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THERMAL DECOMPOSITION OF GAP AND GAP BASED DOUBLE BASE PROPELLANTS

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Abstract

This paper reports the thermal decomposition pattern of GAP and GAP containing double base (DB) compositions. Dynamic and isothermal TGA reveal two stage decomposition process for GAP. At temperatures below 200 deg C reactant-product interface diffusion while at higher temperatures, nucleation based diffusion processes appear to be operative. Inclusion of GAP resulted in drop in temperature for onset of free radical reaction.

Introduction

Double base propellants (DBP) have limitation regarding performance, as maximum nitroglycerine (NG) content is restricted to the extent of about 45% of the composition [1]. Further, the hazard considerations demand the mixing of NG with non-explosive plasticizers like phthalates before processing. Glycidyl azide polymer (GAP) offers a unique energetic plasticizer system for advanced propellants and plastic bonded explosives (PBX). Its chief advantages include higher density (1.3 g/cc), positive heat of formation (42 kcal/mole) and capability to desensitize explosive plasticizers like NG [2]. GAP contains higher concentration of carbon atoms and therefore its high combustion potential could be exploited by the inclusion of oxidisers in the formulation [3]. The main demerit of GAP is relatively high glass transition temperature (T_g), which varies between 20 to 50 °C, depending upon the molecular weight, linearity or branching of chain [4].

In view of the tremendous potential of GAP as binder cum energetic fuel, energetic plasticizer/additive, knowledge about its thermal behaviour assumes great importance. Further, kinetics of exothermic reactions are important in assessing the hazard potential of materials for their handling, processing, storage and shipping. Kinetic parameters many times provide useful information on thermal stability, rate of decomposition and life time prediction of materials under different environmental conditions. A few studies have been conducted in the past on thermal decomposition of GAP, using DTA, TG, mass spectrometry and rapid scan fourier transform IR spectroscopy (RSFTIR) [5–9]. However, information available are limited on GAP based propellants. Thermal analysis techniques particularly DTA, TG, DSC are proven methods for the evaluation of kinetic parameters of various reactions [12–17]. One of the most widely used DSC methods is the variable programme rate method developed by Kissinger [15]. Later Ozawa [16] developed a simpler method for the calculation of kinetic parameters from TG and DSC. Ozawa method is basically a plot of log heating rate versus $1/T$, where T is peak maximum temperature.

This paper reports results from dynamic, isothermal gravimetric analysis, DTA (in air) and DSC. An attempt has been made to explain the decomposition behaviour of GAP and its role as energetic component for propellant systems.

Experimental

GAP prepolymer (mol. weight ~ 400) was synthesized by a method established in our laboratory, on the lines of the procedure reported by Ahad [18]. Propellant compositions were prepared by slurry cast technique invol-

ving mixing of ingredients with and without vacuum, casting, curing, extraction and machining in required shape and size [49]. TG and DTA were carried out using indigenously fabricated furnace with Pt — Rh 13 % thermocouples in static air. DSC was carried out on simultaneous TG/DSC analyzer of Perkin Elmer make under nitrogen atmosphere. Calorimetric values (Cal-val) were determined by Julius — Peters apparatus at loading density of 0.016 g/cc.

Results and Discussion

Results of dynamic TGA reveal two stage decomposition process for GAP (Fig. 1). In the first stage weight loss was 85 % between 127 and 210 °C, which was followed by a gradual loss to 95 % upto 300 °C. Kinetics of first stage of decomposition of GAP suggest two different trends (two slopes) one between 127—200 °C with a steady slope corresponding to activation energy (E_a) of 37 kcal/mole as computed using Coats and Redfern equation [17] and another between 200—210 °C with a higher slope. This suggests that the decomposition does not appear to follow the same mechanism during its total path. In order to get a better picture of the decomposition process of GAP, isothermal gravimetric analyses (IGA) was carried out at 165, 170, 190, 195 and 200 °C. At all temperatures except at 200 °C, α (represents the fraction decomposed, dw/dt) vs time data fits the mechanistic equation $D_3(\alpha)$ (Fig. 2), suggesting a diffusion type mechanism. The decomposition was rapid beyond 200 °C. Kubota [3] attributed exothermic peak between 202 and 277 °C to decomposition and gasification reactions, whereas Farber et al. [6] felt that primary decomposition starts at 120 °C (E_a 42 Kcal/mole) and secondary decomposition involving rupture of carbon backbone takes place at 200 °C. Leu et al. [9], however, observed first stage decomposition at 240 °C and second stage degradation around 260 °C. Mishra et al. [8] have reported onset of exothermic decomposition of GAP at 217 °C (E_a 38.2 kcal/mole) and have concluded that nitrogen atom loss is the preliminary step in the decomposition of GAP. By and large our results are in agreement with the findings of Kubota and Mishra et al. E from isothermal curves calculated was 57.6 kcal/mole between 165 and 195 °C. In the temperature range below 200 °C, reaction appears to be based on reactant-product interface diffusion while at higher temperatures a nucleation based diffusion appears to be predominant. It is a known fact that decomposition of an explosive material depends upon the creation of free radical, which form the nucleus of the chain process and hence materials which help in creation of free radical or removal of barrier in creation of free radicals would lower activation energy. The process of nucleation continues for some time with change in temperature but the curve changes with the onset of formation of radicals. DTA thermograms show two peaks which get more resolved with higher heating rates. At higher temperatures radicals formed may undergo further polymerisation reactions coupled with different fragmentation reactions. The radical based decomposition would be a slightly delayed process attributing to higher temperature peak. DSC

