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A study on the microstructure of a nitrate ester plasticized polyether propellant dissolved in HCl and KOH solutions

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Abstract: Understanding of how the properties and performance of nitrate ester plasticized polyether (NEPE) propellants relate to microstructure is complicated by numerous components that have different characteristics. One approach to alleviating these complications is to observe a microstructure that has lost one or several components. This article examines the dissolution process, mass loss and change of the ion concentration of propellants in acid and alkali solutions. A scanning electron microscope was used to observe the dissolved residual of the propellants. The results revealed that the main constituents of NEPE propellant have different dissolving properties in solutions of HCl and KOH. By monitoring the dissolution process of NEPE propellant in HCl and KOH solutions, it was found that the microstructure of the propellant is generally compact and the polymer binder not only binds all the other components, but also protects the inner part of the propellant in solution.

Keywords: NEPE propellants; microstructure; interfaces; scanning electron microscope (SEM); swelling.

INTRODUCTION

Nitrate ester plasticized polyether (NEPE) propellants are high-energetic composite solid propellants that use a polyether, such as polyethylene glycol (PEG) or an ethylene oxide–tetrahydrofuran co-polyether, as a polymeric binder, and mixed nitrates (BG), usually 1,2,4-butanetriol trinitrate nitrate (BTTN) and nitroglycerin (NG), as plasticizer. Large amounts of solid particles, such as aluminum powder (Al), octogen or cyclotetramethylene-tetranitramine (HMX) and ammonium perchlorate (AP) are contained in the propellants.^{1,2} This type of propellant integrates the advantages of double-base propellants and composite pro-

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pellants, and adds excellent low temperature mechanical properties. Therefore, this type has been studied extensively and applied broadly in many countries since it was first developed in the USA in the 1970s.^{3,4} However, the microstructure of the propellant, which decisively affects its performance, has not been clearly studied.⁵⁻⁷ To obtain more energy or decrease the sensitivity of a NEPE propellant, it is necessary to obtain detailed characteristics of the microstructure of the propellant in advance. An NEPE propellant is a kind of composite containing many components. Through the study of solution processes and the specialty in different solvents, the state of different materials in the composite can be deduced. This is another way to obtain knowledge about the structural characters of a composite besides direct observation. Based on a former study concerning the microstructure and dissolution differences of a NEPE propellant in water and trichloromethane,⁸ the present article sequentially studies the dissolution differences of the propellant in HCl and KOH solutions and examines the dissolution peculiarities of different components of the propellant. Through these studies, it was expected that the microstructures of the propellant could be understood more thoroughly.

EXPERIMENTAL

The main constituents of the studied solid propellant, which was taken from a rocket, were PEG, BG, Al, HMX and AP in the approximate mass percentages 6–9, 15–21, 19, 43 and 8, respectively. The content of the other auxiliary agents, such as the crosslinking agent, was about 1–2 %.

The HCl and KOH employed in the dissolution experiments were analytically pure reagents. All the water used in the present study was distilled water.

The concentrations of NH_4^+ , Al^{3+} and AlO_2^- in the HCl and KOH solutions were measured using a Metrohm 761 Compact Ion Chromatograph (IC) (Switzerland) and Varion Vista-MPX inductively coupled plasma-atomic emission spectrometer (ICPES) (USA).

The microstructure of the NEPE was observed using a Hitachi S-4500 scanning electron microscope (SEM) (Japan). The samples were sprayed with gold for 5 min before observation.

RESULTS AND DISCUSSION

Solubility of the NEPE propellant in HCl

Concentrated HCl (36.5 %) (10 ml) was diluted with water (40 ml) in a beaker; five NEPE propellant samples, each about 2 mm×2 mm×1 mm, were put into the diluted HCl. Five days later, the samples had broken up into a powder. A translucent film had appeared on the bottoms of the beakers. Some small bubbles were observed in the film and small dust-like particles floated on the surface of the solutions. The powders were observed with the SEM; the morphology is shown in Fig. 1. For comparison, the SEM microphotograph of original NEPE propellant is presented in Fig. 2.⁸

