VOL. 12, NO. 1, JANUARY 1974 AIAA JOURNAL 9

Combustion of Polystyrene and Oxygen-Styrene Copolymer/Ammonium Perchlorate Propellants

R. P. RASTOGI,[*] K. KISHORE,[†] AND GURDIP SINGH[‡]
University of Gorakhpur, Gorakhpur, India

Theme

A COMPARATIVE study of combustion of polystyrene and oxygen-styrene copolymer/ammonium perchlorate (AP) composite propellants has been made in order a) to investigate the role of peroxide-linkage in the latter and b) to study the role of surface reactions in combustion.

Contents

Burning rate, heat of combustion, flame temperature, and surface temperature of the two composites have been measured. Studies on thermal degradation kinetics and differential scanning calorimetry (DSC) of the propellants have also been made.

The inhibitor-free styrene was polymerized by benzoyl peroxide. To prepare the oxygen-styrene copolymer, azobis isobutyronitrile was used as the intiator and oxygen was passed at 1 atm pressure for 24 hr through the styrene. The reaction was completed by adding benzoyl peroxide and maintaining the solution in thermostat at 50°C for another 24 hr until it became sufficiently viscous. The yield of styrene peroxide was of the order of 21–22%. Styrene peroxide was characterized by microanalysis and infrared spectroscopy. Infrared spectra have weak characteristic absorption bands at 7.42 μ and 11.15 μ and a broad absorption band at 9.75 μ characteristic of peroxide linkage.

Burning rate was measured in a manner described earlier.[1] The products of combustion were analyzed by an Orsat Gas Analyzer. The heat of combustion of the PS and copolymer propellant was determined by a Parr Bomb Calorimeter. Thermal degradation of the propellants was determined by the weight-loss method.

The flame temperature was measured by the sodium-line reversal technique.[2] The stray light incident on the spectroscope was minimized by putting a diaphragm between the flame and the lens. The measured temperature was corrected for a shift in wavelength on account of the red filter in the pyrometer which was used for calibration.[2] For the polystyrene +70% AP propellant, the flame temperature was found to be 1550 ± 30°C whereas for the corresponding copolymer propellant, the value was 1850 ± 30°C.

The surface temperature of the PS and copolymer propellants during burning was determined by using a Pt-Pt (Rh 10%) thermocouple (0.45-mm-diam). The hot junction was kept touching the surface by putting a load of 60–80 g. The cold junction was kept in water at room temperature. The thermocouple was calibrated beforehand by taking measurements on the melting points of silver nitrate, potassium dichromate, and potassium iodide, and on the boiling point of sulphur. The emf developed was recorded by a potentiometer using a lamp and scale arrangement. The scale was calibrated by applying known emf. The surface temperature was found to be the same throughout the run. The reproducibility was better than 1%.

The differential scanning calorimetry of PS and copolymer containing different amounts of AP was investigated by one of the authors (K. Kishore) at the Univ. of Leeds, U.K., using a Perkin Elmer DSC-IB instrument. The measurements were made at the scan speeds of 8, 16, 32, and 64°K min^{-1}. The sample mass was about 0.6 mg and range settings used were 4, 8, 16, and 32 mcal sec^{-1} for full scale deflection. The sample was sealed in an aluminum pan and a small hole was made in the lid to allow the gases produced to escape.

Discussion of results: The data on burning rate, analysis of gaseous products, and heat of combustion and surface temperature are recorded in Tables 1, 2, and 3, respectively. The

Table 1 Burning rate of polymer/AP (100–150 mesh) propellants[a]

Polymer (wt %)	AP (wt %)	Burning rate (cm/sec) PS propellants	 Copolymer propellants
15	85	0.109 ± 0.003	0.123 ± 0.002
20	80	0.104 ± 0.002	0.124 ± 0.002
23	77	0.091 ± 0.003	0.111 ± 0.003
25	75	0.083 ± 0.002	0.092 ± 0.002
28	72	0.073 ± 0.002	0.087 ± 0.004
30	70	0.057 ± 0.003	0.061 ± 0.002
33	67	0.045 ± 0.003	0.055 ± 0.004

[a] Room temperature = 27.5°C.

Table 2 Analysis of gaseous products of combustion

Propellant system	Polymer (wt %)	Volume percentage of gases HCl	 CO_2	 O_2	 CO
PS/Ap	25	2.59	9.69	4.16	32.37
Copolymer/AP	25	1.85	11.74	4.12	21.18

Table 3 Surface temperature[a] and heat of combustion of propellants

	Surface temperature (°C)		Heat of Combustion (Cal/gm)	
Polymer (wt %)	PS propellants	Copolymer propellants	PS propellants	Copolymer propellants
30	1040 ± 5	1120 ± 12	1017 ± 15	1109 ± 10
25	1117 ± 9	1307 ± 12	1101 ± 10	1168 ± 23
20	1245 ± 4	1403 ± 5	1291 ± 5	1301 ± 8

[a] Room temperature = 30°C.

Received January 31, 1973; synoptic received July 13, 1973; revision received September 7, 1973. Full paper available from National Technical Information Service, Springfield Va., 22151, as N73-31687 at the standard price (available upon request). The authors wish to thank the Ministry of Defence, India, for the grant of a research fellowship to G. Singh.

Index categories: Fuels and Propellants, Properties of; Solid and Hybrid Rocket Engines.

[*] Professor, Department of Chemistry. Associate Fellow AIAA.

[†] Lecturer, Department of Chemistry.

[‡] Research Fellow, Department of Chemistry.