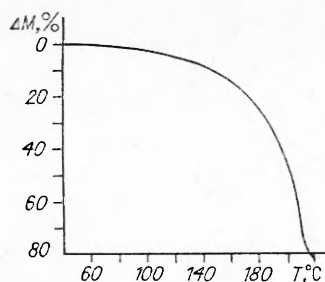


Fig. 1. Dynamic thermogravimetry of GAP.

(Fig. 3) also revealed asymmetric exothermic peak supporting the DTA observation. The overall heat of reaction in DSC was about 900 J/g.

Oyumi and Brill [7] have also reported the commencement of decomposition of GAP at 215 °C as revealed by the diminishing intensity of the band corresponding to the azide group along with the appearance of peaks at 1630—1730 cm^{-1} in FTIR. They observed an accelerated rate of decomposition as the temperature further increased. The spectral features of polymer backbone remain essentially unchanged after the complete disappearance of azide group.

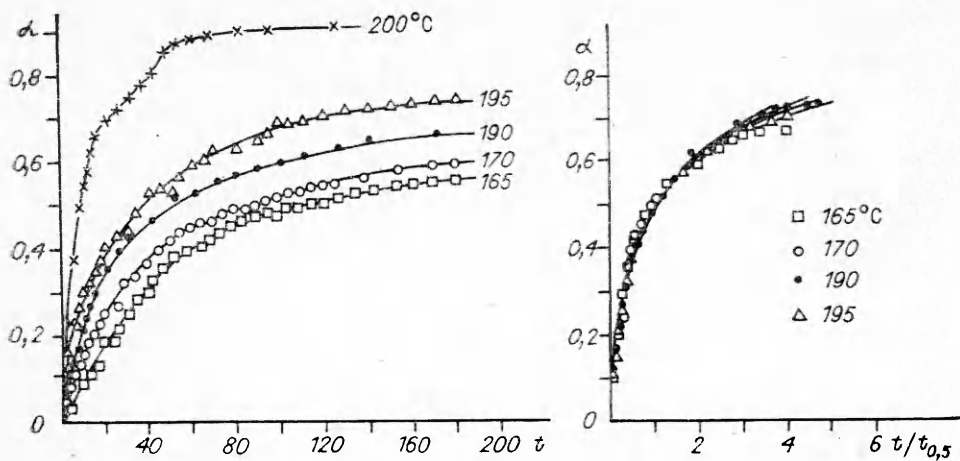


Fig. 2. Isothermal gravimetric analysis of GAP.

GAP based DB propellants containing 60 % NC, 32 % NG, 7.2 % DEP and 0.8 % 2NDPA were also subjected to thermal analyses in order to assess the effect of GAP on their decomposition pattern. DEP plasticized DB propellant exhibit maximum weight loss at 174 °C (see the Table). On incremental replacement of DEP by GAP the decomposition temperature was brought down to 162–170 °C. E_a of 70, 65.2 and 44 kcal/mole respectively was computed for DBP containing DEP, 4 % GAP and 7.2 % GAP. These results bring out that inclusion of GAP facilitates the decomposition of DB propellants at lower temperature. Plots of $F(\alpha)$ vs $(1/T)$ reflects the process of nucleation for a small range of temperature. When the decomposition process approaches the radical formation the curve changes its slope and the break point indicates the onset of radical formation. Free radical formation temperature for composition containing 7.2 % GAP was markedly lower (131 °C) as compared to control DB propellant (164 °C) (see the Table). These results indicate the ease of formation of free radical on total replacement of DEP by GAP.

In case of DEP plasticized DB propellant composition wherein NG was replaced by GAP (4–8 %), the maximum weight loss took place at almost same temperature (166 °C), whereas in a propellant composition having 12 % GAP the maximum weight loss was observed at 158 °C. This data corresponds to E of 49.3, 38.4 and 28.3 kcal/mole respectively. When NG was replaced by GAP in increments of 4, 8 and 12 % in GAP plasticized DB propellant the free radical formation temperatures were almost similar (119–120 °C) (see the Table). This was lower than that for control DB propellant by about 45 °C. E_a for thermal decomposition for these compositions were in the range of 34–39 kcal/mole. Another propellant composition containing NG – GAP in almost 1:1 ratio recorded the lowest maximum weight loss temperature of 146 °C.

