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Preparation and Characterization of a Novel HMX/AP/EP Nanocomposite

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Abstract: The cyclotetramethylene tetranitramine (HMX)/ammonium perchlorate (AP)/energetic polymer (EP) nanocomposite was prepared by a co-precipitation method using a novel EP as matrix. Its structure and properties were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), specific surface area (Brunauer-Emmett-Teller (BET)) measurement, Infrared (IR) spectrometry, and differential scanning calorimetry (DSC). Results show that the HMX/AP/EP nanocomposite possesses the three-dimensional nano-network structure. The HMX and AP particles are uniformly deposited on EP, whose size is in the range of 50–200 nm. HMX, AP and EP are closely bonded each other with good compatibility. The thermal decomposition temperature of the HMX/AP/EP nanocomposite is far lower than that of HMX. When the oxygen balance of HMX/AP/EP nanocomposite is zero, its decomposition heat is up to 2570 $J \cdot g^{-1}$. Compared with the characteristic drop height of impact sensitivity (H_{50}) of 27 cm of HMX, the value of H_{50} of the HMX/AP/EP nanocomposite is 50.49 cm, revealing that the latter has lower mechanical sensitivity.

Key words: energetic materials; nanocomposite; cyclotetramethylene tetranitramine (HMX)/ammonium perchlorate (AP)/energetic polymer (EP); thermal performance

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1 Introduction

Nanocomposite energetic materials (NCEMs) are often composed of a fuel and an oxidizer, which are homogenous at nanometer scale [1]. Generally, the nanocomposites possess excellent thermodynamic characteristics of fuel-oxidizer mixtures and high energy release rate [2]. Numerous energetic composites, such as cyclotrimethylenetrinitramine (RDX)/AP/SiO_2, HMX/AP/resorcinol-formaldehyde (RF), RDX/bacterial cellulose (BC) [3-5], have been prepared. Compared with conventional mixtures, these nanocomposites have less sensitivity and faster burning rate. However, RF, SiO_2, and BC are not energetic materials or components of rocket propellants. Cyclotetramethylene tetranitramine (HMX) and ammonium perchlorate (AP) are the most reactive components in formulations of a large number of high performance explosives and solid propellants[6]. If the well-distributed composites of HMX and AP are prepared according to a certain percentage reaching or being close to zero oxygen balance (ZOB), it will be hopeful to obtain competitive energetic compounds [7]. In this work, a novel energetic polymer (EP) is used as the matrix to prepare NCEMs HMX/AP/EP with different oxygen balance by co-precipitation method.

2 Experimental

HMX, AP and EP were dissolved in a good solvent (ketones) under a magnetic stirrer and ultrasonic dispersion, and then this mixed solution was added into a bad solution (haloalkane) to form the solution with co-precipitation product. The products were filtered from the solution after keeping stirring 2 h, and finally dried through freeze-drying. The oxygen balance of HMX/AP/EP composites was moderated through changing the mass ratio of HMX/AP/EP including positive oxygen balance(POB), negative oxygen balance(NOB) and zero oxygen balance.

3 Results and discussion

3.1 Microstructures of HMX/AP/EP composite

In all HMX/AP/EP composites the content of EP is controlled to be 5.6%, HMX and AP particles uniformly deposit on the nano-network structure of EP and the network size vary in the range of 50–200 nm (Fig. 1). The EDS elemental mapping results can confirm that AP (Cl) and HMX (C) are homogenous dispersion, the content of element C is higher than that of Cl, because of EP contribution for element C (Fig. 2). Compared with the pure EP, the specific surface area of the HMX/AP/EP nanocomposite is reduced from 34.7 $m^2 \cdot g^{-1}$ to

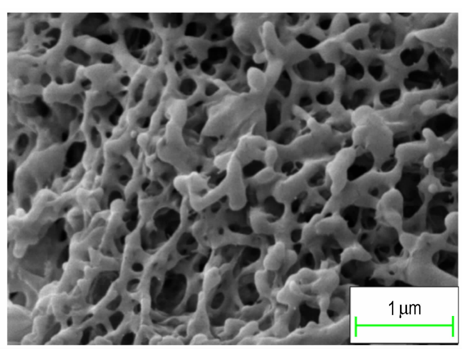

Fig. 1 SEM image of HMX/AP/EP composite

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10.3 $m^2 \cdot g^{-1}$, and the distribution of pore-size decreases from the range of 3–90 nm to 2–40 nm (Fig. 3). According to the Scherer equation [8], the mean particle diameter of HMX and AP in different samples are 59, 62 nm and 63 nm, respectively, indicating that the crystallite size prepared by our method is uniform. The grains of HMX, AP and nano-network are closely bonded each other with good compatibility in a microsystem and there should be molecular interactions, such as hydrogen bonding and electrostatic interactions.

