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Thermal Decomposition Kinetics of Polybutadiene Binders

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Introduction

THE thermal decomposition of polymeric fuel binders plays an important role in the combustion of solid propellants.[1,2] Thermogravimetry (TG) has been extensively used for the determination of the thermal decomposition kinetics of polymers.[3] The kinetic parameters (energy of activation, E, and preexponential factor, A) calculated from TG curves are affected, in certain cases, by procedural factors like heating rate and sample mass.[4] The effect of heating rate on the pyrolysis of binders has been described.[5] It is, therefore, necessary to establish the effect of the procedural factors on E and A of the binder decomposition, for any meaningful correlation of the kinetic parameters with propellant combustion. Carboxyl and hydroxyl terminated polybutadienes (CTPB and HTPB) are used as binders for modern solid propellants. In this investigation, we have attempted to study the effect of the procedural factors, the functional groups, and the method of polymerization on the kinetics of their thermal decomposition.

Experimental

Samples

Three CTPB and two HTPB resins, obtained from different sources and prepared by different methods (free radical and anionic polymerization), were used in the study and their details are shown in Table 1.

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Table 1 Details of resins used in the study

Code	Type of resin	Method of preparation	Source
ISRO-CTPB	CTPB	Free radical	VSSC, India
HC-434	CTPB	Free radical	Thiokol, U.S.A.
Butarez CTL	CTPB	Anionic	Phillips, U.S.A.
ISRO-HTPB	HTPB	Free radical	VSSC, India
Butarez HTS	HTPB	Anionic	Phillips, U.S.A.

TG Experiments

The TG experiments were carried out with DuPont 990 Thermal Analyzer in an atmosphere of dry nitrogen purged at a flow rate of 50 $cm^3\ min^{-1}$. Seven heating rates (1, 2, 5, 10, 20, 50, and 100°C min^{-1}) at a constant sample mass (5 ± 0.1 mg) and seven sample masses (1, 2.5, 5, 7.5, 10, 15, and 20 mg) at a constant heating rate (10°C min^{-1}) were employed. Since heating rate has a more pronounced effect on the kinetic parameters,[4] the TG curves of all five samples were taken at the seven heating rates. The effect of sample mass was studied only for HC-434.

Results and Discussion

The kinetic parameters were calculated using three well-known integral equations[4]:

1) Coats-Redfern equation

$$\ell n\left(\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right)=\ell n\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}$$

2) MacCallum-Tanner equation

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right)=\log\left(\frac{AE}{\phi R}\right)-0.483\,E^{0.435}-\frac{(0.449+0.217E)\times 10^3}{T}$$

3) Horowitz-Metzger equation

$$\ell n\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right)=\ell n\left(\frac{ART_s^2}{\phi E}\right)-\frac{E}{RT_s}+\frac{E\theta}{RT_s^2}$$

[where $g(\alpha)=(1-(1-\alpha)^{1-n})/(1-n)$, α = fraction decomposed, n = order parameter, T = temperature (K), ϕ = heating rate, R = gas constant, T_s = DTG peak temperature, and $\theta = T - T_s$].

The order parameter was evaluated with the Coats-Redfern equation. Using a computer, linear plots of $\ell n(g(\alpha)/T^2)$ vs $1/T$ were drawn by the method of least squares for different values of n in the range 0 to 2 and the order parameter was obtained from the value of n which gave the best fit. It was found to be zero in all the cases. With this value of n and using each of the three kinetic equations, E and A were calculated for all the TG curves and the correlation coefficient was also determined in each case.

Tables 2-6 give the values of E, A, and r, calculated using the three equations, for the thermal decomposition of the five resins at different heating rates. Table 7 gives the corresponding values of HC-434 for different sample masses.

Table 2 Kinetic parameters of ISRO-CTPB for different heating rates

Heating rate	Kinetic equations: Coats-Redfern E	A	r	MacCallum-Tanner E	A	r	Horowitz-Metzger E	A	r
1	132.6	2.26×10^{6}	0.9802	136.4	4.38×10^{6}	0.9829	156.5	1.41×10^{8}	0.9875
2	108.6	4.54×10^{4}	0.9826	112.2	8.55×10^{4}	0.9854	133.1	3.02×10^{6}	0.9906
5	110.5	1.19×10^{5}	0.9910	114.4	2.82×10^{5}	0.9924	134.8	7.04×10^{6}	0.9961
10	105.5	7.06×10^{4}	0.9934	109.6	1.42×10^{5}	0.9945	129.5	3.73×10^{6}	0.9974
20	115.4	5.39×10^{5}	0.9934	119.8	1.14×10^{6}	0.9961	138.8	2.44×10^{7}	0.9981
50	110.5	6.17×10^{5}	0.9970	114.9	1.32×10^{6}	0.9975	133.3	2.47×10^{7}	0.9974
100	87.5	1.85×10^{4}	0.9770	91.9	4.00×10^{4}	0.9825	109.7	6.18×10^{5}	0.9804

