Polymer Pyrolysis over a Wide Range of Heating Rates

A. D. Baer,* J. H. Hedges,† J. D. Seader,* K. M. Jayakar,† and L. H. Wojcik‡
The University of Utah, Salt Lake City, Utah

Experimental weight loss data are presented for the pyrolysis of three reinforced polymeric materials that were heated in nitrogen to temperatures as high as 700°C at constant heating rates from 10°C/min to 4200°C/min. Tests at low heating rates were conducted with a Mettler Thermoanalyzer. A thin-film technique was used to obtain high heating rate data. Extrapolation of low heating rate results to high heating rate conditions is not reliable. However, data for each material over a wide range of heating rates are correlated quite satisfactorily by a single kinetic equation, wherein the kinetic parameters are determined by the quasilinearization technique.

Introduction

ALTHOUGH the various laboratory thermal analysis techniques, differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), etc., are basically quantitative techniques, test results for many materials are often only qualitatively useful when applied outside the range of laboratory conditions. Test sample thickness or degree of subdivision, test cell characteristics, etc.,[1] significantly affect test results in an unpredictable fashion. Since laboratory tests on materials are often restricted to heating rates less than 10°C/min, which are several orders of magnitude lower than anticipated heating rates in practical applications, approximate extrapolation techniques have been developed. Extrapolations are usually based upon simplified kinetic models, but the validity of these models has not been adequately tested. Examples of specific areas where extrapolation of thermal analysis methods has been employed are in the burning of combustible solids,[2] ablation of insulation materials,[3,4] decomposition of unstable materials,[5] and combustion of propellants.[6,7] In each case direct verification of extrapolated results has not been possible, although agreement between some predictions and observations is usually noted.

In recent years a number of studies concerned with these heating rate effects have been reported.[8,9] However, none have really evaluated the extrapolation procedures. Very high heating rate tests (10^3 to 10^5 °C/min)[10-12] have been reported which employ very thin films deposited on electrically heated wires; evolved gas analysis rather than residue evaluation is employed to characterize the reactions. An important result of these flash pyrolysis tests is the confirmation of earlier observations[13] that sample thickness is an important parameter. Apparently, with sufficiently thin samples, primary decomposition products diffuse from the sample without further reaction; and the primary decomposition steps can be characterized.

The work discussed here was undertaken in an attempt to characterize several materials for application as ablative insulators under moderate-heat flux, low-velocity conditions. Pseudo-kinetic parameters were obtained in a form suitable for use in a complex "ablative-insulation" computer program. Conventional laboratory data were obtained with a commercial TGA apparatus at heating rates of 1, 10, and 25°C/min. A new, high heating rate technique was employed with the same materials to obtain mass loss from sample films at heating rates from 25 to 4200°C/min. The proposed application of these materials was at a heating rate of approximately 10,000°C/min. By use of results from these two types of tests, an evaluation of various extrapolation procedures could be made. Although several materials were evaluated during this work, only three ablative insulators designated as A, B, and C are considered here, since they exhibited all the types of behavior noted. Table 1 presents a listing of the major constituents of each of the three materials.

Experimental Techniques

Thermogravimetric analysis on samples of the various insulators was made by a Mettler Thermoanalyzer Model 1 operated at a constant heating rate. The weight-temperature history of the sample was used as direct input to a digital computer, where the data were fitted to a simplified kinetic model. The tests were conducted in nitrogen at 0.85-atm pressure at heating rates of 1, 10, and 25 °C/min. Temperatures as high as 1000°C were attained.

In most cases, samples for thermogravimetric analysis were prepared by grinding the material after cooling in liquid nitrogen to obtain the required rigidity, collecting that part of the material that would pass an 18-mesh sieve, and drying it under vacuum at 56°C. Portions of the ground, dried material equal to 10±0.2 mg were weighed out on a microbalance. Gas flow for these experiments was maintained at 100±10 ml/min to obtain constant buoyancy effects in a given atmosphere.

