Thermal Properties of Ammonium Dinitramide, Monomethylamine Nitrate and Urea based Ionic Liquid Gel Propellants

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Gel propellants have been recognized as future propulsion systems. Gel propellants are liquid fuels such as hydrazine, of which the rheological properties have been altered by the addition of gelation agents. Ammonium dinitramide (ADN) based energetic ionic-liquid propellants (EILPs) are expected to be used as replacements for hydrazine, which has high toxicity, and also for ionic liquid gel propellants (ILGPs). However, there have been few studies conducted on ADN based ILGPs. Here, ADN based ILGPs were prepared to obtain a better understanding of their thermal properties. The thermal behavior of the ADN based ILGP samples were measured using differential scanning calorimetry and the evolved gases were analyzed using thermogravimetry–differential thermal analysis with mass spectrometry. An ADN based ionic liquids (ILs) formed a gel using gelation agents of agarose and hydroxypropyl cellulose. The gas evolved from ADN based ILGPs was determined to be different from that from ADN based ILs due to reaction between the IL and the gelation agents.

Key Words: Gel Propellants, Ionic Liquid Propellants, Thermal Analysis

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADN</td>
<td>Ammonium DiNitramide</td>
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<tr>
<td>MMAN</td>
<td>MonoMethylAmine Nitrate</td>
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<tr>
<td>EILPs</td>
<td>Energetic Ionic Liquid Propellants</td>
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<tr>
<td>ILs</td>
<td>Ionic Liquids</td>
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<tr>
<td>EILs</td>
<td>Energetic Ionic Liquids</td>
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<tr>
<td>ILGPs</td>
<td>Ionic Liquid Gel Propellants</td>
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<tr>
<td>AMU</td>
<td>Ammonium dinitramide, Monomethyl amine nitrate and Urea</td>
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<tr>
<td>DESs</td>
<td>Deep Eutectic Solvents</td>
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<tr>
<td>HPC</td>
<td>HydroxyPropyl Cellulose</td>
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1. Introduction

Gel propellants have been recognized as future propulsion systems due to a reduced tendency to spill and the energy advantages they provide over solid and liquid propellants.1) Previous investigations have concentrated on gelled hydrocarbon fuels and oxidizers.2,3) Monopropellants such as monomethylhydrazine and unsymmetrical dimethylhydrazine have also been studied for use as gel propellants.8-10) However, hydrazine derivatives have high toxicity and handling of the liquid propellant is difficult and costly. To resolve this problem, much attention has been paid to the use of energetic ionic liquid propellants (EILPs).11-14) Ionic liquids (ILs) are composed of salts in a liquid state below 100 °C.15) ILs have attractive characteristics such as nonvolatility, and higher chemical and thermal stability than organic solvents.16) These characteristics can be easily tuned by changing the nature of the component ions. Many EILs have been synthesized and their characteristics have been investigated.11-14) However, it is difficult to produce EILs on a large scale in terms of their purification and isolation. Therefore, we have focused on deep eutectic solvents (DESs), which is one type of EIL, for application as EILPs. A DES is a fluid generally composed of two solid components. The preparation of EILPs from DESs is easier than with other EILs. Ammonium dinitramide (ADN) based EILPs are expected to be employed as a replacement for hydrazine. ADN is a highly energetic material, and many studies on ADN for use as a solid propellant have been reported.17-24) ADN forms DESs with monomethylamine nitrate (MMAN) and urea.25,26) A mixture of ADN, MMAN and urea (AMU) at a mass mixing ratio of 4/2/2 (AMU442) is a liquid at around 0 °C. The melting point is lower than that of hydrazine and vacuum specific impulse of AMU442 mixture is little higher than that of hydrazine.27) AMU631 mixture, which is a liquid at around 25 °C, has the highest specific impulse of AMU liquid mixtures.25-28) Although it has higher melting point than hydrazine, the vacuum specific impulse of AMU631 mixture is 1.2 times higher than that of hydrazine and density is 1.5 times as high as that of hydrazine.27) Therefore, ADN based EILPs are expected to be used for ionic liquid gel propellants (ILGPs). However, there have been few studies on
ADN based ILGPs. Therefore, ADN based ILGP samples were prepared to obtain a better understanding of the thermal properties of ADN based ILGPs. The thermal properties of these samples were measured using differential scanning calorimetry (DSC), and the gases evolved from the samples were analyzed using thermogravimetry–differential thermal analysis (TG-DTA) with mass spectrometry (MS).

