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Original scientific paper

An SEM and EDS study of the microstructure of nitrate ester plasticized polyether propellants

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Abstract: To probe the microstructures of nitrate ester plasticized polyether (NEPE) composite propellants and observe the morphology of each constitute in the propellant, the microstructure and elemental constitutes of NEPE propellants were investigated using scanning electron microscopy and energy dispersive X-ray spectroscopy. The ammonium perchlorate (AP) grains had a scraggy surface and were difficult to disperse uniformly. The compatibility between the AP grains and the polymer binder was poor, especially for large grains. The size distribution range of the AP and octogen (HMX) grains in propellants varied from several to several hundreds μm for the former while for the latter from several to several tens μm. Contrasting images before and after dissolution the propellant in trichloromethane showed that at the degree of crosslinking of the polymer binder was low since non-crosslinked binder on the surface areas was easily removed by the solvent, and that the plasticizer was near the HMX grains and contributed more O to the element analysis of HMX.

Keywords: composite solid propellants; scanning electron microscopy; microstructure; element analysis.

INTRODUCTION

NEPE (nitrate ester plasticized polyether) propellants are a type of highly energetic, composite solid propellant.[1–3] This type of propellant uses a polyether polymer binder, such as polyethylene glycol (PEG) or ethylene oxide (tetrahydrofuran-co-polyether), and a plasticizer of mixed nitrate (BG), usually using nitroglycerin (NG) and 1,2,4-butanetriol trinitrate (BTTN).[4–6] The balance of the propellant consists of large amounts of solid grains, including aluminum powder (Al), octogen (HMX), ammonium perchlorate (AP), *etc*. The interactions between the polymer binder and the other constituents, which are mostly inorganic, are not good. However, after crosslinking, the polymer binder can wrap all the

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solid grains as shown in a previous study.[7] This type of propellant integrates the advantages of double-base propellants and composite propellants, and adds excellent low temperature mechanical properties.[8,9] Therefore, this type of propellant has been studied extensively and applied broadly in many countries since its first development in the USA in the 1970s.[10–12] However, the microstructure of the propellant, which decisively affects its performance, has hitherto not been clearly investigated.[13–15] In this study, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were employed to directly observe the micro-morphology and distribution of the constituents in the propellant, whereby a detailed understanding of its special microstructure was obtained.

EXPERIMENTAL

The microstructure of NEPE solid propellant, which was taken from a rocket, was observed using Hitachi S-4500 and S-6301 scanning electron microscopes (Japan). The grains in the SEM figures were measured using the measuring tool incorporated into Imagenet 2000 software. The elemental constitutes of a small area were analyzed using an Inca energy dispersive X-ray spectrometer (The Netherlands) combined with the S-6301 microscope. The samples were sprayed with gold for 5 minutes before observation.

The main constitutes of the NEPE propellants by mass percentage were: PEG, 6 to 9; BG, 15 to 21; Al, 19; HMX, 43 and AP, 8. The content of some other auxiliary agents were about 1–2 %. The analytical reagent trichloromethane was used to extract the plasticizer from the NEPE propellants.

RESULTS AND DISCUSSION

SEM Analyzes for Al and AP in NEPE propellants

In the NEPE propellants, the polymer binder PEG is the continuous phase while solid grains, such as Al, AP and HMX, are dispersed in the PEG. By the process of elimination, if the morphologies of any two among three kinds of solid grains are determined then the remaining kind of solid grain is also identified. Hence, first the microstructure of two raw materials, AP and Al, were observed, as shown by the images in Fig. 1. HMX was not selected for direct observation since these grains in the propellant are covered closely by bonding agent, making it difficult to obtain their real morphology.

An SEM image of several AP grains is shown in Fig. 1a. This image clearly shows that most of AP grains are anomaly shaped with a size from approximately 100–300 μm, with a few even smaller grains. The SEM image in Fig. 1b is zoomed in on a single AP grain which exhibits a dense, small protuberance on its surface. This grain has the characteristic of a scraggy morphology. Elemental analysis using EDS was performed on this same grain to determine its composition: N:O:Cl is 17:56:15 (the element H cannot be determined), which basically conforms to the molecular composition of AP (NH_4ClO_4). The SEM image in Fig. 1c shows several Al grains with not only ellipsoid shapes but also spherical shapes.[15] The size of the Al grains was mostly below 15 μm, with a wide size distribution.