The experimental technique used in this study for tests at high heating rates is a recent development and has not been previously described. Therefore, a fairly detailed discussion of this technique is presented as follows.

Table 1 Major constituents of materials tested

	Material A	 B	 C
Composition, Wt, %			
EPDM/Neoprene[a]	68.38	...	...
Acrylonitrile butadiene	...	56.34[c]	29.54[b]
Phenolic (BKR 2620)	...	...	35.45
Silica hydrate	23.93	11.27	...
Asbestos	...	28.17	...
Powdered boric acid	...	...	23.63
Sulfur	1.37	1.13	...
Other[d]	6.32	3.09	11.37
Totals	100.00	100.00	100.00
Calculated nonvolatile in N_2 (700°C)[e]	27.4	42.3	47.4
Measured nonvolatile in N_2 (700°C)[f]	26	39	48

[a] Nordel 1040 (ethylene-Propylene-1, 4 hexadiene monomer) and Neoprene FB in ratio of 4 to 1. [b] Hycar 1051. [c] Chemigum N-7. [d] Curative, stabilizers, antioxidants, flame retardants, ZnO, etc. [e] Total of silica hydrate, asbestos, glass fibers, carbon fibers, B_2O_3, ZnO, Sb_2O_3, phenolic char. [f] Heating rate was 170°C/min.

Received Feb. 15, 1977; revision received July 8, 1977.

Index category: Ablation, Pyrolysis, Thermal Decomposition and Degradation (including Refractories).

*Professor of Chemical Engineering, Department of Chemical Engineering. Associate Fellow AIAA.

†Research Assistant, Department of Chemical Engineering.

‡Research Assistant, Flammability Research Center.

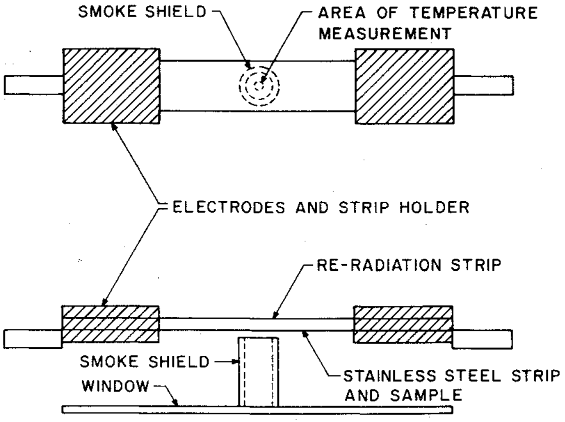

Fig. 1 Sample mounting system for thin films. The test samples were mounted on the lower strip facing the reradiation strip.

Test samples, nominally 0.0125-cm thick × 1.27-cm wide × 12.7-cm long, of the various insulation materials were supplied for these tests. The films were bonded to 0.0025-cm thick × 1.27-cm wide strips of preoxidized stainless steel. The steel strips were clamped between copper electrodes and were heated electrically at a predetermined rate under control of a servo system. Figure 1 is a sketch of the sample miniature system. In all of the tests discussed here, the plane of the strips was horizontal. The sample was bonded to the lower strip with the exposed surface of the sample facing the reradiation strip. The temperature of a 0.3-cm-diameter region at the center and bottom of the lower strip was measured by use of a Raytek Model S/L-300 infrared thermometer. The thermometer was dynamically calibrated for use with the oxidized stainless-steel strips at the zinc and aluminum melting points of 419.4 and 660°C, respectively.

Preweighed samples were heated at a constant rate to a predetermined maximum temperature, the electrical current was stopped, and the strip and sample temperature were quickly reduced by use of a blast of cold nitrogen. Quenching rates of 5×10^4 °C/min were achieved. Weight loss of each sample was determined by reweighing the strip and sample on an analytical balance.

