DECOMPOSITION KINETICS OF GAP BINDER IN THE PRESENCE OF AN ENERGETIC COMPONENT

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Abstract:

Glycidyl Azide Polymers (GAP) are promising candidates as energetic binders for future solid composite propellants. They produce minimum smoke, cause reduced pollution, and have low sensitivity. In our hands, we have undertaken a study of the decomposition kinetics of energetic binder in the presence of the energetic oxidizer, to assess the stability of the composite formulation.

We now report the decomposition kinetics of GAP binder in the presence of two high performance and environment friendly oxidizers like Ammonium Dinitramide (ADN) and 4,10-dinitro-2,6,8,12-4,10-diazatetracyclo-[5.5.0.0^{5,9} 0^{3,11}]dodecane (TEX). Thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) were used to investigate the decomposition characteristics and heat of decomposition of TEX/GAP and ADN/GAP gum formulations. Addition of GAP has improved the thermal stabilities of both AND and TEX. GAP has been found to be more vulnerable to thermal decomposition in the presence of TEX than in the presence of ADN.

Keywords: *glycidyl azide polymer, thermal stability, thermal decomposition, activation energy*

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1. INTRODUCTION

Nitramine based energetic materials such as RDX and HMX are widely used as propellant ingredients for increased specific impulse at low flame temperatures. However, nitramines have low burning rates coupled with a relatively high and undesirable burning rate exponent. Therefore research efforts were directed to employ nitramine explosives as fillers in oxidizer/binder matrix propellants.

Glycidyl Azide Polymers (GAP) are promising candidates as energetic binders for rocket propellant applications. Owing to its highly exothermic decomposition, high burning rates are usually observed during the combustion of GAP. Also, its fuel rich composition results in low flame temperature. Composite propellants of nitramines and energetic azido polymers are characterized by low flame temperature, high detonation velocity, low vulnerability and high thermal stability **[1]**.

In this paper, we report the study of thermal decomposition characteristics of two nitramine/GAP pseudo propellants using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The nitramines used for this study are Ammonium Dinitramide (ADN) **[2]** and 4,10-dinitro-2,6,8,12-4,10-diazatetracyclo-[5.5.0.05,9 03,11]dodecane (TEX) **[3]**. ADN and TEX are two high performance environment friendly oxidizers. ADN

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is a potential halogen free replacement to ammonium perchlorate (AP) in solid rocket propellants. TEX is envisioned as a prospective oxidizer component in nitramine based composite propellant formulations.

It is important to understand the thermal decomposition processes that occur in the condensed phase of composite propellants because; these processes control the burn rate of the propellant. Moreover, an understanding of the underlying molecular processes behind the thermal decomposition behavior of propellants will provide insight into their relative stability. This information will in turn provide guidance into the development of more stable composite propellants.

2. EXPERIMENTAL

GAP, ADN and TEX were synthesized in our laboratory by adopting standard procedures. All the synthesized compounds were characterized using GPC, NMR, and IR analysis. Requisite amounts of the compounds were hand mixed in a vacuum chamber at room temperature and the samples were degassed for 1hr prior to testing.

Thermo gravimetric analyses were carried out using a Shimadzu Hires TG-50 equipped with thermal analysis software for data analysis.

Differential scanning calorimetry measurements were carried out in TA DSC 2010 equipment containing thermal analysis software for data interpretation. In representative runs, 2-3 mg of samples in sealed hermetic pans were ramped from room temperature to 320^0C at varying rates of 2^0C/min, 5^0C/min, 10^0C/min and 15^0C/min in a steady flow of nitrogen (50ml/min).

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

TGA curves of ADN, GAP and ADN+ GAP compounds are presented in figure 1.

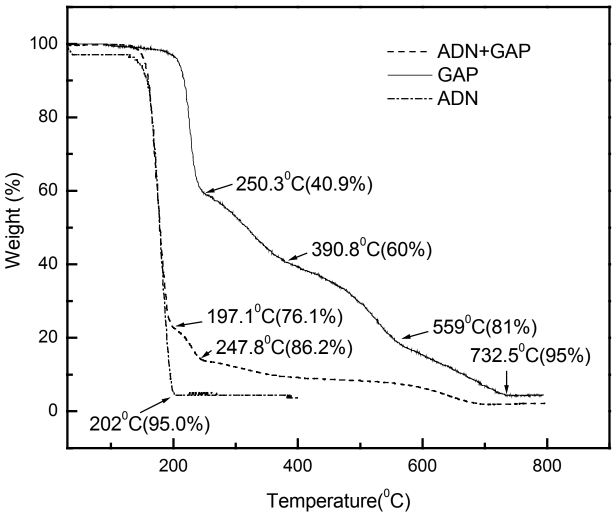

Fig 1. TGA curves of GAP,ADN and ADN +GAP formulations

GAP decomposes in multiple stages. The predominant weight loss of 37% between 197^0C and 250^0C is due to the decomposition of azide groups, which is the common decomposition mechanism associated with the azido polymers [4]. After 250^0 C, GAP exhibits a gradual weight loss until 732^{0}C due to the decomposition of the polymer back bone.

