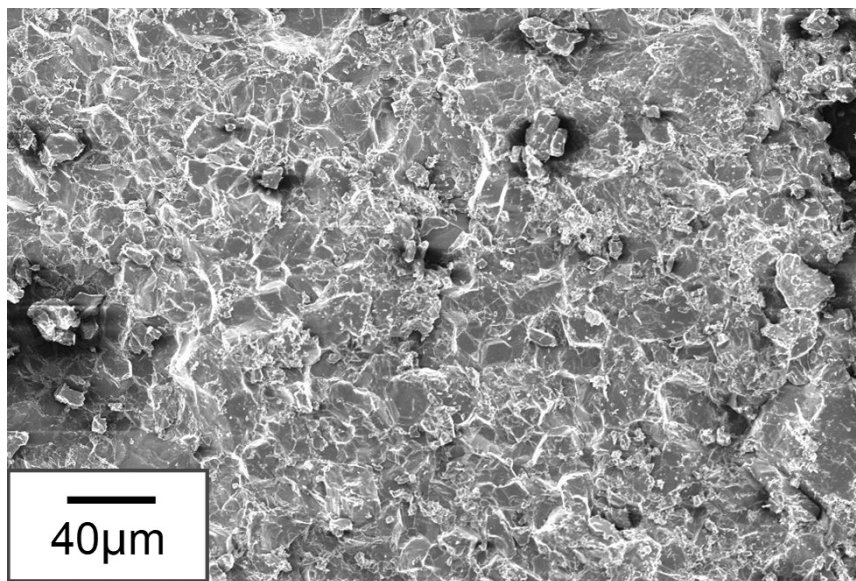
(c)

Figure 9.   SEM images of impacted tablets: (a) PBX-1-H, (b) PBX-2-H, (c) PBX-3-H

It is known that the ignition mechanism is heavily dependent on the properties of the materials and stimuli conditions in which hot-spots are being created. There are several possible hot-spot mechanisms which have been proposed by previous studies [16]: pore collapse, friction between particles, adiabatic shear banding, particle crack, *etc*. For pressed PBX-3, as the size of the pores between the PBX particles is relatively large (several microns) and its compressive strength is relatively low, inter-granular pores could be easily compressed, generating high temperature hot-spots. However, for pressed PBX-1 and PBX-2, as the inter-granular pores are quite small (tens to hundreds nanometers) and the samples are harder to deform, compression of the pores is unable to produce high temperatures. Instead, slipping and shearing between the particle layers become the dominant effects under fall hammer impact. This difference indicates that the formation mechanism of hot-spots under impact is affected by particle size. Coarse PBX tends to be ignited by pore collapse while fine PBX tends to be ignited by adiabatic shearing.

Combined with the results of the mechanical and thermal properties tests, the effect of particle size on impact sensitivity could be elucidated according to hot-spot theory. At the same porosity, size reduction leads to smaller pore sizes and larger pore numbers. Numerical simulation studies [24, 25] have concluded that the critical temperature and pressure for initiation increases exponentially with a decrease in pore size, *i.e.* small pores are more difficult to initiate. Furthermore, due to the increased inter-granular pore number, the mechanical energy of the drop weight is dispersed and homogenized by the nano-structure. During the development of a hot-spot, the competition between the exothermic reaction and the thermal dissipation determines whether a hot-spot leads to a sustained reaction or quenches by thermal conduction. With high thermal conductivity, the heat created by hot-spots would dissipate rapidly. Although improved mechanical strength leads to a higher stress during impact, experiments have shown that the effect of particle size on impact pressure is less significant. Desensitization by reducing the particle size is perceived as an integrative effect resulting from pore size reduction, pore structure homogenization and thermal conductivity enhancement. All of these factors soften heat localization, resulting in a significant resistance to initiation under impact stimuli.

4   Conclusion

The influence of particle size and pressed density on mechanical and thermal properties, and impact sensitivity was studied. Compressive strength,

compressive modulus, thermal conductivity and thermal diffusivity all increase dramatically with decreasing particle size and increasing pressed density. The influence of particle size on thermal stability can be negligible. Samples with small particle size and low pressed density are less sensitive to impact. Under the same impact conditions, peak pressure at impact increases with increasing pressed density or decreasing particle size. Impact causes pore collapse in large particle size PBX, and shearing slip of particle layers in small particle size PBX. By eliminating variation in pressed density of sample tested, the sensitivity test using pressed samples has been shown to be a promising method for impact sensitivity determination.

Acknowledgements

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