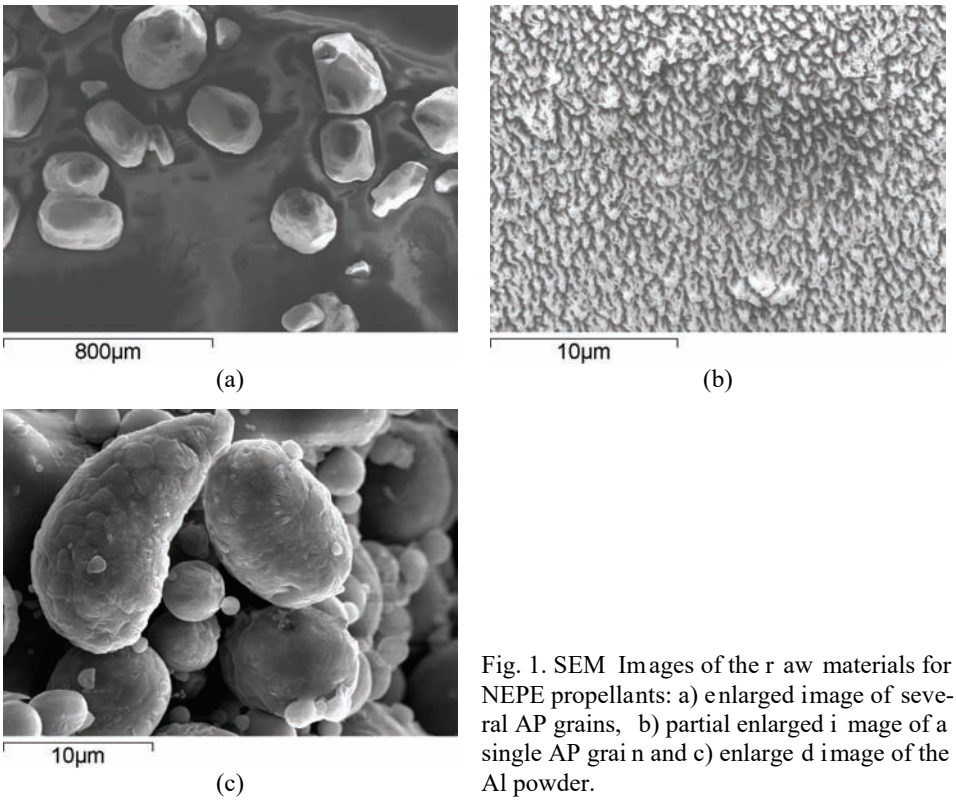
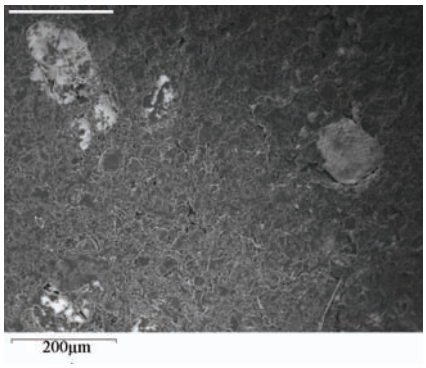


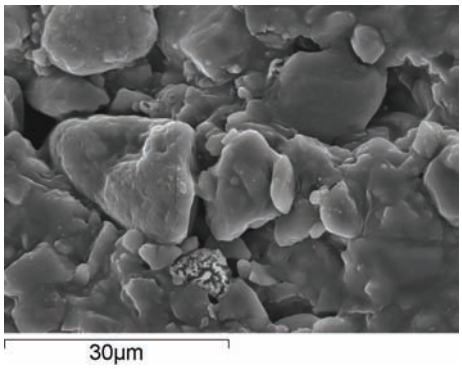
Fig. 1. SEM Images of the raw materials for NEPE propellants: a) enlarged image of several AP grains, b) partial enlarged image of a single AP grain and c) enlarged image of the Al powder.

