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Fabrication and characterization of HMX@TPEE energetic microspheres with reduced sensitivity and superior toughness properties

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A B S T R A C T

The development of a facile method for improvement of interface interaction between rigid particles and coating polymer is of great importance for energetic composite materials, especially for military purpose. In this paper, energetic composites with spherical morphology, toughness property and low sensitivity are firstly fabricated by using Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as core material and thermoplastic polyester-ether elastomer (TPEE) as shell material via an emulsion solvent evaporation (ESV) method. From the morphology and structure characteristic of as-prepared energetic microspheres, it is found that the HMX@TPEE energetic microspheres have uniform spherical morphologies, narrow size distribution and honeycomb coating structure under the circumstance of compound emulsifiers and appropriate core-shell ratio. The good toughness of HMX@TPEE microspheres in Brazilian test and dynamic mechanical analysis (DMA) demonstrates a new route to enhance interface interaction between HMX particles and TPEE matrix. Moreover, because of the favorable energy-decentralizing property of this exotic honeycomb structure, the sensitivity of HMX@TPEE microspheres measured by BAM impact sensitivity instrument can be markedly decreased and the impact energy ($\boldsymbol{E}_{li}$) can be improved from 3.5 J to 8.0 J at the HMX/TPEE ratio of 5/1. This fabrication of HMX@TPEE microspheres with adjustable coating content via a facile ESV process might provide a promising approach for HMX based energetic composites to enhance the safety and toughness properties when used in advanced weapon system.

1. Introduction

Energetic crystal is an important class of organic functional material, which contains large amounts of chemical energy in its molecule and can rapidly react and release abundant amounts of gases and heat [1,2]. These crystals are applied extensively to civil as well as military affairs. The safeties, mechanical and thermal properties of energetic materials are several vital properties, which may restrict their application in many fields. For example, energetic crystals are very sensitive to external stimuli (e.g., impact, friction, and thermal), causing a common hazard in the manufacture, storage and use procedure, often results in many catastrophic explosions [3]. As a result, much interest has been generated on how to reduce the sensitivity of energetic crystals. One way to reduce the sensitivity towards the external stimuli is to control the morphology to spherical or cubic shape [4]. Furthermore, surface coating has been another important technology to reduce the sensitivity of explosives [5].

For decades, various alternative methods have been developed for the coating of energetic crystals [6], including conventional water slurry coating [7], crystallization coating [8], spray-drying coating [9], and in situ polymerization coating [10]. However, these processes are subject to a number of problems related to their sensitivity and stored energy. Many research results indicated that when nitroamine explosives were coated with some inert materials [11–13], the mechanical sensitivity could be reduced, whereas there are still some deficiencies need to be improved. Firstly, the interfacial action between inert material and explosive is not strong enough, which may cause some pores at the interface of different components. Secondly, the coverage on the explosive surface is

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insufficiently high. Thirdly, the strength of coating layer is relatively weak, so the functional structure would be destroyed when this material undergoes some external mechanical impact. Finally, sometimes the coating materials maybe deposit solely from the solution, no effective coverage can be formed on the surface of explosive. Therefore, enhancement of the interfacial properties through coating is a very difficult thing and research hotspot.

The fracture toughness is an important material property. In classical fracture mechanics, the J-integral has been widely used as a fracture characterizing parameter in macroscale mechanics to measure materials inherent resistance to crack growth [14]. The fracture energy or toughness is the sum of the fracture energy at all the scales where fracture is taking place. However, the conventional methods are unable to precisely measure the J-integral of polymer composites at the nanoscale. Many researchers are devoted to develop the effective calculation method for predicting the J integral of polymer composites. For example, M. Silani and T. Rabczuk presented some modified simulation method to predict the fracture behavior of reinforced polymer composites via quantitative studying the strength and J-integral versus its composition, which can help to achieve a successful design and characterization of the nanocomposites [15,16]. From the point of view of fabrication for composites, the interface is of great importance to the final properties [17]. Actually, almost all the issue about composite materials can be ascribed to interfacial issue. It is a vital importance to improve properties of composites by enhancing the interface interaction between energetic crystal and polymer matrix. Although surface modification is a commonsensible method for particles, its adhesion efficiency is not always enough. A universal reason which cause the performance of composites to be inadequate excellent is that the surface coverage is dissatisfactory by reason of the poor interface interaction. Therefore, novel coating techniques for energetic crystal should be explored to essentially transform the mode of interfacial contact.