2. Experimental

2.1. Materials

The ADN used in this study was manufactured by Hosoya Pyro-Engineering Co. Ltd. Japan. The MMAN was synthesized from a methylamine solution (40 wt%, Wako Pure Chemical Industries, Ltd. Japan) and nitrate acid (60 wt%, Wako Pure Chemical Industries, Ltd. Japan). Urea with a purity of 99% was manufactured by Wako Pure Chemical Industries, Ltd. Japan. Agarose (Wako Pure Chemical Industries, Ltd. Japan) and hydroxypropyl cellulose (HPC; Wako Pure Chemical Industries, Ltd. Japan) were selected for use as gelation agents with reference to previous studies. 1,29)

2.2. Sample preparation for ADN based gel mixture

To produce gel samples, AMU mixtures were first prepared. 200 mg samples of powdered ADN, MMAN and urea with two mixing ratios were prepared in glass vials. The mass mixing ratio for the AMU mixtures was 4/4/2 (AMU442) and 6/3/1 (AMU631). There samples were prepared in a glove box with a relative humidity of 20 RH%. To melt these samples quickly, they were kept in a constant-temperature oven at 50 °C for 24 h. After 24 h, the samples were left out at room temperature around 15 °C and at 20 RH%. We checked the state of these samples.

2.3. Thermal properties and evolved gas

The thermal properties of AMU442 mixture, AMU631 mixture, AMU442 mixture with agarose (AMU442/agarose), AMU442 mixture with HPC (AMU442/HPC), AMU631/agarose, and AMU631/HPC mixtures were characterized using sealed cell DSC (SC-DSC; TA Instruments, Q200). The DSC apparatus was calibrated for temperature and heat flow based on the melting of high-purity indium (99.99%) at a scanning rate of 10 K min⁻¹. For SC-DSC measurements, approximately 1.5 mg of sample was loaded into a stainless-steel container (SUS303), sealed in air and then heated from -30 to 400 °C at a rate of 10 K min⁻¹. We sampled gelation part from the mixture. For the AMU mixtures with and without gelation agents, the thermal characteristics and evolved gases were evaluated using TG-DTA (Rigaku TG/DTA-8120) connected with a MS instrument (Shimadzu GC/MSQP2010). 2 mg samples were heated from room temperature to 300 °C at a rate of 10 K min⁻¹ under helium flow (200 mL min⁻¹) in an open aluminum cell. The evolved gases were transferred to the MS by the helium carrier gas and analyzed. The mass spectrometer was operated in electron impact ionization mode with selected ion monitoring (m/z=16, 17, 18, 28, 29, 30, 43, 44 and 46) by reference to previous studies.25,30)

3. Results and Discussion

3.1. Sample preparation of ADN based gel mixture

Figure 1 shows the appearance of the AMU442 and AMU631 mixtures kept in sample vials at 60 °C for 24 h. The AMU442 and AMU631 mixtures shown in Figs. 1(a) and 1(b) are liquids, which is consistent with previous study. 29 Figure 1(c) shows that the appearance of AMU631 mixture cooled to approximately 15 °C for a few days after heat treatment. Needle-like crystals are formed in the liquid phase. The AMU442 mixture remained in the liquid state after cooling. Therefore, gelation agents were mixed with AMU631 mixture and the sample reheated to form a liquid phase. Agarose, which is a powder reagent, was easily dispersed in the AMU mixtures liquid mixture, whereas powdered HPC did not disperse but settled on the bottom as a lump. Figure 2 shows AMU and gelation agent mixtures kept at 60 °C for 24 h.

Fig. 1. Appearance of AMU mixtures.
(a) AMU442 and (b) AMU631 mixtures kept at 60 °C for 24 h, and (c) AMU631 mixture cooled to around 15 °C for a few days.

Figure 2 shows the appearance of the AMU442 and AMU631 mixtures with agarose and HPC gelation agents. Figures 2(a) and 2(c) show that the AMU mixtures with agarose are solids and contain many bubbles. The mixtures of AMU mixtures with HPC (Figs. 2(b) and 2(d)) contain two distinct layers. The upper layer is whitish and the lower layer is transparent. After stirring the mixtures, the upper layer forms a membrane and the lower layer forms a liquid with a fluidity similar to that for the AMU mixture. After cooling the sample to around 15 °C, needle-like crystals formed in the liquid phase of the AMU631/HPC mixture. These results indicate that the AMU mixtures form a gel when mixed with agarose, whereas those mixed with HPC only partially form a gel under these experimental conditions.
3.2. Thermal properties and evolved gas