Comparing Figs. 1 and 2, it is apparent that only solid particles were stacked in Fig. 1, while a film covered almost all the solid particles in Fig. 2. This phe-

nomenon can be attributed to the fact that the polymer binder in the NEPE propellants broke down into small molecules, such as ethylene glycol, in the HCl solution. After the polymer chains had decomposed into fragments, the solid particles, such as AP, HMX and Al, which had been bonded by the chains, fell to pieces and then became powder. The dust particles on the solution surface may be very small solid particles that had a relatively large specific surface area. These small particles collected together and floated on the liquid surface because they were subjected to strong surface tension. To confirm this deduction, some Al powder was put into dilute HCl. A little Al powder floated on the surface even after vigorous shaking, which validates the above supposition. The solid component HMX is a chemically stable material that generally does not react with dilute HCl or KOH at normal temperatures.⁹ The AP and Al particles can react with dilute HCl and dissolve into the solution:^{10,11}

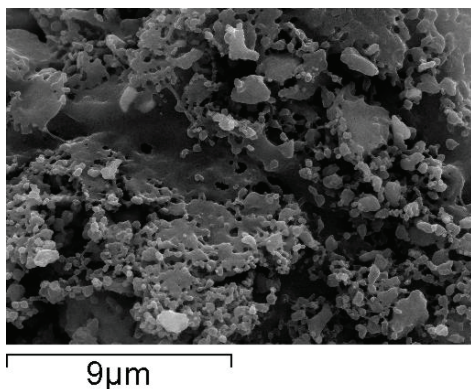
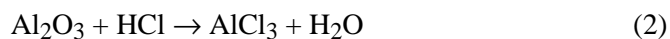
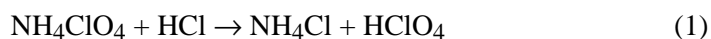


Fig. 1. SEM Image of the NEPE propellant powder treated with HCl solution.

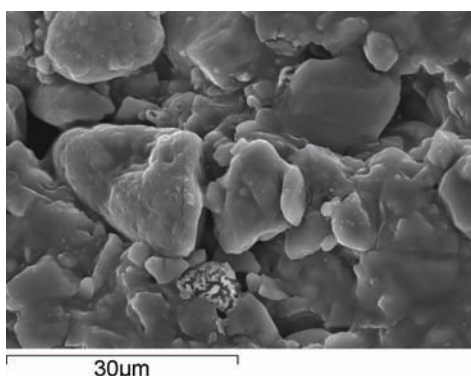


Fig. 2. SEM Image of the untreated NEPE propellant.

However, the quantity of these two reagents was large and the reactions are slow. As a result, at the end of the experiment, some of the AP and Al particles remained. For this reason, Fig. 1 shows small balls (Al), particles with a scraggy surface (AP) and numerous middle-size particles (HMX).⁸ The densities of the liquid plasticizers NG and BTTN are both greater than water. In addition, the plasticizers both are barely dissolved in water and HCl, hence they formed a translucent film at the bottom of the beakers. As some components react with HCl and produce gases such as H₂, some mini bubbles appeared in the film.

Information about the mass loss of a composite material in solution will reflect to some extent the microstructure of the composite, especially when the components have specific solubility in different solutions. The mass loss experiment with NEPE propellants in dilute HCl was performed as follows:

1. The propellant was cut into samples about 2 mm×1.5 mm×1 mm, weighed, and put into 5 weighing bottles.
2. Five ml 0.042 mol L⁻¹ HCl was put into each bottle.
3. The solution was poured out from each bottle after a certain interval.
4. The bottles with their remaining solution were dried at 30 °C for 24 h.
5. The residues were weighed and the mass losses were calculated and the results are shown in Fig. 3.

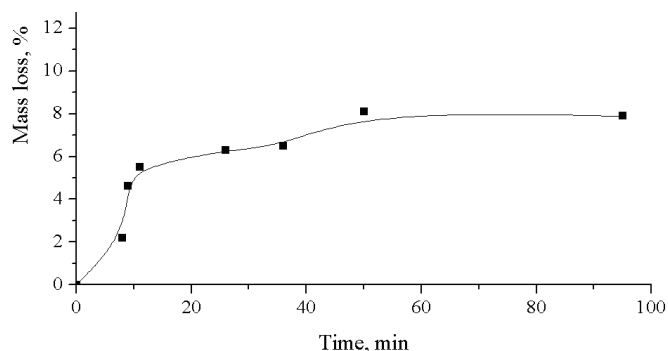


Fig. 3. Mass loss curve of the NEPE propellant soaked in dilute HCl.