Table 3 Kinetic parameters of HC-434 for different heating rates

Heating rate	Kinetic equations: Coats-Redfern E	A	r	MacCallum-Tanner E	A	r	Horowitz-Metzger E	A	r
1	118.4	1.48×10^{5}	0.9841	122.1	2.81×10^{5}	0.9865	142.7	9.70×10^{6}	0.9914
2	113.6	1.16×10^{5}	0.9867	117.3	2.18×10^{5}	0.9878	138.5	8.16×10^{6}	0.9929
5	100.7	2.51×10^{4}	0.9919	104.3	4.76×10^{4}	0.9933	124.2	1.37×10^{6}	0.9968
10	102.6	4.70×10^{4}	0.9928	106.6	9.31×10^{4}	0.9939	127.3	2.83×10^{6}	0.9972
20	100.3	5.13×10^{4}	0.9960	104.4	1.09×10^{5}	0.9967	124.9	2.90×10^{6}	0.9984
50	103.9	1.57×10^{5}	0.9968	119.6	3.35×10^{5}	0.9974	128.7	8.30×10^{6}	0.9978
100	93.7	4.86×10^{4}	0.9884	98.2	1.05×10^{5}	0.9909	117.3	2.05×10^{6}	0.9908

Table 4 Kinetic parameters of Butarez CTL for different heating rates

Heating rate	Kinetic equations: Coats-Redfern E	A	r	MacCallum-Tanner E	A	r	Horowitz-Metzger E	A	r
1	120.2	2.24×10^{5}	0.9948	123.9	4.25×10^{5}	0.9955	143.4	1.22×10^{7}	0.9977
2	105.8	2.75×10^{4}	0.9946	109.5	5.21×10^{4}	0.9946	129.4	1.57×10^{6}	0.9974
5	107.6	6.91×10^{4}	0.9954	111.5	1.36×10^{5}	0.9961	131.5	3.73×10^{6}	0.9982
10	109.9	1.55×10^{5}	0.9936	114.1	3.17×10^{5}	0.9946	133.9	8.08×10^{6}	0.9966
20	115.2	5.48×10^{5}	0.9949	119.6	1.17×10^{6}	0.9957	138.6	2.44×10^{7}	0.9972
50	108.5	2.68×10^{5}	0.9950	113.1	5.90×10^{5}	0.9959	132.8	1.24×10^{7}	0.9962
100	94.0	5.69×10^{4}	0.9898	98.4	1.22×10^{5}	0.9920	116.7	2.11×10^{6}	0.9913

Table 5 Kinetic parameters of ISRO-HTPB for different heating rates

Heating rate	Kinetic equations: Coats-Redfern E	A	r	MacCallum-Tanner E	A	r	Horowitz-Metzger E	A	r
1	97.6	3.85×10^{3}	0.9809	101.3	6.95×10^{3}	0.9841	123.2	3.26×10^{5}	0.9909
2	112.5	8.22×10^{4}	0.9759	116.2	1.58×10^{5}	0.9797	137.2	5.54×10^{6}	0.9859
5	109.8	9.11×10^{4}	0.9790	113.7	1.79×10^{5}	0.9823	135.5	6.49×10^{6}	0.9884
10	121.5	1.03×10^{6}	0.9886	125.8	2.15×10^{6}	0.9864	146.1	5.83×10^{7}	0.9895
20	107.7	1.39×10^{5}	0.9981	112.0	2.93×10^{5}	0.9942	132.1	7.24×10^{6}	0.9973
50	94.2	2.54×10^{4}	0.9946	98.6	5.47×10^{4}	0.9967	118.7	1.25×10^{6}	0.9975
100	82.0	7.44×10^{3}	0.9913	86.2	1.59×10^{4}	0.9934	104.5	2.75×10^{5}	0.9928