Figure 3 shows DSC curves for ADN, MMAN, AMU442 mixture, AMU631 mixture and AMU mixtures with gelation agent mixtures. We sampled gelation part from the mixture. For the AMU442 mixture, three exothermic reactions are observed around 160, 270 and 310 °C. ADN and MMAN binary mixture which is mixed 1:1 of mass ratio shows roughly two exothermic peaks at 130-220 °C and 220-260 °C in sealed condition and second peak is derived from MMAN. It is considered that the first and second exotherms are derived from ADN and Urea or decomposition of Urea affect reaction onset temperature of MMAN. AMU631 mixture has two exotherms. Since the amount of Urea in the AMU631 mixture is lower than that of AMU442 mixture, reaction onset temperature of AMU631 mixture result from MMAN is lower than that of AMU442 mixture. The second peak of AMU631 mixture includes reaction of ADN and MMAN. Since the amount of Urea in the AMU631 mixture is lower than that of AMU442 mixture, reaction onset temperature of AMU631 mixture result from MMAN is lower than that of AMU442 mixture. The second peak of AMU631 mixture includes reaction of ADN and MMAN. Since the amount of Urea in the AMU631 mixture is lower than that of AMU442 mixture, reaction onset temperature of AMU631 mixture result from MMAN is lower than that of AMU442 mixture. The second peak of AMU442 gel mixtures occur at lower temperature than that of AMU442 mixture. Gelation agent may inhibit the effect of Urea on reaction onset temperature of MMAN. AMU631 mixture has two exotherms. Since the amount of Urea in the AMU631 mixture is lower than that of AMU442 mixture, reaction onset temperature of AMU631 mixture result from MMAN is lower than that of AMU442 mixture. The second peak of AMU631 mixture includes reaction of ADN and MMAN. The AMU442/agarose and AMU442/HPC mixtures show exotherms similar to AMU442 mixture around 160 °C. The second exotherm of AMU442 gel mixtures occur at lower temperature than that of AMU442 mixture. Gelation agent may inhibit the effect of Urea on reaction onset temperature of MMAN. The heat of the exothermic reaction for the AMU442 gel mixtures around 160 °C is lower than that for the AMU442 mixture due to the latter being fuel rich and the lack of ADN as an oxidizer. The exotherm onset temperatures for the AMU442 gel mixtures are lower than that for the AMU442 mixture. Therefore, agarose and HPC affect the exothermic reaction of MMAN in the AMU442 mixtures. No obvious changes associated with solidification or melting are observed for the AMU442/agarose and AMU442/HPC mixtures. The onset temperature for the first exotherm for AMU631/agarose mixture is higher than that for the AMU631 mixture. The onset temperature and heat of reaction for AMU631/HPC mixture are the same as that for AMU631 mixture. In the case of AMU631 mixture, agarose has a greater effect on the thermal behavior than HPC.

The DTA and TG curves for AMU442 and the AMU442/agarose mixtures are shown in Fig. 4. The thermal behavior of AMU442 mixture and AMU442/agarose mixture is different. The exotherm for AMU442/agarose mixture starts around 160 °C and accelerates around 190 °C. The endotherm observed for AMU442 mixture around 220 °C is not observed for the AMU442/agarose mixture. This result is different from the DSC result. The difference seems to be due to the open conditions and the sample mass. TG curves indicate that the mass loss rate for AMU442/agarose mixture is lower between 170 and 200 °C. AMU442 mixture was completely gasified, while AMU442/agarose mixture was gasified by 90% and formed a residue which is considered carbide of agarose.
The mass spectra in Fig. 5 show the average relative intensities of the ions generated from AMU442 mixture and AMU442/agarose between 150 and 250 °C, in which the m/z values are 16, 17, 18, 28, 29, 30, 43, 44 and 46. These values are attributed to the production of N2 (m/z = 28), N2O (m/z = 44, 30), NO (m/z =30, 46), NH3 (m/z = 17, 16), HNCO (m/z=43, 29), CO2 (m/z=44) and H2O (m/z = 18, 17). These gases have been reported as the major gases evolved during the reaction of AMU442 mixture.25,31) The mass spectrum for AMU442/agarose mixture indicates that H2O (m/z=18, 17) is the major evolved gas. H2O is considered to be formed by the decomposition of agarose and oxidation reaction between agarose and the oxidizer. Furthermore, the amount HNCO (m/z=43, 29) of AMU442/agarose mixture is less than that of AMU442 mixture. From the TG result and the oxidation reactions of the gases in the gel phase, it is assumed that gas fuel such as HNCO is difficult to evolve from a gel phase. These reactions produce H2O.

4. Conclusion

To obtain a better understanding of the thermal properties of ADN based ILGPs, AMU samples were prepared and thermal analysis of the samples was conducted using SC-DSC and TG-DTA-MS. During sample preparation, AMU442 and AMU631 mixtures with agarose as a gelation agent formed a gel state. On the other hand, HPC as a gelation agent only partially formed a gel with AMU mixtures under the experimental conditions. SC-DSC measurements indicated that agarose has a greater effect on the thermal characteristics of AMU631 mixture than HPC. TG-DTA-MS results showed that different reactions occur between AMU442 and the AMU442/agarose mixtures. Agarose gel was found to have an effect on the oxidation reactions of AMU442 mixture.

Acknowledgments

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References