The microstructure of the NEPE propellant was observed using SEM (Fig. 2). The wide-angle SEM image of the NEPE propellant sample in Fig. 2a clearly shows that the large grains are AP due to both their scraggy morphological characteristic and their relatively large size. The spatial distribution of this kind of grain is uneven since four can be seen located close to the top left corner of the image while none is seen in the middle. Two AP grains, the top left and the bottom ones, are obviously cracked. This cracking likely occurred during cutting the propellant using a knife to obtain the SEM samples. From the distribution of AP grains in this image, it can be inferred that the large AP grains are difficult to disperse evenly. The SEM image in Fig. 2b is zoomed in to show a smaller area of propellant. Almost all the solid grains (no bigger than approximately 30 μm) are covered with polymer binder. Only one solid grain, in the lower part of the Fig. 2b, is exposed and its surface is scraggy — perhaps a small AP grain or a corner of large one. An SEM picture of a single AP grain in the propellant is shown in Fig. 2c. Obviously the surface of this AP grain has two kinds of morphology: grooves on the left and protuberances on the right. The right morphology, grooves, is the same as those of the raw AP material. The possible reason for the two

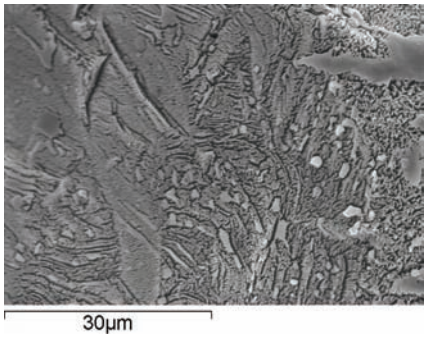
kinds of morphology appearing simultaneously is that an AP grain, as a crystal, has several surfaces of which two of them appeared in this observation area. Different observation angles showed different morphologies. The three images in Fig. 2 show the poor compatibility of AP (especially the large grains) with the polymer binder in this propellant, since only AP grains were visible, the other solid grains being covered with binder. A further easy deduction is that the bad compatibility will result in the AP grains being the point of stress concentration within the propellant. Thus, the mechanical performance of the propellants could be improved by improving the compatibility between the AP grains and the polymer binder, possibly by using a bonding agent.



(a)



(b)



(c)

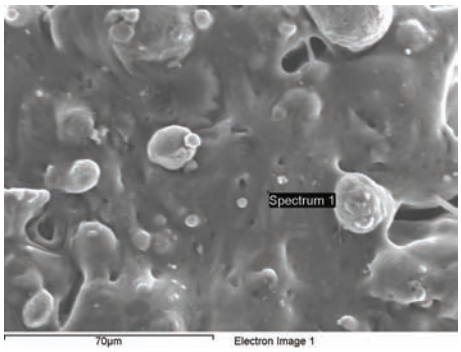
Fig. 2. SEM Images of the original NEPE propellant: a) image of a large area of the propellant, b) image of a small area of propellant and c) image of a partial AP grain in the propellant.

SEM and EDS analyses of NEPE propellants

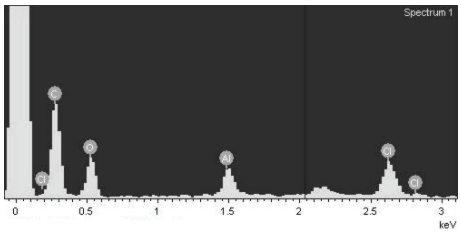
According to the formulation of NEPE propellants, most of the solid grains in Fig. 2b should be HMX. However, the ellipsoid Al and small AP grains could possibly be covered with polymer binder, which is an additional difficulty in ascertaining whether or not a certain grain is HMX. In order to assure the material attributes of a grain in NEPE propellants and to determine the dimension distri-

bution of HMX grains, elemental analysis using EDS combined with the S-6301 SEM was performed on a few of the solid grains and some polymer binder areas.

