Small-angle X-ray analysis of the effect of grain size on the thermal damage of octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7 tetrazocine-based plastic-bounded expolsives*

Yan Guan-Yun(闫冠云)[a], Tian Qiang(田 强)[a,†], Liu Jia-Hui(刘佳辉)[b], Chen Bo(陈 波)[a], Sun Guang-Ai(孙光爱)[a], Huang Ming(黄 明)[b], and Li Xiu-Hong(李秀宏)[c]

[a] *Key Laboratory for Neutron Physics and Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang* 621900, *China*
[b] *Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang* 621900, *China*
[c] *Institute of Shanghai Apply Physics, Chinese Academy of Sciences, Shanghai* 201800, *China*

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The microstructure evolution of plastic-bonded explosives (PBXs) after thermal stimulus plays a key role in PBX performance. In this paper, the nanoscale pores of thermal-treated octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX)-based PBXs with different HMX particle sizes [approximately 40 (FHP) and 100 μm (LHP)] were measured using small-angle X-ray scattering (SAXS). No obvious pore variations were found in the LHP samples heated at 160 °C for 6 h, whereas the amount of pores of FHP decreased when subjected to 160 °C for 6 h. At 180 °C, the average pore radii of FHP and LHP decreased from approximately 45 nm to 25 nm, and the total pore volume increased distinctively because of phase transformation. The LHP sample reached a high level of pore content after being held at 180 °C for 1 h, whereas FHP required 3 h. Both FHP and LHP had relatively high pore volumes when subjected to 200 °C for 1 and 3 h.

Keywords: HMX-based plastic-bonded explosives, small-angle X-ray scattering, pores, thermal-treated

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1. Introduction

When energetic materials are subjected to unexpected heat (such as fire), earthquake, a fall, sudden climate change, and combat operations in battle fields, thermal effects may result in pores, cracking, phase transition, thermal expansion, and gaseous decomposition. All these modifications change the physical and chemical properties, as well as the equations of state of energetic materials. The resulting damaged energetic materials will become more sensitive to shock or impact initiation.[1] It is known that pores (or voids) play a major role in controlling the detonation process as some kind of energy concentrator or, rather, "hot spots". It is not clear what kind of characteristic the pores (e.g., size and/or shape) possess in order to change the sensitivity of high energy materials. It is also not clear whether the ultimate pore characteristic originates from either the processing or the initial stage of detonation.[2] Therefore, characterizing and understanding the thermal effects on nanoscale pores of energetic materials is important.

Octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX) is of interest because of its use in the area of explosives. It exists in many polymorphic forms, δ-, γ-, α-, and β-, and β-phase is the most stable and δ-phase is the most unstable. HMX-based plastic-bonded explosives (PBXs) change remarkably due to shock sensitivity and self-supported accelerated burning[3,4] when subjected to thermal stimulus. These changes may be induced by the β–δ phase transition, thermal decomposition, and decrease in binder viscosity at elevated temperature.[5,6] The microstructure evolution of HMX-based PBX after thermal stimulus plays a key role in its performance. Understanding the thermal effects on HMX-based PBXs is important to the development of models that can predict the response of munitions in abnormal thermal environments and obtain an understanding of the chemical processes that control their long-term degradations.

Small-angle scattering is a useful tool in measuring the microstructure of explosives.[7–13] Peterson *et al.*[14] investigated the pore variations of PBX 9501 subjected to thermal stimulus through polarized light microscopy and small angle X-ray scattering (SAXS). A previous study has reported that the thermal stability of HMX was greatly dependent on particle size.[2] However, to date, investigations on the nano-scale pores of HMX-based PBX with different HMX particle sizes have not been reported. In the present study, the influence of particle size on the thermal damage in HMX-based PBXs is examined using SAXS.