The length of the samples was selected to make use of the cooling effect of the copper electrodes to prevent overheating of the outer ends of the sample. Because of the heat capacity of the polymer, the central portion of the metallic strip bonded to the film would be at a lower temperature than the uncovered end of the strip, in the absence of heat losses. An optimum sample length for each heating rate was determined analytically, and the calculation was experimentally verified.

For heating rates less than 5000°C/min, the temperature difference between the stainless-steel strip and the surface of a 0.0125-cm thick sample would be less than 5°C in the absence of heat losses. Both radiative and convective heat losses from the sample surface were effectively eliminated by the reradiation strip located 0.32 cm above the sample surface, as shown in Fig. 1. The reradiation strip was electrically in parallel with the sample strip and was, thus, always at a slightly higher temperature than the sample during a test.

The strip, sample, and electrodes were mounted in a partially sealed, clear plastic container for a test. A volume of a pure nitrogen gas equal to 10 times the container volume was passed through the container prior to a test to remove the air. All tests were in nitrogen at atmospheric (0.85 atm) pressure. Also, these insulating materials tended to produce a large amount of dense smoke during pyrolysis. The smoke shield shown in Fig. 1 was installed to prevent this smoke from obscuring the view of the infrared sensor.

Preliminary tests showed that approximately 5% of the sample mass was lost during heating of the samples to 250°C. It appears that this early loss of material was responsible for some bubble formation in the films and a tendency for some areas of the film to lift-off of the steel strips. In most cases, 10-20% of the sample area was not in direct contact with the strip. Motion pictures taken of the samples during a test showed that bubbling was not observed at temperatures greater than 250°C. Fortunately, this effect does not lead to serious errors in measurement of the mean sample temperatures except at very high heating rates. Because the samples were very thin, radiant heating between the two stainless-steel strips was effective in maintaining the raised areas at the strip temperature. In order to maintain an accuracy of reported mean film temperatures to about ±10°C, it was necessary to limit heating rates to less than 5000°C/min in these tests.

Analysis of the data for the materials tested indicated that an asymptotic limit in the fractional mass retention of the films was reached at a temperature less than 700°C. Table 1 indicates the values of this asymptotic limit for each material. A comparison is also shown of this limit to a calculated value based on the assumption that all film constituents would vaporize except for the inorganic materials and phenolic char. The fact that the ratio of the measured to the calculated value of the fraction retention is near one suggests that most of the organic materials were lost. Very large amounts of carbonaceous chars from the polymers were not formed at these heating rates during pyrolysis in nitrogen.

Experimental Results

Figure 2 illustrates the mass retention-temperature curves obtained by TGA at 10°C/min for the three materials of interest. During a single run, this type of information was collected by a data acquisition system assembled about a Hewlett-Packard Model 2100S computer. The stored, digitized data were then used to generate kinetic constants for each run by means of the ratio method of Mickelson and Einhorn[14] using the pyrolysis model described below. The range of weight loss values used as input to the computer to generate parameters was selected to give minimum errors over the region where the maximum rate of weight loss occurred. Except for material C, where an apparent two-stage reaction

Table 2 Pyrolysis model constants and kinetic parameters

Material	Type of test[a]	Fraction retained at 350°C (w_0)	Fraction retained at T_{max}[b] (w_r)	Reaction order n	Activation energy, E, cal/gm mole	Frequency factor, A, min^{-1}	Reference figure no.
A	TGA	0.95	0.32	0.58	58000	0.47×10^{17}	3
B	TGA	0.96	0.338	0.74	25700	0.13×10^{8}	4
C	TGA	0.92	0.484	2.12	39200	0.37×10^{12}	5
A	HHR	0.96	0.26	1.56	36000	0.18×10^{11}	6
B	HHR	0.93	0.39	1.82	38500	0.76×10^{12}	7
C	HHR	0.89	0.48	2.48	59000	0.36×10^{18}	8

[a] TGA refers to test using the Mettler thermoanalyzer at a heating rate of 10°C/min with data analysis using Eq. (1) by ratio method. HHR refers to high heating rate tests with data analysis using Eq. (2) by quasilinearization method. [b] For TGA tests, T_{max} was 1000°C. For the HHR tests, T_{max} was 700°C achieved at a heating rate of 170°C/min.