Table 4 Kinetic parameters for the thermal degradation of propellants

Temperature (°C)	Rate constant k (sec^{-1}) PS (30%) propellants	Rate constant k (sec^{-1}) Copolymer (30%) propellants	Energy of activation (Kcal/mole) PS (30%) propellants	Energy of activation (Kcal/mole) Copolymer (30%) propellants
160	4.100	0.542	5.72	3.29
200	1.398	0.310		
240	1.077	0.297		
280	0.806	0.206		

kinetic parameters for thermal degradation have been given in Table 4.

Results recorded in Table 1 show that the burning rate increases with the increase in oxidizer percentage for both polystyrene and copolymer propellants. However, the burning rate is consistently higher for the latter by about 20%. This may be due to either of the following factors: a) lower degradation rate constant in case of copolymer, b) more exothermic surface reactions in the case of copolymer, or c) higher flame temperature in the case of copolymer.

The degradation of both the propellants was investigated and the results satisfy the following equation:

$$(2/t)\ln W = kW + \text{const} \qquad (1)$$

where k is a constant which depends on temperature, W is the weight fraction volatilized, and t is the time. Values of k for various temperatures are recorded in Table 4. It is obvious that k is lower in case of copolymer propellants. Accordingly, the rate of degradation dW/dt would be higher. This is one of the causes of the higher burning rate of the copolymer propellants. The energy of activation calculated by using the Arrhenius equation is found to be lower for the copolymer propellant (Table 4). The reason for the enhanced degradation of copolymer is due to the fact that the bond energy of an –O–O– bond is lower than that of a –C–C– bond, so that the former breaks easily. There is also the likelihood of the formation of a peroxy radical on the termal decomposition of copolymer.[3] If this is so the degradation rate would be increased. However the heat of combustion of copolymer propellants is higher than that of polystyrene propellants, as is clear from Table 3. This is due to the additional –O–O– and –C–O– bonds in the copolymer.

We shall now assess the role of surface reactions or the reactions at the polymer/oxidizer interface. It is generally believed that the initial step in ammonium perchlorate decomposition involves proton transfer[4] viz.,

$$NH_4^+ClO_4^-(s) \rightleftharpoons NH_3(a) + HClO_4(a)$$

yielding adsorbed ammonia and perchloric acid, and there is a distinct possibility of solid-state reactions between the latter and the products of polymer degradation. Differential scanning, calorimetric studies, and surface temperature measurements of the propellants were undertaken to understand such reactions.

The results on DSC for both types of propellants show that an endothermic process occurs in the temperature range 515 ± 5°K–525 ± 5°K. Further an exothermic decomposition takes place in the temperature range 550 ± 10°K–710 ± 10°K. It has been observed that both the endothermic and the exothermic processes occur at a fixed temperature range (Fig. 1) and that this range is independent of the percentage of AP for a fixed scan speed. This clearly indicates that basic combustion reactions are the same in all cases. It appears that the endothermic process involves the degradation of the polymer and that the products of the degradation enter into some sort of exothermic solid state reaction with the ammonium perchlorate. The detailed DSC analysis for the kinetics, mechanism, and thermochemistry of the propellant decomposition would be published elsewhere.

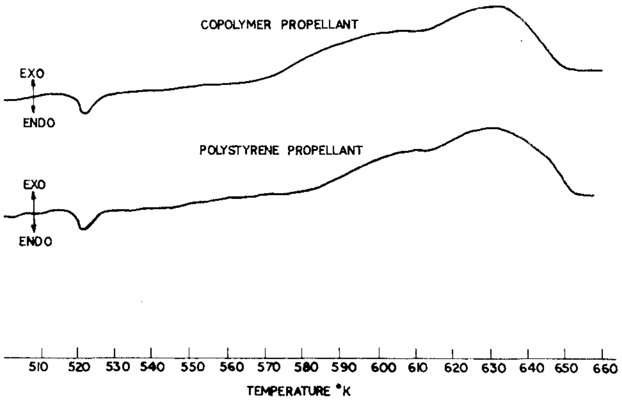

Fig. 1 DSC thermograms of PS/AP (75% by wt) and copolymer/AP (75% by wt) propellants (scan speed = 8, range = 4).

Our measurements on surface temperature (Table 3) are higher than those reported by earlier workers.[5] The constancy of surface temperature during the burning of the strand, as well as visual observation, supports the view that a liquid layer is formed at the burning surface. This view gets further support from a number of recent observations.[6,7] The molten layer is expected to have a thickness of the order of a few hundredths of a millimeter.[8] Since we used a thermocouple having a 0.45-mm-diam, this would be exposed to the reaction zone or fizz zone, and the thermocouple would measure the resultant temperature. However, it is surprising that the values are reproducible. It should be noted that the results do qualitatively support the contention that the surface temperature would be higher in the case of copolymer propellants. An enhanced surface temperature would result on account of a) exothermic surface or interface reactions and/or b) higher flame temperature. The measurements on flame temperature show that the flame temperature for the copolymer/AP (70%) propellant is higher by 300°C as compared to that of the PS/AP (70%) propellant.

The reason for the higher flame temperature can easily be understood. The break-up of the copolymer releases extra oxygen which is capable of taking part in gas-phase reactions. The results on the analysis of the combustion gases recorded in Table 2 show that percentage of CO_2 is increased in the case of the copolymer propellants, confirming the previous point.

In summation, burning rate, degradation rate, surface temperature, and flame temperature are higher in the case of the copolymer propellants as compared to that of the PS propellants. The DSC data show that both types of propellant undergo endothermic degradation of polymer which is followed by an exothermic solid state reaction.

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