Stabilizer Effect on Thermal Decomposition of Aged Solid Propellant

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Abstract. Composite solid propellants experience aging process during storage, and their properties will alter. The stabilizer added was used to reduce the effects of aging. This research studied the influence of the stabilizer on changes of the composite solid propellant thermal decomposition due to the onset of aging during the 40 days of storage at a temperature of 333 K. AO 2246 as a stabilizer added by as much as 0 to 1% by weight of propellant binders. The testing method used is heating the samples at various heating rate using DSC. And the Ozawa method was used to determine the values of the activation energy and frequency factor on the Arrhenius parameters. The optimal composition of stabilizer was 0.5 wt% for those on the value of activation energy and frequency factors for unaged and aged propellants were nearly the same i.e. 196 kJ/mol and 1.22 x1012 min⁻¹.

1. Introduction

The composite solid propellant is widely used for missiles rocket and launch vehicles. The composite solid propellants consist of oxidizing agents, binders, and additives. Ammonium Perchlorate (AP) had good characteristics, performances, compatibility, and availability so it most widely used as an oxidizing agent [1]. Hydroxyl Terminated Polybutadiene (HTPB) acts as a binder, also serves as a fuel which would be oxidized in the combustion reaction. The selection of HTPB as fuel binder because of its nature and can allow high solid content up to 90% weight [2,3].

The propellants experience aging during storage, and their properties will alter. An additive that serves as a stabilizer can be added to reduce the effects of aging. For example, amine and hindered phenols act as H donor on free radicals thus preventing the propagation of a chain reaction [4]. Hindered phenol compounds, such as types of AO 2246 is used because it was evidence that AO 2246 was a proper stabilizer for HTPB that used as a propellant binder [5].

Combustion of the propellant is a complex process. At the burning surface area, gas decomposition of Ammonium Perchlorate and HTPB, are inter-diffused and produce diffusion flame streams [6]. A various research was conducted to study the propellant thermal decomposition processes. A variety of mathematical and analytical methods used to determine kinetic parameters of thermal decomposition. Differential Thermal Gravimetry (DTG) and Differential Scanning Calorimetry (DSC) were the most widely used instrument in the study of the thermal decomposition of the material. The value of the kinetic parameters of thermal decomposition of the material such as activation energy (E) and
frequency factor (A) can be determined using some methods such as Ozawa, Kissinger, or Flynn Wall Ozawa (FWO).

This research studied the influence of the AO 2246 as a stabilizer on changes of the composite solid propellant thermal decomposition due to the onset of aging during the 40 days of storage at a temperature of 333 K.

2. Experimental

2.1. Material

The composition of the composite solid propellant was HTPB as a fuel binder with curing agent Isophorone Di Isocyanate (IPDI) with a 17.6 wt%, 2.25 wt% of DiOctyl Adipate (DOA) as the plasticizer, and 80 wt% of solid content. Ammonium Perchlorate acts as an oxidizing agent with three-grain size 200 μm, 100μm, and 50 μm, while the Aluminum powder serves as a metal fuel. The type of hindered phenols, AO 2246 as a stabilizer added by as much as 0%; 0.2%; 0.5%; and 1% by weight of the binder. The samples code, S00, S02, S05, and S10 represent the amount of AO 2246 added.

Manufacture of propellant was done in batches planetary mixer for 135 minutes. The mixing stages started with mixing HTPB and DOA, followed by the addition of Aluminum powder, stabilizer and other additives. The addition of Ammonium Perchlorate is done in two stages, and the last stage was the addition of the IPDI. The propellant is cured in an oven at a temperature of 60 C (333 K) for three days.

Testing of thermal decomposition conducted for the unaged propellant and aged propellant that has been stored for 40 days at a temperature of 333 K

2.2. Testing

Thermal decomposition of unaged and aged samples were tested using DCS 60 Shimadzu instrument. They were heating at the range 303 – 823 K of temperature at four heating rates, i.e. 15, 20, 25, and 30 K/min under nitrogen atmosphere. Because of high heating rates and explosivity of propellant, the only small sample size was used about 1.5 – 1.8 mg. Ozawa or iso conversional method was used to determine the activation energy (E) and frequency factor (A).

2.3. Methods

The Ozawa method that used to determine the activation energy (E) and frequency factor (A) is based on basic kinetic equation for heterogeneous chemical processes and not necessary to know the reaction order. Activation energies determined by this method were the sum of activation energies of chemical and physical reactions in the thermal decomposition process. The relationship between reciprocal of an absolute exothermic peak (Tp⁻¹) and a logarithm of heating rates (log β) is a linear equation and described in equation (1) can be used to determine the activation energy and frequency factor.

\[ \log \beta = aT_p^{-1} + b \]  

(1)

Where a and b are the parameters of linear equation, a (slope)= -0.4567E/R and R is gas constant.