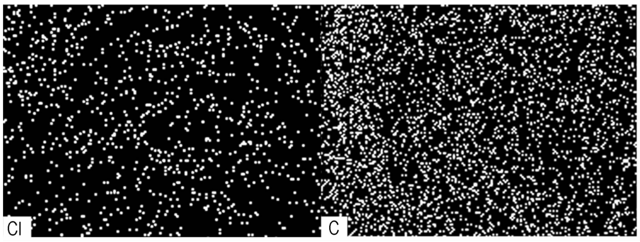

Fig. 2 Distribution of elements Cl and C for HMX/AP/EP composite

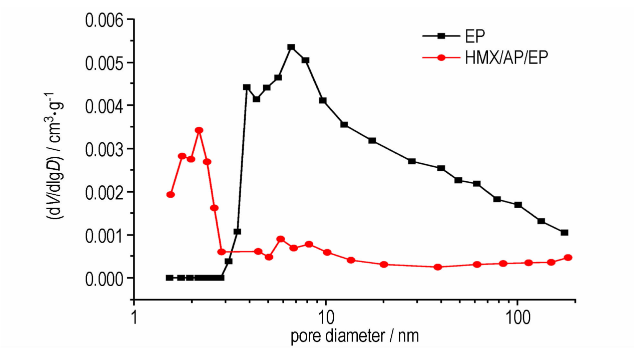

Fig. 3 The pore-size distribution of EP and HMX/AP/NBC composite

3.2 Thermal behavior and sensitivity characteristic

The thermal behavior of HMX/AP/EP nanocomposite is greatly different from that of pure HMX and AP. The ZOB NECM has a sharp exothermic peak at 232.4 ℃. The peak temperature is much lower than that of HMX. The decomposition heat of the composite reaches to 2570 $J \cdot g^{-1}$. This value is the highest among all the samples in Fig. 4. The EP can boost the decomposition and enhance the interaction of AP and HMX. The unique nanostructure of the composite broadens the contact surface. The optimum mass ratio of AP/HMX/EP contributes to the excellent decomposition heat.

The characteristic drop height of impact sensitivity (H_{50}) of the nanocomposite reaches to 50.49 cm, which is much higher than that of H_{50} of 27 cm of HMX, showing that EP as matrix can reduce the sensitivity of this energetic material. Meanwhile, the presence of AP and the nano-effects have also obvious desensitization function.

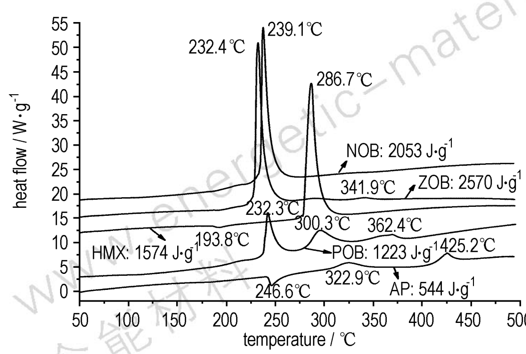

Fig. 4 DSC curves for pure HMX, AP and nanocomposites with POB, NOB and ZOB

4 Conclusion

A novel HMX/AP/EP nanocomposite has been prepared by the co-precipitation method which enables to easily control the stoichiometry to different OBs and the homogeneity of the HMX/AP/EP nanocomposites. This material possesses the three-dimensional nano-network structure with size of 50–200 nm, HMX and AP are uniformly deposited on EP matrix with good compatibility. EP and the optimal mass ratio to ZOB are able to boost the decomposition of the composite and make its decomposition heat up to 2570 $J \cdot g^{-1}$. Its impact sensitivity is lower than that of HMX. It will be hopefully applied in formulations of high performance explosive and solid propellant.

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新型 HMX/AP/EP 纳米复合物的制备及表征

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摘　要：以含能聚合物(EP)为基底通过共沉淀法制备了奥克托今(HMX)/高氯酸铵(AP)/含能聚合物(EP)纳米复合物。用扫描电镜(SEM),能量色散 X 射线能谱(EDS)、比表面积(Brunauer-Emmett-Teller(BET))测定、红外(IR)光谱法和差示扫描量热法(DSC)表征了它的结构及性能。结果表明,HMX/AP/EP 纳米复合物具有三维纳米网状结构。HMX 和 AP 均匀沉积在 EP 上面,其尺寸为 50~200 nm。HMX、AP 和 EP 紧密结合在一起,具有良好的相容性。HMX/AP/EP 纳米复合物的分解温度远低于 HMX 的。当 HMX/AP/EP 纳米复合物的氧平衡为零时,其分解热高达 2570 J·g^{-1}。HMX/AP/EP 纳米复合物的撞击特性落高 H_{50} 为 50.49 cm,与 HMX 的撞击感度的特性落高(27 cm)相比,其机械感度较低。

关键词：含能材料；纳米复合物；奥克托今(HMX)/高氯酸铵(AP)/含能聚合物(EP)；热性能
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《含能材料》高品质炸药晶体研究专栏征稿

高品质炸药晶体的出现为钝感弹药的研究与应用开辟了一条重要途径,高品质炸药晶体因而也成为目前国内外含能材料研究领域的热点之一。为促进高品质炸药晶体的研究和应用,《含能材料》将于 2015 年开设高品质炸药晶体研究专栏,专题报道高品质炸药晶体的制备、表征、性能、应用等领域的最新研究成果,促进学者间的交流。欢迎相关研究学者投稿。来稿建议为英文。来稿时请选择对应的专栏。

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