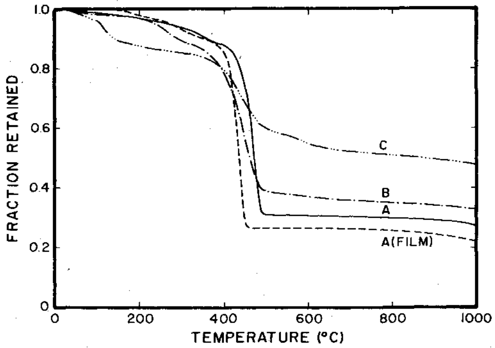

Fig. 2 TGA curves for 10°C/min in nitrogen. Except as noted, all materials were in the form of – 18-mesh granules.

is indicated, the values predicted from the simple pyrolysis model using the best-fit parameters were almost indistinguishable from the experimental data for fractional retention between 0.4 and 0.8.

The pyrolysis model parameters derived from the TGA tests are summarized in Table 2. The parameters apply to the mathematical pyrolysis model represented by

$$-\frac{\mathrm{d}W_l}{\mathrm{d}t}=AW_l^n\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where $W=(w-w_r)/w_0-w_r$, w is the fraction retained at time t, w_0 is the fraction retained at the minimum temperature of interest, w_r is the asymptotic fraction remaining at high temperature, A is the pre-exponential factor in the rate law, n is the empirical order of the reaction, and E, R, and T are the activation energy, gas constant, and temperature, respectively. The value of w_0 was taken as the fraction retained at 350°C as measured from the high heating rate tests. The value of w_r was taken to be the fraction retained at 1000°C in the TGA tests. As noted earlier, the fractional retention at 1000°C was determined primarily by the quantity of nonvolatile inorganic materials included in the formulation. Only the parameters n, E, and A were obtained by analysis of the 10°C/min TGA results.

Thermogravimetric analysis was also made on 10-mg samples of the 125-μm-thick films used in the high heating rate tests. In the case of the B and C materials, no significant differences were noted between film or powdered material. However, results for the A material films, shown in Fig. 2, indicate some differences for the two forms. The fact that the high-temperature asymptotic retention limit is not the same indicates that there were, in fact, compositional differences. In the following discussion, for the sake of consistency, the comparisons are between TGA data on powdered material and high heating rate tests on films. In the case of the A material, it is apparent that the comparison should be to TGA tests on the film; however, the final conclusions are not changed.

Results of the high heating rate tests are shown in Figs. 3-5. Data points of the fractional weight retention of the various films are plotted as a function of maximum film temperature. The light solid lines through the data points in all three plots are simply approximate "eye-fits" to the data, wherein some artistic license has been exercised. Also, shown in these figures are dashed lines which represent predictions for 25, 170, 850, and 4200°C/min based on Eq. (1) using the parameters derived from the TGA tests at a 10°C/min heating rate.

A direct comparison between results obtained by the TGA equipment and the high heating rate apparatus was made by performing tests at a heating rate of 25°C/min in both devices. The results are included in Fig. 3, where the leftmost dashed line accurately represents the TGA data. Since each device was operated at the limit of its practical operating range, data scatter and the uncertainties in the results were higher than normal. For a given fractional weight retention, it is seen that the thin-film temperatures are as much as 25°C different from the corresponding TGA temperature, although the average error of 4°C for the six central data points is less than the sum of the uncertainties in the temperature measurement in the two apparatuses. For practical purposes, the results at 25°C/min were essentially the same.