With assumed that reaction kinetics followed the Arrhenius law and exothermic reaction was a single step process, the value of frequency factor (A) can be calculated using equation (2)

\[ A = \frac{E}{R} e^b \]  

(2)

3. Result and Discussion

Figure (1) shows the DSC patterns for unaged propellant with 1% stabilizer at various heating rates. There is an endothermic and an exothermic peak on the curve. Endothermic peak has almost the same value for different heating rate, which is about 520 K. This peak represents the
phase transition of Ammonium Perchlorate from orthorhombic to cubic [7,8]. While, an exothermic peak is the temperature where thermal decomposition reaction occurred, which is different for various heating rates. The higher of heating rates, the higher of exothermic temperature.

**Figure 1.** DSC Curve For Unaged Propellant at 1% Stabilizer

**Figure 2.** Ozawa Plot For Unaged Propellant
Figure 3. Ozawa Plot for Aged Propellant

Figure (2) and (3) show the relationship between the reciprocal of absolute exothermic peak and logarithm of heating rates for unaged and aged propellant. Based on Ozawa method and using equation (1) and (2) the value of activation energy (E) and frequency factor (A) can be determined as seen in Table 1.

Figure 4. Activation Energy For Unaged and Aged Propellants
Figure 5. Logarithmic of Frequency Factor for Unaged and Aged Propellants

Figure (4) and (5) show the changes in the value of activation energy and frequency factor respectively. The greater the amount of stabilizer was added, the value of the activation energy and the frequency factor are increased for unaged propellant. However, after experiencing aging, the changes of the values of activation energy and frequency factor were different for various stabilizer composition.

Table 1 shows the results of activation energy and frequency factor for unaged and aged propellant. The value of activation energy is about 127 – 200 kJ/mol for unaged propellant and 175 – 306 for aged propellant. These values are accordance with the literature. Sell et.al studied about the kinetics of AP/HTPB propellant thermal decomposition using thermogravimetry. The activation energies calculated by Ozawa method were between 100 – 230 kJ/mol [9]. Goncalves et.al studied about kinetics of unaged propellant thermal degradation using DSC and Ozawa method and the calculated activation energy and frequency factor were 134 kJ/mol and $2.04 \times 10^{10}$ min$^{-1}$ [10].

Table 1. Thermal Decomposition Parameters For Unaged and Aged Solid Propellants

| Code | % Stabilizer | Unaged E,kJ/mol | A, min$^{-1}$ | Log A | Aged E,kJ/mol | A, min$^{-1}$ | Log A |
|------|--------------|-----------------|--------------|--------|--------------|--------------|--------|
| S00  | 0            | 127.58          | $2.91 \times 10^4$ | 9.46   | 175.24       | $2.31 \times 10^{11}$ | 11.36  |
| S02  | 0.2          | 145.75          | $1.63 \times 10^{10}$ | 10.21  | 306.67       | $2.10 \times 10^{16}$ | 16.32  |
| S05  | 0.5          | 195.98          | $1.22 \times 10^{12}$ | 12.08  | 196.35       | $1.22 \times 10^{12}$ | 12.09  |
| S10  | 1.0          | 200.26          | $2.62 \times 10^{12}$ | 12.08  | 183.37       | $5.51 \times 10^{11}$ | 11.74  |

On the propellant S00 and S02, the value of activation energy and a frequency factor of aged propellant were increased very significantly. It means, that the aged propellant are less reactive, but the decomposition reaction rate is higher than unaged ones. In the other hand, the propellant S05, had no changes. So, the reactivity and thermal decomposition rate of propellant do not change for aging of 40 days at a temperature of 333 K. The S10 propellant, with an addition of stabilizer 1%, the value of E and A were slightly decline. It said that on the propellant S05 and S10, the AO 2246 stabilizer has an optimal influence by minimizing the changes of the propellant properties due to aging, in this case, the thermal properties. Otherwise, on the addition of stabilizer of less than 0.5% by weight of binders, the changes of propellant thermal properties are still significant.

4. Conclusion

The changes of thermal properties propellant due to aging can be minimize by addition of AO 2246 as a stabilizer. For unaged propellant, the greater stabilizer added, the greater the activation energy and
frequency factor. The AO 2246 stabilizer gives an optimal effect for the composite solid propellant at an addition of more than 0.5 wt% due to the changes of thermal decomposition properties after experiencing aging for 40 days at a temperature 333 K are very slightly. The value of activation energy and frequency factors for unaged and aged propellants at 0.5 wt% AO 2246 were nearly the same i.e. 196 kJ/mol and 1.22 x10^{12} min^{-1}.

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