

Role of oxygen balance on the thermal decomposition behaviour of composite propellants

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Differential thermal analysis (DTA) on ammonium perchlorate (AP), hydroxy terminated polybutadiene (HTPB) based polyurethane (PU) and other composite propellant compositions consisting of AP and PU matrix has been studied. The data show that as the oxygen balance (OB) of the propellant composition decreases, the decomposition rate of AP during the second stage (deflagration exotherm-Exo II) around 360°C rises very significantly due to the increase in calorific values.

Thermal decomposition and combustion studies on ammonium perchlorate (AP), the most commonly used oxidizer in composite propellants (CP) have been extensively carried out to get a better insight into the mechanism of CP combustion¹⁻⁵. Differential Thermal Analysis (DTA) study on AP clearly reveals three peaks, viz., an endothermic peak around 240°C corresponding to reversible crystallographic transition from orthorhombic to cubic structure, a low temperature exothermic decomposition (EXO-I) around 290°C which ceases after partial decomposition, and a high temperature exothermic decomposition (EXO-II) around 360°C which goes to completion. The thermal decomposition behaviour of AP in a composite propellant may be expected to depend on the composition of composite propellant, especially with reference to its overall oxygen balance (OB). Effect of oxygen balance on the thermal decomposition of composite propellant has not been reported and, therefore, an attempt has been made to study the effect of OB on the thermal decomposition pattern of the CP compositions by carrying out DTA studies.

Experimental Procedures

CP compositions containing various percentages of coarse AP (mean particle size ~ 200 µm) and hydroxy terminated polybutadiene (HTPB) based polyurethane (PU) binder fuel were made with varying OB from +17 to -53% corresponding to 95 and 75% solid loading by weight, respectively. The specifications of AP, HTPB and TDI used are given below:

Ammonium perchlorate (AP)—Conforming to specification JSS 1078 and having average particle size ~ 200 µm. (WIMCO, Bombay).

Hydroxy terminated polybutadiene (HTPB)—Having following characteristics (i) number average molecular weight (\bar{M}_n) = 2200 g per mol; (ii) hydroxyl value = 40 mg KOH per g and (iii) viscosity at 30°C = 35-65 Poises (ARCO, USA).

Toluene-di-isocyanate (TDI)—Consisting of isomers 2,4-TDI = 80 ± 2%, 2,6-TDI = 20 ± 2% and NCO content ≠ < 99% (M/s Bayer, Germany).

HTPB was dissolved in minimum amount of an inert organic solvent such as CCl₄ and calculated quantity of AP was added with thorough mixing. The calculated quantity of toluene-di-isocyanate (TDI), based on hydroxyl value of HTPB was added, and mixed thoroughly with the AP slurry, cast in small trays and cured at 70°C for 7 days.

10 mg of the fully cured propellant was used to carry out DTA studies on the Micro-DTA apparatus fabricated in ERDL itself and described earlier⁶.

Samples with varying oxygen balances were evaluated for their calorific values by using Julius-Peters Adiabatic Calorimeter. 1 g of the sample was accurately weighed and ignited using a nichrome wire in the calorimeter that has been filled with excess of oxygen. The calorific value was calculated by measuring the temperature rise and knowing the water equivalent of the calorimeter.

Calculation of OB

Calculation of OB (expressed as percentage) of AP as well as the cured polymer was done by the conventional method⁷. By convention, +ve sign for oxygen-rich composition and -ve sign for oxygen-deficient composition have been assigned.

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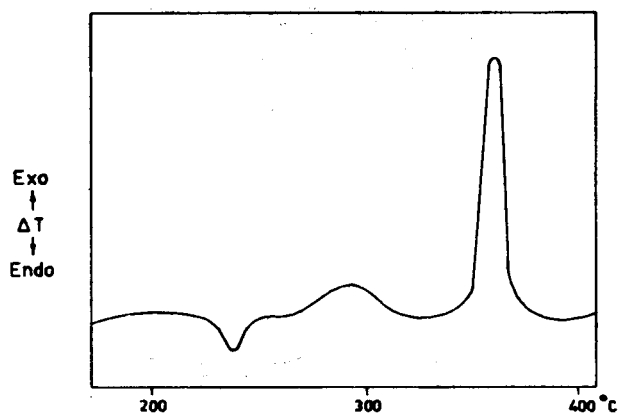