Nowadays, a spherical composite particle gets more attention because of its profitable processing performance and lower mechanical sensitivity [18]. Emulsion solvent evaporation (ESV) method is an effective way to prepare spherical particles, and the process parameters are easy to control [19–21]. Polymer microspheres generated by this method have attracted increasing interests in modern science and technology, due to their diverse potential applications such as catalysis, delivery and controlled release, microcavity resonance and contaminated waste removal [22–26]. But few works about the forming and properties of polymeric microsphere containing energetic crystals via ESV method have been investigated. This method employs generally an oil-in-water system in which the emulsifiers are usually required. The polymer is dissolved in a suitable water immiscible solvent, and the energetic crystal is dispersed in this polymeric solution. The resultant dispersion is then emulsified in an aqueous continuous phase to form discrete droplets. As solvent evaporates, the polymer in droplets hardens and free flowing microspheres are obtained after suitable filtration and drying. Obviously, the merit of this method is that the interface interaction between energetic crystals and polymer can be definitely improved as compared with traditional water slurry method. As for water slurry coating, the surface of energetic crystal is directly contacted with water, then polymer molecule precipitates into water phase and adheres onto the crystal surface via weak physical adsorption. Whereas in ESV method, energetic crystal firstly contacts with polymer molecule, followed by a plenary interaction in oil solution, which mean the crystal surface is saturated adequately by polymer solution. Additionally, the stable emulsion droplets in ESV can afford dispersive coating microspheres, but the coating particles in slurry method are difficult to avoid aggregation.

The organic nitramine 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), is a representative energetic crystal that is widely used in explosive composites and propellants [27]. Thermoplastic polyester-ether elastomer (TPEE) is a segmented copolymer with hard and soft segments as repeating units in the main chain (molecular structure shown in Fig. 1). Due to its favorable mechanical properties (e.g., elongation at break, tear strength, tensile strength, and abrasion resistance) [28], TPEE has already been proven providing beneficial performances for a wide variety of applications in automotive, electronics and various other industrial field. However, few works have reported the use of TPEE coating on the energetic materials, such as HMX crystal.

Herein, we demonstrate a general and facile approach to distribute energetic crystals into the polymer microsphere through an ESV method. A simple oil-in-water emulsion of energetic crystals-TPEE solution dispersing in an aqueous solution following by solvent evaporation can lead to the spontaneous deposition of TPEE film on the microspheres. Systematical structure characterizations on the HMX@TPEE energetic microspheres indicated favorable spherical morphology with high quality coverage. The present work potentially provides a novel method for the fabrication of spherical composites. Interestingly, a significant desensitization effect and visibly improved toughness on the impact of microspheres were also achieved through the honeycomb-like coating structure.

2. Experimental

2.1. Materials

As for thermoplastic polyester-ether elastomer (TPEE, molecular weight 10,000), which is composed of polybutylene terephthalate (PBT) as hard segment, and polytetramethylene glycol (PTMG) as soft segment (Fig. 1), was purchased from Sunshine Plastics Co., Ltd. (Sichuan, China). HMX, fine particles (mean size 25 μm), were purchased from Yingguang Chemical Industry Group Co., Ltd. (Gansu, China). Poly (vinyl alcohol) (PVA-1788, average degree of polymerization 1,700, degree of hydrolysis 88%), which was provided by Sinopec Sichuan Vinylon Works (Chongqing, China), was used as a stabilizer for water phase. Sodium dodecylbenzene sulfonate (SDBS) and nonaphenol polyethyleneoxy ether (OP-10) of biochemical grade, purchased from Tianjin Kermel Chemical Reagent Ltd. (Tianjin, China), were selected as emulsifiers of the water phase. Besides, dichloromethane (DCM, AR) was obtained from Tianjin ZhiYuan Reagent Co. Ltd. (Tianjin, China). Considering the other reagents, they were of analytical grade and used without further purification.

2.2. Preparation of energetic HMX@TPEE microspheres

Energetic HMX@TPEE microspheres were prepared by the above oil-in-water emulsion solvent evaporation (ESV) method, including an oil-in-water emulsion and of organic solvent evaporation process (Fig. 2).

First, stabilizer polyvinyl PVA, emulsifier SDBS and OP-10 were dissolved into deionized water, their concentration were 2.0 wt-%, 2.0 wt-% and 1.0 wt-%, respectively. The water phase (W) was formed by blending stabilizer and emulsifier solution. In this process, DCM was used as organic solvent because it was good solvent for TPEE and its low boiling point enable it can be easily removed by evaporation. In addition, HMX with narrow size distribution was used as a core material in order to improve the conventional process via the assistant of ultrasonic. Thus, an oil phase (O) can be achieved. Next, these two phases were mixed and homogenized at a stirring rate of 1000 rpm for 3–5 min by using a high-speed