From the mass loss curve in Fig. 3, it can be seen that at the initial stage (about 0–10 min) the propellant dissolved very quickly. During the second period (about 10–50 min), the dissolution slowed. Finally, after about 50 min, almost no components were dissolving. Considering the previous solubility of the components NEPE propellants in more concentrated HCl, the reason for the mass loss curve may be that when the small propellant particles are put into dilute HCl, the AP and Al on the surface dissolve quickly, but the polymer binder reacts with the HCl very slowly. About 10 minutes later, the inner AP and Al begin to dissolve, but the outer binder forms a protective covering that blocked the reaction of the

inner AP and Al with the HCl; hence the mass loss became slower and slower. By the end of the process, the dissolution reached a balance.

To examine the solubility of large NEPE propellant samples in dilute HCl, a 9.7 mm×10 mm×10.5 mm propellant cube was put into 500 ml 0.042 mol L⁻¹ HCl solution. The solution was stirred continuously and 1 ml aliquots were taken at intervals to measure, using the IC and ICPEs, the concentration of NH₄⁺ and Al³⁺ in the solution. The results are shown in Fig. 4.

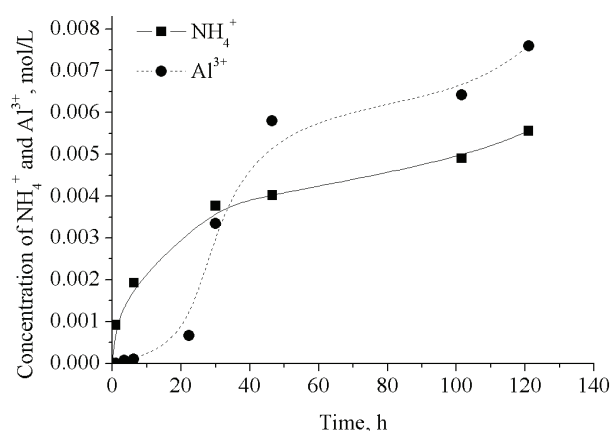


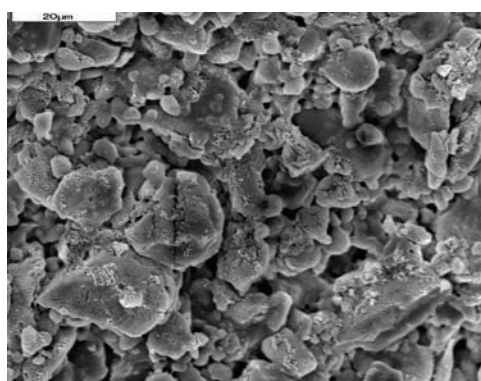
Fig. 4. Curves of the change in the concentrations of NH₄⁺ and Al³⁺ in dilute HCl with time.

From Fig. 4, it is apparent that the curve of NH₄⁺ concentration increased rapidly because the AP readily dissolved in the HCl solution. After the outer AP had dissolved, the rate of increase of the NH₄⁺ concentration slowed, illustrating that the polymer binder in the outer part blocked the HCl solution from entering the propellant. In contrast, the curve of the Al³⁺ concentration in Fig. 4 can be divided into three stages. During the first stage (about 0–20 h), the increase of the Al³⁺ concentration was slow. The reason may be that there was an oxide film on the Al surface, which reacted with HCl slowly and protected the inner Al. Thus, after the oxide film had been dissolved, the inner Al reacted rapidly with the HCl. As a result, the concentration of Al³⁺ increased very rapidly in the second stage (about 20–50 h). After the AP and Al in the surface layer of the propellants had dissolved, the polymer binder reacted with the dilute HCl very slowly and became a protective cover to the inner contents. The binder cover blocked the penetration of HCl into the propellant; for this reason, at the third stage (after about 50 h), the concentration of both Al³⁺ and NH₄⁺ increased slower and slower.