We have reported earlier that replacement of DEP by GAP resulted in increase of burn rates considerably but substitution of NG by GAP produced lower burn rates due to reduction in cal-val of resultant propellant [11, 12]. Burn rates of GAP based propellants depend largely on its concentration in the formulation and initial temperature. The flame structure of NC – NC – GAP based propellant is expected to be similar to DBP containing NC – NG – plasticizer, comprising of foam, fizz, dark and luminous zones. The major products of decomposition (CO, CO₂, N₂, H₂, NO, H₂O) are reported to be similar in both the cases. The higher burn rates, however, with GAP based DBP may be due to exothermic decomposition at propellant surface, resulting in higher heat output. Further, the peak decomposition temperature and energy of activation being comparatively lower may affect the kinetics of the reaction. Thus, higher heat output and same reactions taking place at lower temperature appear to be the reason of very high burn rates

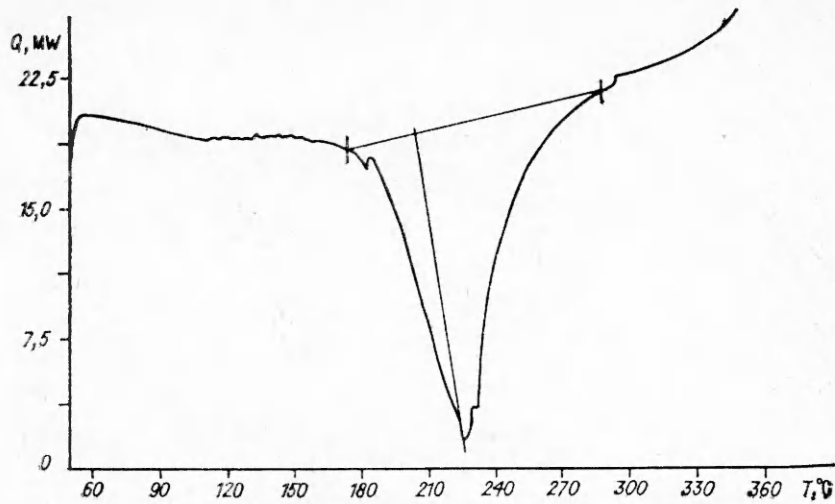


Fig. 3. Differential scanning calorimetric analysis of GAP.
Scanning rate, 10 °C/min.

THERMAL DECOMPOSITION PATTERN FROM DYNAMIC TG OF GAP PLASTICIZED
AND GAP BASED COMPOSITIONS

COMPOSITION	INCEPTION (°c)	PEAK (°c)	Ea(kcal/mole)
CONTROL :DEP:7,2, NG:32	164	174	70.1
GAP-I :DEP:3,2, GAP:4, NG:32	162	170	65.2
GAP-II:GAP:7,2, NG:32	131	162	44
GAP-III:GAP:4, DEP:7,2, NG:28	122	166	49.3
GAP-IV:GAP:8, DEP:7,2, NG:24	140	166	38.4
GAP-V:GAP:12, DEP:7,2, NG:20	119	158	28.3
GAP-VI:GAP:11,2, NG:28	119	160	38.9
GAP-VII:GAP:15,2, NG:24	120	156	35.6
GAP-VIII:GAP:19,2, NG:20	120	146	34.4

obtained with GAP based propellants and initial decomposition is caused due to degradation of $-\text{CH}_2-\text{N}_3$ to $-\text{C}\equiv\text{N} + \text{N}_2 + \text{H}_2$. N - N bond energy (39 kcal/mole) being lower than N - O bond (53 kcal/mole) in nitric esters.

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**UNSTEADY COMBUSTION OF SOLID
PROPELLANTS SUBJECT
TO DYNAMIC EXTERNAL RADIANT HEATING**
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Abstract

A theoretical and experimental investigation is being conducted on the effect of a dynamic external radiant heat flux on the combustion of energetic materials. These studies have illustrated the need for including the effect of the mean radiant heat flux and in-depth absorption. Also, a method for obtaining the linear frequency response function over a range of frequencies from a single test using series of radiant pulses is demonstrated. Experimental results have been obtained for an AP/HTPB propellant.

Introduction

There is a growing recognition of the advantages of studying the combustion of energetic solids, particularly solid propellants, using unsteady external radiant energy sources such as lasers. A reason this particular approach has recently received renewed interest is that it is easier to control a radiant flux and to simultaneously measure the instantaneous burning rate than to perform a similar experiment with an unsteady pressure field. The purpose of this paper is to illustrate the effect of primary parameters