Fig. 1—DTA thermogram of ammonium perchlorate (Heating Rate $10^{\circ}\text{C min}^{-1}$)

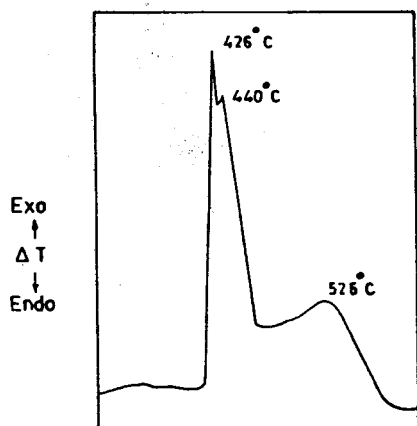
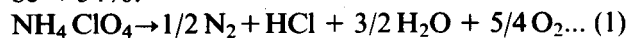


Fig. 2—DTA thermogram of fuel (PU binder) (Heating Rate $10^{\circ}\text{C min}^{-1}$)

The OB of AP was calculated based on the following decomposition reaction and it was found to be +34%.



The OB of PU binder matrix was calculated assuming \bar{M}_n -2200 and OH value of 40 mg KOH per g, the formula of HTPB used in this experiment can be deduced as $(\text{C}_4\text{H}_6)_40 (\text{OH})_{1.5}$. As one TDI molecule forms two PU linkages with two OH groups, the formula of a cross-linked unit of HTPB can be written as $(\text{C}_4\text{H}_6)_40 [(\text{NHCOO}) (\text{C}_3\text{H}_3)]_{1.5}$ or roughly $\text{C}_{166}\text{H}_{246}\text{O}_3\text{N}_2$ the OB of which works out to be -313%.

Results and Discussion

Differential thermograms of pure AP, the PU resin and mixtures of AP and PU resin in various proportions are shown in Figs 1, 2 and 3, respectively.

In case of pure AP, the endothermic peak around

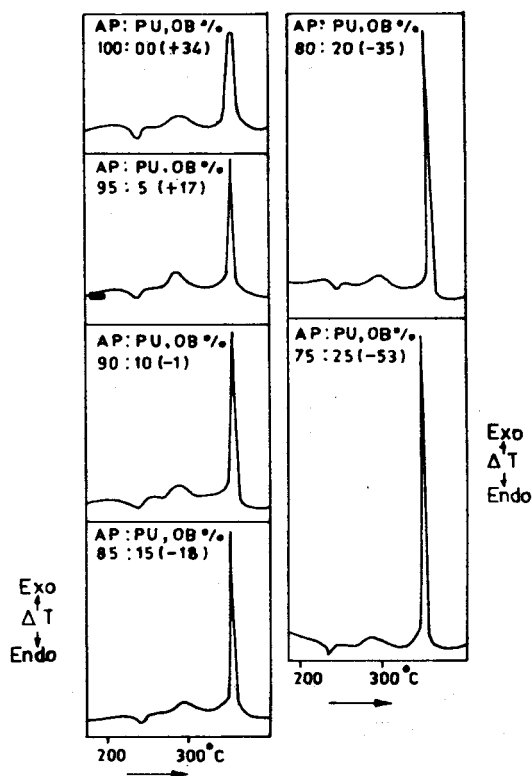


Fig. 3—DTA thermograms of AP and CP compositions with varying OB (Heating Rate $10^{\circ}\text{C min}^{-1}$)

240°C is attributed to the phase change of AP crystals from orthorhombic to cubic form. Around 290°C (EXO-I) a part of AP decomposes to form NH_3 and HClO_4 gases of which the former gets adsorbed on the remaining portion of AP. This adsorbed ammonia inhibits further decomposition of AP. However, around 360°C (EXO-II), the ammonia gets desorbed facilitating further decomposition of the leftover AP^{1-5} .

DTA of HTPB based PU matrix shows primarily two exothermic peaks, one at 431°C (with a shoulder at 440°C) and the other at 525°C . This is in agreement with the reported results⁸⁻¹². It is clear that the decomposition of the PU commences around 427°C and the degradation mechanism involves two stages. In the first stage, HTPB based PU polymer depolymerizes yielding the monomer butadiene, cyclopentene etc. and in the second stage, the remaining residue cyclizes, crosslinks and then undergoes further degradation to gaseous products.