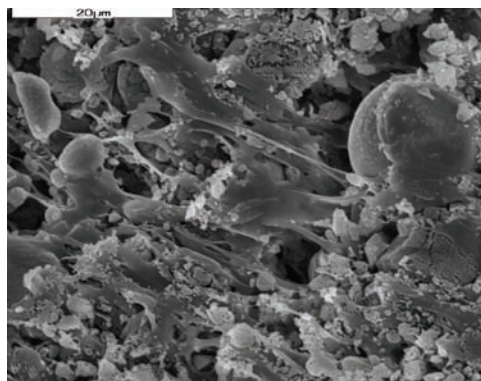
Solubility of the NEPE propellant in KOH solution

Similar to the experiment of NEPE propellants dissolved in HCl, a 2 mm×2 mm×1 mm NEPE propellant sample was put into 0.022 mol L⁻¹ KOH solution. The sample floated in the solution just under the surface of the liquid. About 24 h

later, a corner of the sample appeared to swell, and some mini blobs appeared on the sample. Four days later, the outer layer of the sample became translucent, like a gel. The color of the solution became yellowish. Six days later, the whole sample had swelled, and some mini pores could be observed on the surface of the sample. Some particles were suspended in the solution and the yellowish color deepened. After fourteen days, the sample was taken out, dried, and observed by SEM. The results are shown in Fig. 5.



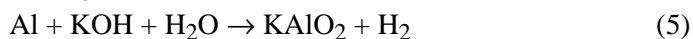
(a)



(b)

Fig. 5. SEM images of the NEPE propellant soaked in KOH solution, a) surface of the sample; b) interior of the sample.

The propellant sample may have a relatively strong surface tension in alkaline solutions, hence the sample floated in the solution near the surface. Initially, the polymer binder absorbed water and swelled, and then it reacted slowly with the KOH. This was the cause of the swell. A few polymer binders appeared on the surface, as shown in the SEM image (Fig. 5a). Both Al and its oxide film Al_2O_3 can react with KOH and then dissolve in the solution:



Finally, the reactions created a flock of $\text{Al}(\text{OH})_3$ sedimentation. These suspensions in solution caused the slight amount of ball-like Al that can be seen in Fig. 5a. HMX and AP are crystals and perhaps react with KOH very slowly; hence, after the grey Al had disappeared, the outer sample became translucent. It can be seen from Fig. 5a that many big scraggy particles (AP) and small, smooth particles (HMX) appeared on the image.⁸ Due to the swell and the dissolution of some components, mini pores became visible on the surface of the sample. The plasticizers BTTN and NG are yellow oil-like liquids. They hardly dissolve in a dilute alkali solution at normal temperature, hence the solution did not immediately become yellowish. However, over a long time period, the plasticizer dissolved a little and then the solution became yellow. Comparing Figs. 5a and 5b, the difference is apparent in that there are more polymer binders and ball-like Al in Fig. 5b, although the sample plumped. Thus, it can be concluded that the Al components reacted with difficulty with KOH under these conditions.

The mass loss experiment of the NEPE propellant in KOH was performed in exactly the same manner as that in HCl. The results are shown in Fig. 6.

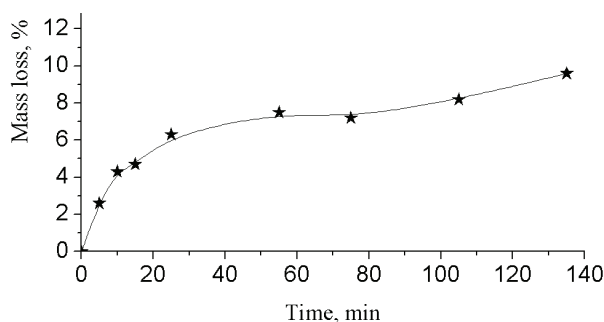


Fig. 6. Mass loss curve of the NEPE propellant soaked in KOH solution.

From the mass loss curve presented in Fig. 6, the dissolution process can be described as follows: when the small particles of propellants were soaked in KOH solution, the AP and Al on the surface layer of propellants promptly began to dissolve, hence the initial mass loss (about 0–20 min) was fast. Then during the following period (about 20–75 min) the dissolution proceeded more and more slowly. The possible reason was that the amount of AP and Al on the surface layer decreased on the one hand and the outer polymer binder blocked the KOH solution from entering the propellant on the other. However, because the propellant solution appeared to swell in KOH during the last period (after 75 min), the inner AP and Al began to dissolve again. The mass loss increased during the third stage.