ADN shows a single step decomposition behavior with 91% weight loss between 135^{0}C and 202^{0}C. The major decomposition mechanism associated with ADN is its breakdown to various oxides of nitrogen (NO_2, N_2O and NO), ammonia, ammonium nitrate and nitrogen [5]. ADN+GAP show multi step decomposition with a major weight loss of 75% between 140^{0}C and 197^{0}C owing to ADN decomposition, followed by a 10% weight loss until 247.8^{0}C due to GAP decomposition. TGA curve of ADN+GAP lies above that of ADN indicating that thermal stability of ADN has improved with the mixing of GAP.

Figure 2 shows the TGA curves of TEX, GAP and TEX+GAP formulations.

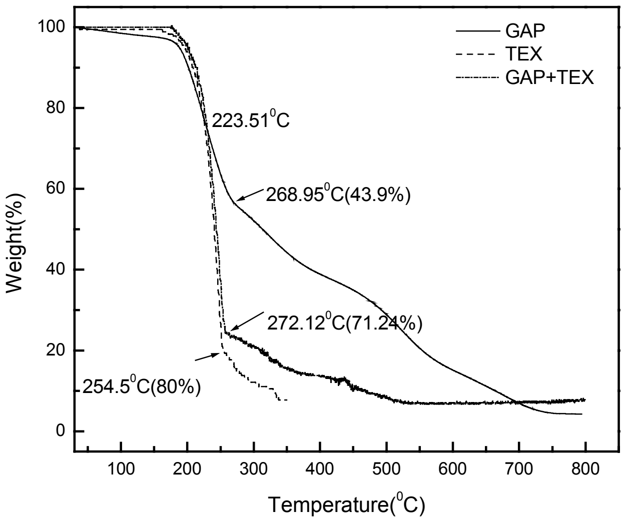

Fig 2. TGA curves of GAP,TEX and TEX+GAP formulations

TGA curve of TEX shows a single step decomposition behavior of 80% weight loss between 1800C and 2540C associated with the scission of N-NO2 bonds in the molecule, the primary decomposition mechanism in nitramines[6]. TEX+ GAP compound also shows a single step decomposition of 80%weight loss between 180^{0}C and 254^{0}C, followed by a gradual weight loss associated with GAP component in the formulation. It is noteworthy that TEX and TEX+GAP compounds exhibit a higher thermal stability than GAP until 223^{0}C. After 250^{0}C, thermal stability of TEX+GAP is higher than that of TEX alone. Clearly addition of GAP has improved the thermal stability of TEX.

Comparing figures 1&2, in ADN + GAP and TEX+GAP pseudo propellant formulations the major mass loss step primarily relates to that of decomposition of ADN and TEX followed by the degradation of GAP binder. Thermal stabilities of ADN + GAP & TEX + GAP formulations have increased with respect to ADN and TEX alone. ADN + GAP propellant formulation shows a gentle slope of variation of mass loss with temperature when compared to that of ADN. On the other hand, for TEX+GAP and TEX, the slopes are the identical.

Activation energy of thermal decomposition was calculated by employing Coats-Redfern method [7]. Activation energy of thermal decomposition of ADN increases from 150KJ/mole to 170KJ/mole in ADN+GAP formulation. For TEX, activation energy increases from 120KJ/mole to 128KJ/mole in TEX + GAP formulation. The increase in the activation energy of ADN+GAP formulation is higher than that for TEX+GAP. Consequently, it could be concluded that, GAP stabilizes the thermal decomposition of ADN more than that of TEX.

3.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a more versatile technique to understand the thermal decomposition process of propellant formulations. Figure 3 presents the DSC curves for GAP, ADN and ADN + GAP formulations.

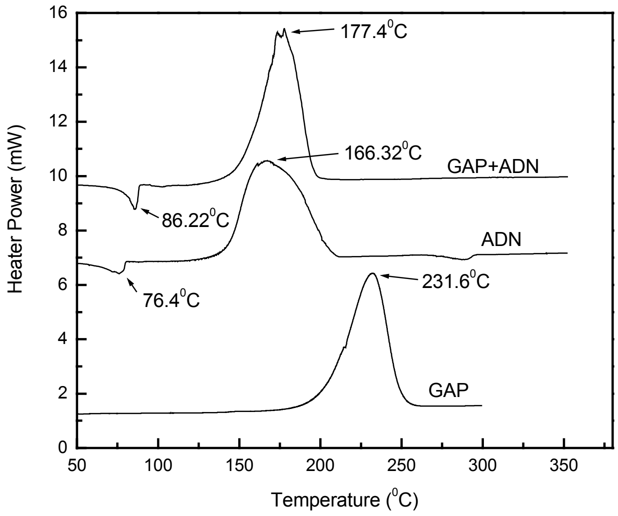

Fig 3. DSC curves of GAP,ADN, and ADN+GAP formulations

GAP exhibits an exothermic decomposition peak at 231.6^{0}C with a heat of decomposition of 1294 J/g. ADN displays an endothermic melting peak at 76.4^{0}C, followed by an exothermic decomposition of the melt at 166.32^{0}C. The heat of decomposition of ADN is 2131J/g. ADN + GAP propellant formulation, also shows an analogous DSC curve as that of ADN. The exothermic decomposition temperature has shifted to 177.4^{0}C. The heat of decomposition is 2042 J/g. Exothermic peak due to decomposition of GAP in the composition could not be observed.