2. Experiment

Two types of HMX-based PBX with HMX particle size distribution centered at 40 μm (FHP) and 100 μm (LHP) were supplied by the Institute of Chemical Materials, China Academy of Engineering Physics. The samples consisted of

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†Corresponding author. E-mail: tqsuperego@163.com
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95% HMX and 5% fluorine rubber. The samples were thermally treated in an aging chamber at 160 °C for 6 h and at 180 °C and 200 °C, respectively, for 1 h, 3 h, and 6 h. The samples were then allowed to cool naturally to room temperature. The SAXS measurements were conducted at the SAXS station (BL16B1) of the Shanghai Synchrotron Radiation Facility (SSRF), China, which is a third-generation light source. The wavelength of the X-ray is 0.124 nm, and the distance from the detector to the sample is 5110 mm. Two-dimensional (2D) scattering patterns were recorded using an image-intensified charge-coupled device detector. The recorded 2D scattering patterns were converted into one-dimensional (1D) curves by MySAS package.[15]

In SAXS experiments, scattering is derived from fluctuations in the electron density $\rho(r)$, which reflects the microscale structure. The scattering intensity $I(q)$ is measured as a function of scattering vector $q = (4\pi \sin\theta)/\lambda$, where λ is the wavelength of the incident radiation, and θ is the half of the scattering angle. The scattering intensity $I(q)$ for a polydisperse system of non-interacting particles dispersed in a uniform medium can be expressed as[16,17]

$$I(q) = |\Delta\rho|^2 \int_0^\infty |F(q,r)|^2 V^2(r) NP(r)\,\mathrm{d}r, \qquad (1)$$

where $\Delta\rho$ is the scattering length density difference between the average scattering length density of the PBX and that of the pores (for PBX materials), and r is the radius of the scattering particles, $F(q,r)$ is the scattering form factor, $V(r)$ is the volume of the particle, N is the total number of minority phase particles, and $P(r)$ is the probability of having a minority phase particle of size r. Pore size distribution, $f(r) = V(r)NP(r)$, as a function of radius r, is presented in this study. The form factor of the pores of a sphere is assumed, and the size distribution of the pore is calculated by the "Irena" package using a maximum entropy algorithm.[17]

3. Results and discussion

The I–q curves of raw and 160 °C heated samples are illustrated in Fig. 1. The scattering intensity of FHP is higher than that of LHP. The intensity of LHP increases after heating at 160 °C, which is contrary to the decrease in the intensity of FHP. The fitted results of the volume-weighted size distribution of pores of the samples are demonstrated in Fig. 2. A decrease in pore magnitude can be seen in the FHP sample heated at 160 °C for 6 h. The high intensity of FHP can be caused by a large number of binder-HMX interfaces induced by the small HMX particle size. The decrease in the pore number of the FHP sample heated at 160 °C may be related to the increased flexibility of the binders[18] that may fill into the inter-particle pores as the temperature increases.

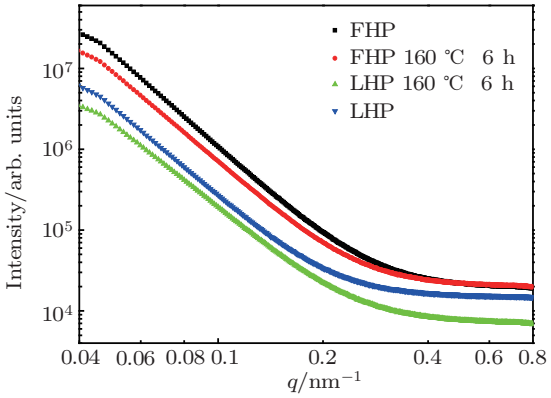


Fig. 1. (color online) SAXS measurements of raw and 160 °C-heated HMX-based PBXs.

