Engineering Notes

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Effect of Heating Rate on Thermal Decomposition Kinetics of Fiberglass Phenolic

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Introduction

FIBERGLASS phenolic laminates are used as an ablative thermal protection system of rockets and their thermal decomposition has been described by different Arrhenius type equations.[1,2] The complexity of the decomposition process in the flight environment makes it impossible to evaluate the kinetic constants in tests conducted in exactly simulated flight conditions. However, thermogravimetry (TG) has been extensively used for determining the kinetic parameters for the thermal decomposition of the polymers used in such heat shield materials.[1,2] The results from TG curves are known[3] to be affected by a number of experimental variables, such as heating rate. Empirical correlations between procedural factors and kinetic parameters have evolved recently.[4,5]

This Note presents the results of our TG studies (carried out at different heating rates) on the thermal decomposition of fiberglass phenolic laminate used as a heat shield in satellite launch vehicles. As the heating rates experienced by the heat shield in the flight environments are different from those employed in usual TG experiments, an attempt to correlate heating rate and the kinetic parameters, viz. energy of activation E and pre-exponential factor A, is made. Such correlations, we hope, would make TG studies more useful in evaluating the heat shield materials.

Experimental

Fiberglass phenolic laminate (67% glass and 33% phenolic) was used as a representative specimen of 10 ± 0.5 mg weight. The TG experiments were carrried out with a Du-Pont 990 Thermal Analyzer in conjunction with a 951 Thermogravimetric Analyzer. The heating rates employed were 1, 2, 5, 10, 20, 50, and 100°C min^{-1}. As the decomposition of the satellite heat shield occurs in the Earth's atmosphere, the furnace atmosphere used was also air purged at a rate of 50 $\text{cm}^3\ \text{min}^{-1}$.

Results and Discussion

The values of the temperature of inception of reaction (T_i), the temperature of completion of reaction (T_f), and the mass loss percentage obtained from the TG experiments are given in Table 1. It can be observed that T_i is not affected much by heating rate while T_f increases with increased heating rate.[4,5] The carbonaceous residue of pyrolysis also gets oxidized by the purging air. This is in agreement with the average 34% mass loss in the TG experiments. Thus the kinetic parameters calculated from these experiments would be for the overall process of the oxidative degradation.

Kinetic Parameters

The kinetic parameters were calculated using the following three integral equations[4]: Coats-Redfern equation, MacCallum-Tanner equation, Horowitz-Metzger equation. The order parameter, n, was evaluated using the Coats-Redfern equation by an iteration method described in our earlier publication[6] and was found to be zero. With this value of n, using each one of the three kinetic equations, E, A, and the corresponding correlation coefficient r were calculated from the TG curves, recorded at the seven heating rates. The results are summarized in Table 2.

The values of the energy of activation are comparatively low; but the slow rate of decomposition can be explained since the values of the pre-exponential factor (which is a measure of the probability that a molecule having energy, E, will participate in the reaction) are also very low. Such low values of A have been reported in the literature.[7]

From Table 2 it can also be seen that the regular trend in the kinetic parameters relative to changes in heating rate makes the data amenable to statistical treatment. Using a computer, different curve fits were done using various functions of the kinetic parameters and the best-fit curve was chosen. It was found that the activation energy vs heating rate could be best represented as a third-degree curve following the equation of the type:

$$\log E = C_1 - C_2\phi + C_3\phi^2 - C_4\phi^3$$

where C_1 to C_4 are empirical constants, different for the three equations, and ϕ is the heating rate. Similarly, A vs ϕ could

Table 1 Thermogravimetry results

Heating rate, °C min^{-1}	T_i, °C	T_f, °C	Mass loss, %
1	310	495	33
2	320	555	35
5	335	595	35
10	330	615	34
20	350	690	35
50	330	760	35
100	340	900	33

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Table 2 Kinetic parameters

Heating rate, °C min^{-1}	Kinetic equations								
	Coats-Redfern			MacCallum-Tanner			Horowitz-Metzger		
	E^a	A^b	r	E^a	A^b	r	E^a	A^b	r
1	77.72	8.253×10^1	0.9979	81.17	1.568×10^2	0.9985	102.8	5.597×10^3	0.9952
2	71.70	2.612×10^1	0.9984	75.77	5.568×10^1	0.9989	96.13	1.257×10^3	0.9963
5	70.78	2.880×10^1	0.9960	75.40	6.718×10^1	0.9997	96.55	1.420×10^3	0.9989
10	66.25	2.007×10^1	09976	71.09	4.890×10^1	0.9981	93.81	1.180×10^3	0.9995
20	62.13	1.262×10^1	0.9953	67.36	3.280×10^1	0.9964	92.45	9.428×10^2	0.9994
50	57.90	1.066×10^1	0.9959	63.76	3.070×10^1	0.9971	85.60	4.388×10^2	0.9967
100	41.77	1.425×10^0	0.9804	48.20	4.671×10^0	0.9907	64.70	2.297×10^1	0.9725

[a] In KJ mole^{-1}. [b] In sec^{-1}.

Table 3 Curve fit constants for correlation of E and A with heating rate

Kinetic equation	Correlation with log E					Correlation with A				
	C_1	$C_2\times10^3$	$C_3\times10^5$	$C_4\times10^7$	F	K_1	$K_2\times10^{-3}$	$K_3\times10^{-3}$	$K_4\times10^{-3}$	F
Coats-Redfern	1.8832	7.2475	14.783	10.160	111.0	2.4576	0.23336	0.59131	0.43803	167.6
MacCallum-Tanner	1.9035	6.0538	12.489	8.6406	107.1	9.7077	0.52231	1.3481	0.97287	61.5
Horowitz-Metzger	2.0003	2.8251	5.0240	4.0933	63.9	131.85	13.262	36.460	28.666	148.5

best be represented by a third-degree curve, following the equation of the type

$$A = K_1 + \frac{K_2}{\phi} + \frac{K_3}{\phi^2} + \frac{K_4}{\phi^3}$$

where K_1 to K_4 are empirical constants, different for the three equations.

The reliability of the curve fittings was evaluated by the F test.[8] The values of C_1 to C_4 along with the corresponding Fisher constant F, the values of K_1 to K_4, and F for the three equations are given in Table 3. The critical value of the Fisher constant[8] for the system at 99% confidence level is 28.7. From Table 3 it can be seen that the confidence level of all the correlations is above 99%. Similar quantitative correlations between kinetic parameters and heating rate have been reported in the case of certain reactions, while for other reactions, the kinetic constants do not depend on the heating rate.[4] No universally acceptable theoretical explanation has been propounded for such systematic dependence.

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Turbulent Reynolds Analogy Factors of Stacked Large-Eddy Breakup Devices

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Nomenclature

A = test (flat-plate) surface area
C_f = area-averaged skin-friction coefficient, $2D/A\rho_\infty U_\infty^2$
D = measured total drag
h = area-averaged heat-transfer coefficient, $Q/A\,(T_w/T_\infty)$
Q = measured heat-transfer rate
Re_θ = momentum thickness Reynolds number
T_w = wall temperature
T_∞ = freestream temperature
U_∞ = freestream velocity
x = streamwise distance from leading edge
δ = boundary-layer thickness

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