DSC curves for GAP, TEX and TEX+ GAP formulations are presented in figure 4. TEX displays a narrow decomposition peak at 297.15^{0}C with a heat of decomposition of 730J/g. In contrast to the ADN + GAP formulation, TEX + GAP exhibits two exothermic decomposition peaks at 228^{0}C and 297.15^{0}C. The heats of decomposition are 600J/g and 380J/g respectively. This double decomposition behavior could not be assessed clearly from the TGA experiments. It is noteworthy that the decomposition temperature of GAP in GAP+TEX formulation shifts to lower values.

Comparing figures 3&4, decomposition temperature of ADN shifts to higher values in the presence of GAP. On the other hand, in the presence of GAP, the decomposition temperature of TEX remains the same. Shift in the decomposition temperature of the solid propellant demonstrates that GAP is capable of enhancing the thermal stability of ADN. This result is consistent with our TGA results.

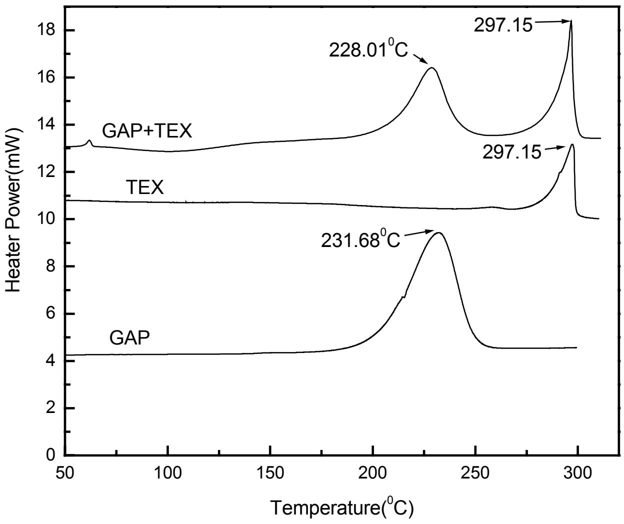

Fig 4. DSC curves of GAP,TEX, and TEX+GAP formulations

Kissinger equation [8] (equation 1) was employed to evaluate the activation energy of thermal decomposition of GAP and the GAP component in GAP+TEX formulation.

$$-\ln\left(\frac{\beta}{T_d^2}\right) = E/_{RT_d} + K \qquad \textbf{(1)}$$

Where β is the heating rate, T_d is the temperature of decomposition, E is the energy of activation for thermal decomposition, R is gas constant and K is a constant. The Kissinger plots are presented in figure 5.

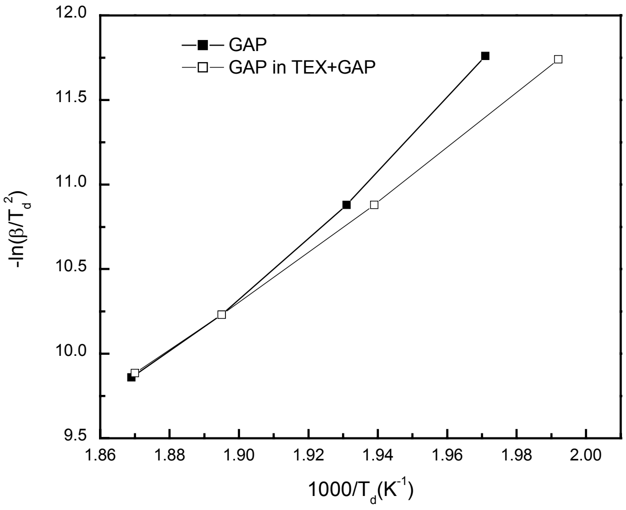

Fig 5. Kissinger plots for GAP and GAP component in TEX+GAP formulation

Activation energies are calculated from the slopes of the Kissinger plots. The activation energy for pure GAP was computed as 155.6 KJ/mole and that for the GAP component in GAP+TEX was computed as 126.6 KJ/mole. It could be concluded that, GAP is more vulnerable to thermal degradation in the presence of TEX.

4. CONCLUSIONS

Thermogravimetry analysis (TGA) and Differential Scanning Calorimetry were used to study the thermal decomposition characteristics of GAP and its two propellant formulations with two high performance oxidizers; ADN & TEX. TGA results indicated that inclusion of GAP has improved the thermal stability of its pseudo propellant formulations with TEX and ADN. Clearly, mixing of nitramine oxidizers with energetic polymers has resulted in the formation of more thermally stable propellant formulations. The thermal stabilizing effect of GAP is more pronounced in ADN when compared to that of TEX. DSC results provided a comprehensive assessment of the thermal degradation process. It was shown that, GAP is more vulnerable to thermal degradation in the presence of TEX.

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