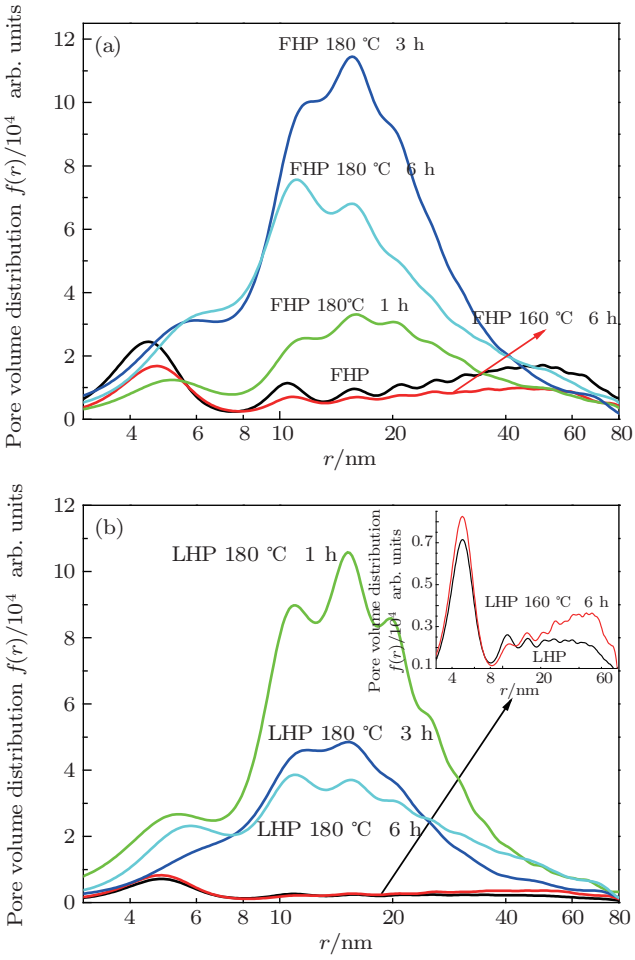


Fig. 2. (color online) SAXS analyses of volume-weighted size distribution of samples heated at 160 °C and 180 °C for (a) FHP and (b) LHP.

Figure 3 shows the SAXS patterns of FHP and LHP samples heated at 180 °C. Compared with the raw materials, the intensities of FHP and LHP increase remarkably after heating at 180 °C. The FHP sample heated at 180 °C for 3 h has the largest intensity among the FHP samples at the same temperature. The LHP sample heated at 180 °C for 1 h has the largest intensity among LHP samples. The relative intensities of FHP heated for 3 h and those of LHP heated for 1 h and 3 h at

180 °C increase at the values of q ranging from 0.08 nm^{-1} to 0.3 nm^{-1} (Fig. 4). A distinct increase in pore sizes from 9 nm to 30 nm can be seen for 180 °C-heated samples in Fig. 2. The FHP heated at 180 °C for 3 h and LHP heated at 180 °C for 1 h each have the highest number of pores.

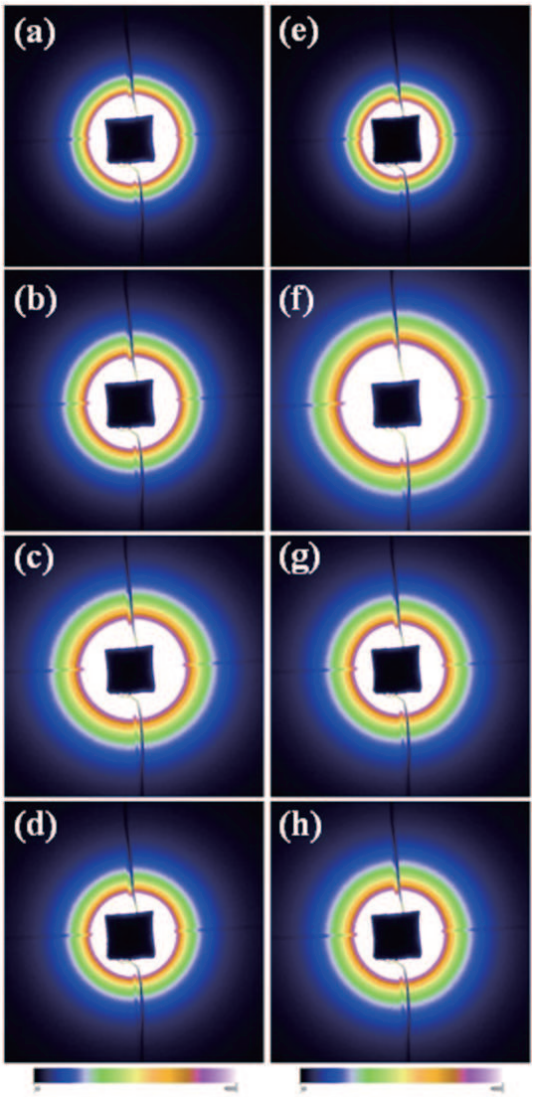


Fig. 3. (color online) The 2D SAXS patterns of raw and 180 °C-heated HMX-based PBXs: (a) raw FHP sample; FHP heated at 180 °C for (b) 1 h and (c) 3 h, and (d) FHP for 6 h; (e) raw LHP sample; LHP heated at 180 °C for (f) 1 h, (g) 3 h, and (h) 6 h.