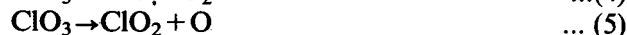
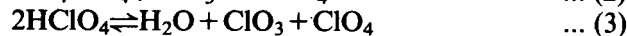
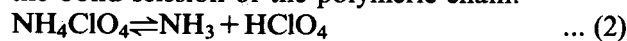
The DTA thermograms for composite propellant compositions are shown in Figs 3b-3f and data are given in Table 1. The thermograms show clearly that the combustion of the propellant is over well before 426°C which is the starting temperature observed during the decomposition of a pure PU matrix. This indicates that PU matrix is attacked by the initial

Table 1—Variation of thermal decomposition parameters and calorific values with OB

AP/PU, % OB, %	Phase change °C	EXO-I peak temp. °C	EXO-II peak temp. °C	EXO-I peak height mm	EXO-II peak height mm	Calorific value cal/g
100/0 (+34)	238	293	363	5.0	34.0	488
95/5 (+17)	240	294	364	7.0	49.0	1473
90/10 (−1)	236	289	365	6.0	63.0	—
85/15 (−18)	240	295	358	5.0	68.0	1808
80/20 (−35)	235	293	348	4.4	103.0	2513
75/25 (−53)	239	282	348	4.0	114.0	3102

decomposition products of AP. It is also observed that in all these cases, there is no significant variation in Exo-I peak temperature as well as Exo-I peak height. It may be pointed out here that the binder in its original state has a high molecular weight and it does not volatilize owing to its low vapour pressure. When heat is supplied to the polymer, the large chains undergo bond scission until the requisite mean size is reached at the surface for volatilization. This is called *Critical Fragment Size* (CFS)¹³. At EXO-I the temperature ($\sim 290^\circ\text{C}$) is too low to degrade the polymer matrix to CFS level so that any change in the composition does not markedly affect the decomposition of AP at EXO-I.

However, after 290°C , i.e., after EXO-I, the PU matrix starts decomposing very fast. This accelerated decomposition appears to be mainly due to HClO_4 (g) and its oxygen-rich decomposition products mostly in the form of free radicals such as $\text{ClO}\cdot$, $\text{O}\cdot$, $\text{O}_2\cdot$ (Eqs (2-5)). These free radicals seem to play a vital role in the bond scission of the polymeric chain.



The most remarkable observation in the DTA of AP/PU compositions is the significant influence of OB of the composition on the rate of decomposition of AP at EXO-II, i.e., the final decomposition-cum-combustion. It can be seen that the decomposition rate at EXO-II becomes remarkably faster as the OB of the composition decreases.

This can be explained by the increase in the calorific values of the AP/PU compositions as they become more and more fuel-rich (Table 1). It is well known that as a propellant becomes richer in fuel content, its calorific value (the heat of combustion in excess of oxygen) significantly increases. This phenomenon has been extensively used in the development of air-breathing fuel-rich propellant based rockets¹⁴. Higher heat output during decomposition/burning

of the composition results in faster heat transfer from gas phase to the condensed phase (AP/PU surface). However, at lower pressures, (below 10 atm) the rate determining step during propellant combustion is the heat transfer from gas phase to condensed phase¹⁵. It is, therefore, expected that as the propellant becomes richer in fuel content (poorer in oxygen balance), the heat transfer process becomes faster because of the increase in calorific value/heat output, thereby, resulting in faster decomposition of the AP/PU surface.

Conclusion

The following conclusions may be drawn from this study:

1. For a given heating rate, the DTA profile of AP/PU composite propellant varies with the OB of the composition. As the OB decreases, there is no significant change in the initial exotherm (EXO-I) indicating that PU matrix at that temperature has not significantly degraded to have any marked influence on the thermal decomposition pattern of AP. However, soon after EXO-I, the primary decomposition products of AP & HClO_4 greatly accelerate the pyrolysis of the PU matrix.

2. At EXO-II, the rate of decomposition remarkably increases with the decrease in OB which is evidently due to the increase in the calorific value/heat output resulting in a faster heat transfer from the gas phase to the condensed phase of the propellant.

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