First, a planar area to make element analysis was selected where the polymer binder seemed to be the main component, Fig. 3a. The mini cross in the image is the center of the area selected for spectrum analysis. The EDS results are listed in Table 1 and shown by Fig. 3b. Al and AP grains were possibly located under the binder area, explaining the small content of the elements Al and Cl in these results. In this area, the constitute ratio of C:O was about 69:25, which is larger than expected for the PEG polymer, the segment molecular formula of which is C_2H_4O. The deviation in the element C content possibly arises from SEM instrumental error, as about 12 % C, was also measured in the element constitute results for pure AP and Al grains.



(a)



(b)

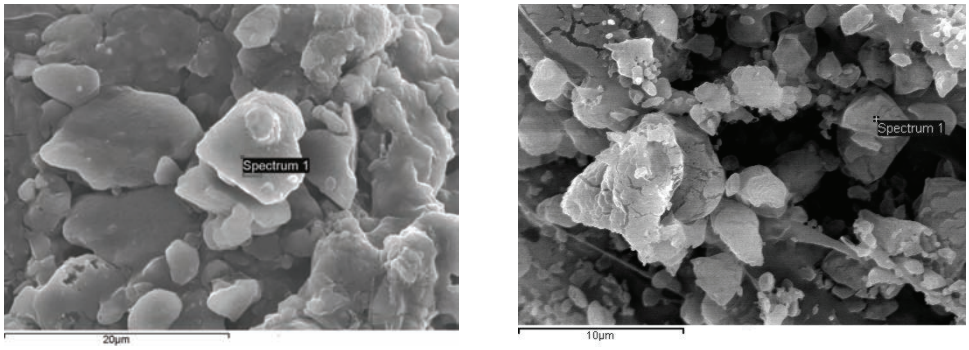
Fig. 3. SEM Image of the NEPE propellant for EDS element analysis: a) binder area; b) spectrum of the analysis.

TABLE I. Element content of the binder determined by EDS analysis

Element	Content, mass %	Content, at. %
C	59.18	69.44
O	28.69	25.27
Al	3.74	1.95
Cl	8.39	3.34

Second, a medium-sized grain having an anomalous shape, as shown in Fig. 4a, was analyzed. Elemental composition was approximately C:N:O = 10:7:8. The molecular formula of HMX is $C_4H_8N_8O_8$, while the formula of NG and BTTN are $C_3H_5O_9N_3$ and $C_4H_7O_9N_3$, respectively. With no Cl or Al evidenced and further with the ratio of the elements N and O nearly 1:1, this solid grain can be confirmed to be HMX. The content of element O is slightly high in the results, possibly because liquid plasticizer near the HMX grain contributed more elemental O. To confirm the above hypothesis, a NEPE propellant sample was left in $CHCl_3$ for 10 days in order to extract the plasticizer. Then another EDS analysis performed on a solid grain, as shown in Fig. 4b. The elemental composition re-

sults for C:N:O was approxim ately 43 :27:27. The elem ent C content was very high. Possible reasons are the SEM instrument and the bondi ng agent which contains a relatively large am ount of elem ent C, coating the HMX grains. The ratio of N:O was 1:1 in these elemental composition results, proving the correctness of the above hypothesis. The plasticizer w ould be near the HMX grain and would contribute a large amount of element O to EDS analysis results. Comparing images in Figs. 4a and 4b, clearly the pol ymer binder covering the solid grains was lower in Fig. 4b, indicating that the degree of crosslinking of the polymer binder was low and that some uncrosslinked polymer binder was dissolve by the $CHCl_3$.



(a) (b)

Fig. 4. SEM Images of middle size grains for EDS element analysis: a) NEPE propellant; b) after soaking in $CHCl_3$.

In Fig. 5, the large grain and the sma ll white one below it were con firmed to be HMX usi ng EDS ele ment analysis. Cracks on th e surfa ce of t he large HM X grain were th e result of the high veloci ty electron i mpulse when observing th e microstructure. The dim ensions of the l arge and sm all HMX grains can be estimated as about 30 and 4 μm, respectively, illustrating that the size distribution of the HMX grains was broad, from several to several tens of μm.