The solubility of a cube of NEPE propellant (10 mm×10 mm×10 mm) in KOH solution was also examined in the same manner as in HCl. The change of the concentrations of NH_4^+ and AlO_2^- are shown in Fig. 7.

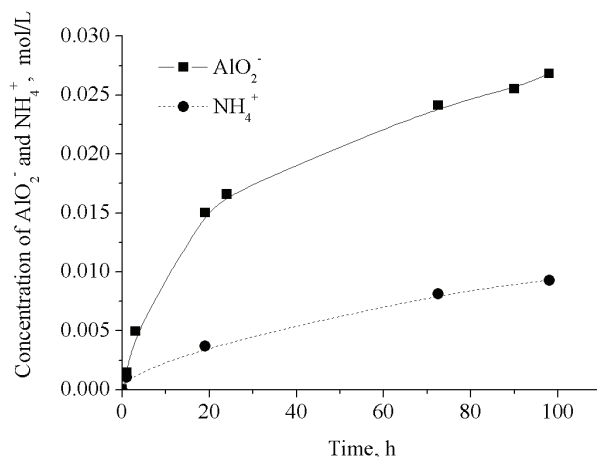


Fig. 7. Curve of the changes in the concentration of NH_4^+ and AlO_2^- in KOH solution with time.

Comparing Fig. 4 and Fig. 7, the change of the NH_4^+ concentration was different. The curve of the concentration of NH_4^+ in Fig. 7 is smooth and shows almost no major changes, while in Fig. 4, the curve changes abruptly during the initial stage, which illustrates that AP is a little difficult to dissolve in KOH. Another reason may be related to the swell of the sample, which allowed relatively greater contact between AP and the KOH solution. Thus, the amount of AP reacting with KOH changed little. The curve of AlO_2^- concentration in Fig. 7 is not like that of Al^{3+} in Fig. 4; it is rather like that of NH_4^+ in Fig. 4. This may be attributed to the fact that the oxide film on the surface of the Al particles reacted more easily than the inner Al with KOH. For this reason, the concentration of AlO_2^- increased faster during the initial 20 h than it did later.

CONCLUSIONS

From the results obtained in this study, the following conclusions can be drawn.

- i)* The NEPE propellant disaggregates in concentrated HCl. In contrast, it swells in a KOH environment, which leads to a loosening of the microstructure.
- ii)* The polymer binder does not react easily with HCl or KOH, and it forms a protective layer around the inner AP and Al particles. Hence the binder in the outer layer results in the interior of the propellant retaining an intact structure.
- iii)* The AP particles dissolve easily in dilute HCl or KOH solutions, while the Al powder has a better solubility in KOH solution than in HCl. The reason

may be that the oxide film on the Al surface is easier to remove in KOH solution than in HCl. The dissolution of the two materials would destroy the structure of the propellant.

iv) The dissolution mechanism of AP is different for big cubes of propellants in HCl and KOH. The swell of the propellant in KOH may be the main reason. More knowledge about the microstructure of the propellants may be obtained by comparing the solubilities of NEPE propellants in HCl and KOH.

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ИЗВОД

АНАЛИЗА МИКРОСТРУКТУРЕ ЕКСПЛОЗИВА НА БАЗИ НИТРАТНИХ ЕСТАРА ПЛАСТИФИКОВАНИХ ПОЛИЕТРИМА И ТРЕТИРАНИХ РАСТВОРИМА HCl И KOH

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Разумевање утицаја микроструктуре на својства и примену композитних експлозива на бази нитратних естара пластификованих полиетрима (NEPE) је веома компликовано јер се састоје од великог броја компоненти различитих карактеристика. Један од начина да се поједностави поступак изучавања микроструктуре је да се уклони једна или више компоненти из композита. У овом раду је приказан поступак растварања NEPE композитних експлозива, праћен губитком масе као и променом концентрације јона у киселој и базној средини. Скенирајућа електронска микроскопија (SEM) је коришћена за анализу микроструктуре у раствору преосталог композита. Резултати су показали да се основне компоненте композитних експлозива различито растварају у киселој и базној средини. Анализом процеса растварања NEPE композитних експлозива у HCl и KOH растворима је показано да је структура композита углавном компактна и да улога полимерног везива није само да повезује компоненте композита већ и да штити унутрашње делове честица у раствору.

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