The increases in intensity of samples heated at 180 °C are attributed to the new populations of pores developed in the $\beta \rightarrow \delta$ phase transitions, during which volume expansions and anisotropic variations of crystals[19] can cause obvious damages.[20] The X-ray diffraction (XRD) patterns of FHP and LHP samples after heating at 180 °C for 1 h and 3 h are shown in Fig. 5. The δ phase peaks are represented by the dashed line. The relative intensity of the δ phase of LHP is higher than that of FHP. That is, the $\beta \rightarrow \delta$ phase conversion rate of FHP is lower than that of LHP because of the influence of particle size[2] and this is the reason why FHP needs 3 h to reach the highest pore number whereas LHP only needs 1 h. The pores grow and coalesce into cracks[14,21] during heat treatment, and part of the pores may be out of the q-range of the instrument, which could be the reason for the decline in pore numbers of the LHP and FHP heated at 180 °C for 6 h in Fig. 2.

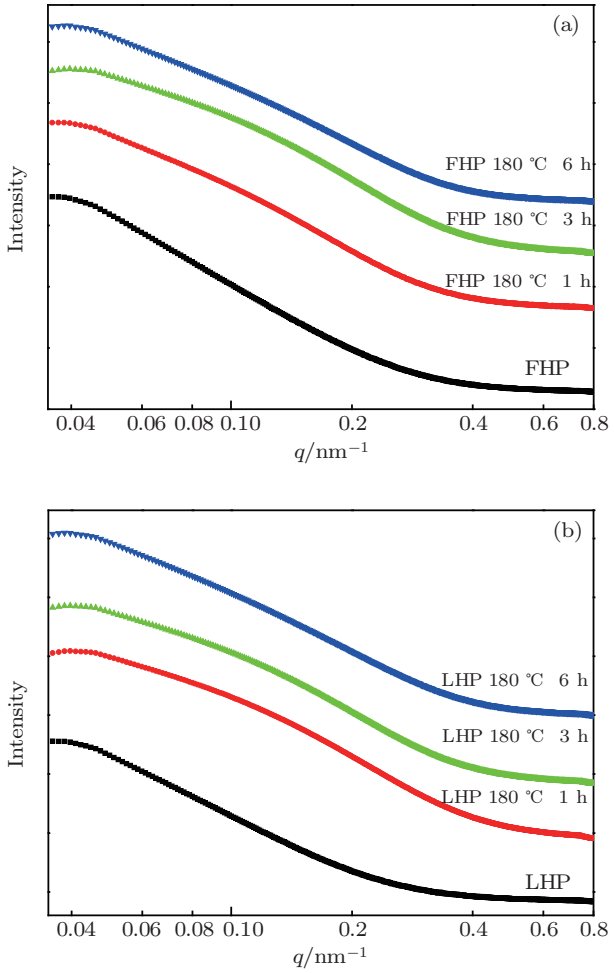


Fig. 4. (color online) Curves of scattering intensity versus q for raw and 180 °C-heated samples: (a) FHP and (b) LHP. Note that the curves have been displaced vertically on the log scale by multiplying a factor.

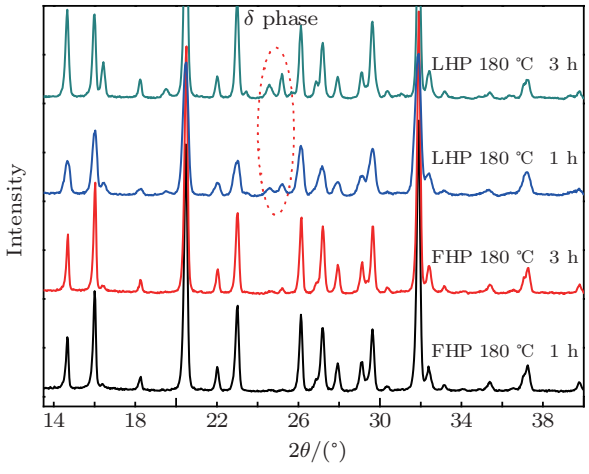


Fig. 5. (color online) XRD patterns of FHP and LHP samples heated at 180 °C for 1 h and 3 h.