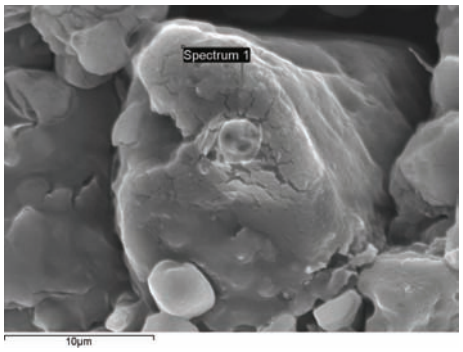


Fig. 5. SEM Im age of one la rge grain i n th e NEPE propellant.

Using the same element analysis method, the small grain marked in Fig. 6 and the other small grain, close to the left of the marked one, were determined to be HMX and AP, respectively. The three spikelet in the left part of the image were the result of image distortion because when observing microstructure the polymer binder tended to flow under the action of the high velocity electrons or the electrical conductivity was bad in this area. Contrasting this image with those in Figs. 2 and 3, it is apparent that the polymer binder covered the small grains more easily than the large ones, especially the large AP grains. Another conclusion is that the size range of the AP grains was larger than that for the HMX grains, being from several to several hundreds μm in size.

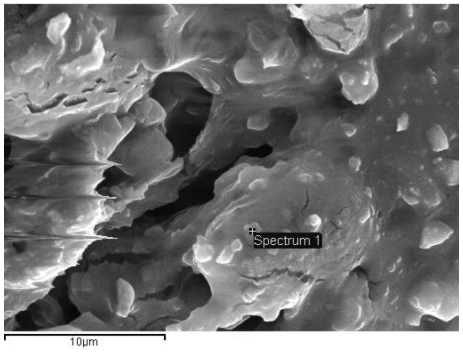


Fig. 6. SEM Image of a small grain in the NEPE propellant.

CONCLUSIONS

The microstructure morphology of AP grains observed using SEM was either dense, small protuberances or groove anomalies on the grain surface. The size distribution range of the grains was wide, from several tens to about 300 μm. The shape of the Al grains varied widely and their size was predominately less than 15 μm, with a broad distribution. Observations of the NEPE propellant using SEM evidenced that the distribution of the large AP grains was not uniform or regular, and that compatibility between the AP grains and the polymer binder was poor, making the AP grains points of stress concentration if the propellant were to be subjected to stress.

The elemental composition of the material in the NEPE propellants was determined using EDS element analysis, enabling the material attributes of the grains and binder to be established. The size range of the HMX grains in these propellants, confirmed using EDS, was from several to several tens of μm. By using $CHCl_3$ to extract the plasticizer from the NEPE propellants, with before and after element analysis, the plasticizer was shown to lie very close to the HMX grains. The contrasted microstructure images allowed the deduction that the degree of cross-linking of the polymer binder in the NEPE propellants is low and that the uncross-linked binder on surface parts can be readily dissolved by solvents.

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ИЗВОД

SEM И EDS СТУДИЈА МИКРОСТРУКТУРЕ ЕКСПЛОЗИВА НА БАЗИ НИТРАТНИХ ЕСТАРА ПЛАСТИФИКОВАНИХ ПОЛИЕТРИМА

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За анализу микроструктуре композитних експлозива на бази нитратних естара пластификованих полиетрима (NEPE) као и морфологије и елементарног састава појединачних компоненти, коришћене су скенирајућа електронска микроскопија (SEM) и спектроскопска анализа карактеристичног рентгенског енергетског зрачења (EDS). Анализа је показала да зрна амонијум-перхлората (AP) имају неравну површину и да нису равномерно распоређена по узорку. Компатибилност између AP зрна и полимерне матрице је веома лоша што је нарочито изражено код већих зрна. Ширина расподеле величине зрна је била за AP и (HMX, експлозиви високе температуре топљења) у опсегу од неколико до неколико стотина μm, односно од неколико до неколино десетина μm. Анализа слике пре и после растварања експлозива у трихлорметану је показала да су брзина и степен реакције умрежавања полимерног везива мали, и то на основу чињенице да је неумрежено полимерно везиво лако уклоњено са површине зрна. На основу елементарне анализе и повећаног садржаја кисеоника закључено је да се полиетарско везиво налази на површини HMX зрна експлозива.

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