Table 6 Kinetic parameters of Butarez HTS for different heating rates

Heating rate	Kinetic equations: Coats-Redfern E	A	r	MacCallum-Tanner E	A	r	Horowitz-Metzger E	A	r
1	118.7	1.46×10^{5}	0.9686	122.3	3.06×10^{5}	0.9734	142.6	1.01×10^{7}	0.9802
2	118.8	2.54×10^{5}	0.9888	122.6	4.94×10^{5}	0.9862	143.3	1.65×10^{7}	0.9911
5	109.3	9.73×10^{4}	0.9930	113.1	1.89×10^{5}	0.9940	133.8	6.12×10^{6}	0.9970
10	117.5	5.72×10^{5}	0.9929	121.7	1.18×10^{6}	0.9989	142.7	3.64×10^{7}	0.9960
20	123.0	1.80×10^{6}	0.9985	127.5	3.88×10^{6}	0.9972	148.9	1.18×10^{8}	0.9968
50	106.4	1.95×10^{5}	0.9900	110.9	4.24×10^{5}	0.9972	131.6	1.08×10^{7}	0.9985
100	105.2	2.69×10^{5}	0.9981	109.9	6.02×10^{5}	0.9944	129.0	1.13×10^{7}	0.9944

Table 7 Kinetic parameters of HC-434 for different sample masses

Sample mass (mg)	Kinetic equations: Coats-Redfern E	Coats-Redfern A	Coats-Redfern r	MacCallum-Tanner E	MacCallum-Tanner A	MacCallum-Tanner r	Horowitz-Metzger E	Horowitz-Metzger A	Horowitz-Metzger r
1.25	111.7	2.18×10^5	0.9952	115.7	4.40×10^5	0.9960	134.2	9.17×10^6	0.9980
2.5	108.8	1.22×10^5	0.9932	112.9	2.48×10^5	0.9943	131.8	5.54×10^6	0.9972
5.1	107.2	9.35×10^4	0.9918	111.2	1.88×10^5	0.9982	131.7	5.36×10^6	0.9963
7.5	110.8	1.57×10^5	0.9900	115.0	3.22×10^5	0.9916	135.3	8.91×10^6	0.9939
10.2	95.8	1.36×10^4	0.9985	99.6	2.06×10^4	0.9946	120.8	8.65×10^5	0.9976
14.9	102.8	3.70×10^4	0.9901	106.9	7.50×10^4	0.9918	128.1	2.33×10^6	0.9957
20.5	105.5	6.03×10^4	0.9891	109.6	1.22×10^5	0.9909	131.8	4.50×10^6	0.9900

The units of E, A, and the heating rate given in the tables are kJ mole^{-1}, s^{-1}, and °C min^{-1}, respectively. From these tables, the following observations can be made:

1) The correlation coefficients are close to unity indicating near-perfect fits.

2) The kinetic parameters calculated with the Horowitz-Metzger method are higher than those with the other two methods; this is due to the approximation technique used in the integration of the former. Similar observation has been made earlier.[4]

3) The kinetic parameters are not significantly affected by either heating rate or sample mass, the deviations being about 10%, which is within the scatter usually observed in TG experiments.[6]

4) Irrespective of the nature of the terminal groups and the method of preparation, the energy of activation for the thermal decomposition of all the five resins is around 110 kJ mole^{-1} and the preexponential factor is of the order of 10^5 s^{-1}, showing that the decomposition kinetics are dependent only on the polymer backbone (which is the same in all the cases studied). The values of E and A are in close agreement with the reported values for CTPB resin.[7]

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Measurement of Nutation Parameters for the Geostationary Telecommunication Satellite Sirio

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Introduction

SIRIO 1 was launched by a Thor-Delta rocket from Cape Kennedy on August 25, 1977. Mission control was at Goddard Space Flight Center (NASA). Sirio 1 is a geostationary, spin-stabilized satellite with a despun super-high-frequency (SHF) antenna, stationed on the equator, 15° W of Greenwich. The spacecraft is cylindrical in shape, with the Apogee Boost Motor (ABM) nozzle protruding at one end and the SHF antenna at the other. The principal axis of inertia coincides with the cylinder geometric axis z. The spacecraft is dynamically stable around the z axis. An accelerometer and a nutation damper (NUD) are placed inside the spacecraft. In this paper the analysis of accelerometer telemetry data is described for the purpose of measuring nutation parameters. The accelerometer is mounted parallel to the spacecraft geometric axis z and measures the acceleration component parallel to that direction in the spacecraft reference system. The algorithms used to analyze rectified acceleration data and acceleration sign are described. The two cases of negligible and non-negligible bias are discussed.

The simple devices that prevent noise and data-flow gaps from affecting measurements are described. A method is found to analyze the sign which can recover a period as short as 1.6 s with a sampling time of 4 s, with an ambiguity on the measured value which is resolved by knowledge of a theoretically expected value or by comparison with the period calculated from amplitude. The program was tested with simulated data before launch, and worked as expected during flight. Measurements are obtained for nutation period, ratio of moments of inertia, nutation amplitude, damping time, misalignment, and bias. The spacecraft behaves as expected and nutation is efficiently damped by NUD and fuel sloshing.

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