As temperature increases to 200 °C, the scattering intensities of the FHP and LHP samples increase with heating time from 1 h to 3 h. The pore volume-weighted size distribution analyses of the 200 °C heated samples are shown in Fig. 6. The pore numbers of the samples heated for 3 h are larger than those of samples heated for 1 h, which is different from the cases of 180 °C heated samples and is likely to be caused by the gaseous products of exothermic decompositions of HMX and binders.[5,22] The decline in the numbers of pores of the samples heated at 200 °C for 6 h is induced by the growth of the pores, which are beyond the probed length scale of the SAXS spectrometer. The pores generated from the phase transition and thermal decomposition can coalesce into macro- and micro-cracks, exposing new reactive surfaces that may result in the variations of shock mechanical sensitivity and thermal stability.[4,23,24]

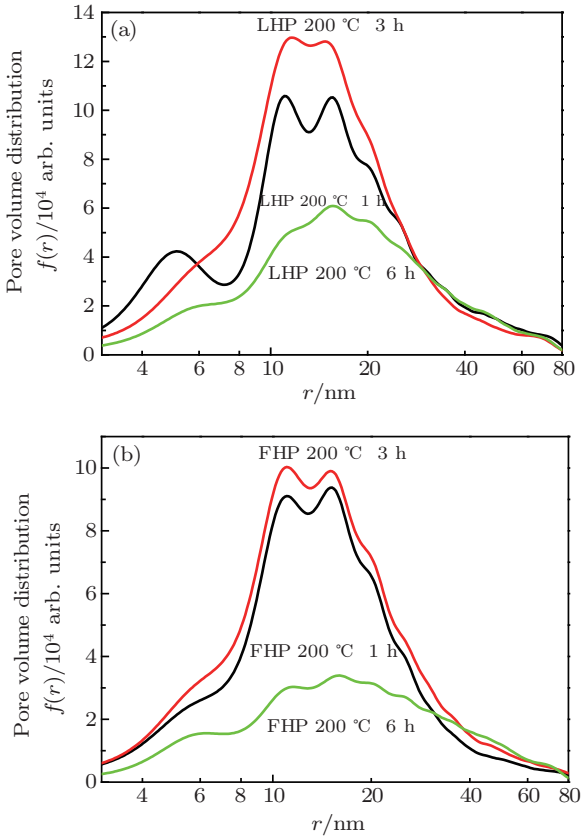


Fig. 6. (color online) SAXS analyses of volume-weighted size distribution of pores for the 200 °C-heated (a) FHP and (b) LHP samples.

The fitted results of the total pore volume (relative to the raw LHP sample) in HMX-based PBXs are summarized in Fig. 7. This study could help understand the mechanisms of the cook-off process of HMX-based PBXs, and it can also be used to estimate the stability of HMX-based PBXs when subjected to unexpected thermal or mechanical stimulus.

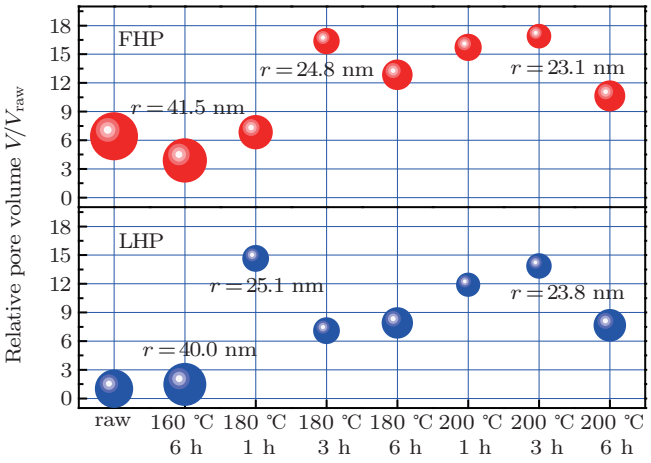


Fig. 7. (color online) Volume-averaged mean pore size and total pore volume from SAXS analyses.

4. Conclusions

Two types of HMX-based PBXs composed of different sizes of HMX particles are characterized by SAXS after thermal stimulus. Generally, FHP has a higher pore number than LHP after the same heat treatment, thereby forming a smaller grain size. The pore number of FHP decreases when heated at 160 °C for 6 h. At 180 °C, the average pore radii of FHP and LHP decrease to approximately 25 nm, and the pore volume increases remarkably due to the HMX β–δ phase transition. The FHP sample heated at 180 °C for 3 h has the largest pore number among the 180 °C-heated FHP samples, whereas the LHP sample heated at 180 °C for 1 h has the largest pore number among LHP samples. The samples heated at 200 °C for 1 h and 3 h each have relatively high pore number, which may be caused by the exothermic decomposition of gaseous products of HMX.

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