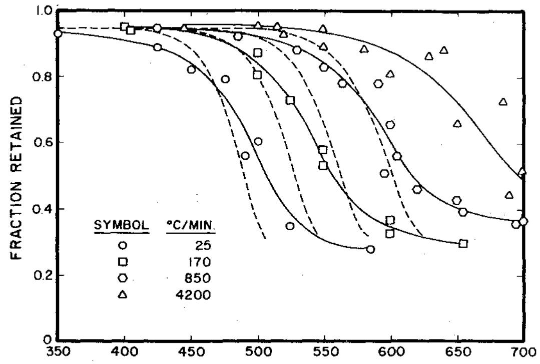

Fig. 3 Comparison of data for high heating rate tests with predictions from TGA model (dashed lines) for material A.

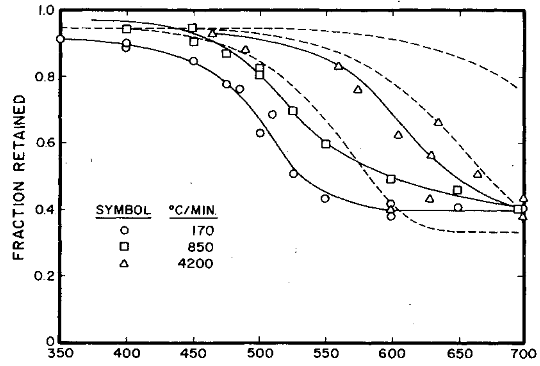

Fig. 4 Comparison of data for high heating rate tests with predictions from TGA model (dashed lines) for material B.

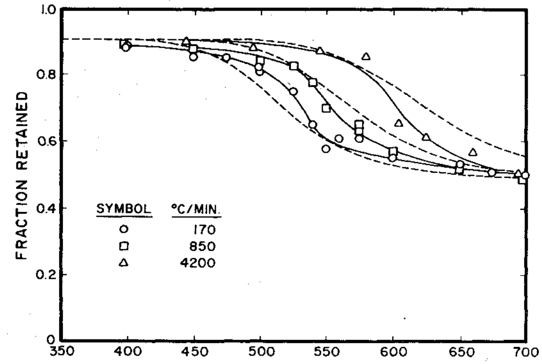

Fig. 5 Comparison of data for high heating rate tests with predictions from TGA model (dashed lines) for material C.

The fraction-retained asymptote at high temperature for the TGA tests is about equal to the value measured in the high heating rate tests for the A and C materials as seen in Figs. 3 and 5. In the case of material B in Fig. 4, chemically bound oxygen in the inorganic materials likely had time to react with the organic matter at the low heating rate of the TGA test, thus increasing the volatilization of carbon or the inorganic materials.

For materials A and B, the predicted curves of fraction retained based upon the TGA data are not in very good agreement with the values measured at high heating rates. At a heating rate of 850°C/min (nearly two orders of magnitude extrapolation of the heating rate), the predicted temperature of half-mass loss is low for material A and high for material B. The maximum error is about 100°C. The maximum slopes and the shape of the tail-off to the high-temperature asymptote for the predicted fraction-retention vs temperature curves are very different from experimental observation. In contrast, the predictions for material C are in reasonably good agreement with the experimental curves, both with respect to the temperature of half-weight loss and to curve shape.

The lack of agreement between measurement at high heating rates and prediction based on data obtained at low heating rates is likely the result of two factors. First, Eq. (1) is only an approximate representation of a very complex phenomenon. Extrapolation of a questionable model is risky. Also, the parameters listed in Table 2 are strongly affected by small changes in pyrolysis results. At low heating rates such small changes could be traced to effects of minority constituents; at high heating rates, these effects should be minimized.

These results show that the extrapolation procedure employing Eq. (1) simply is not generally accurate. Even worse, because all possible qualitative differences were noted, one cannot even use such a procedure to insure a conservative prediction. A better pyrolysis model is required. However, because of the complexity of the degradation process, it is unlikely that an improved model can be generated. A less attractive alternate is to use essentially the same model but to improve the evaluation of the parameters by use of data obtained over a wide range of heating rates. This is the approach used here, and the next section briefly describes a technique for obtaining an optimum set of parameters for any selected pyrolysis model.

Quasilinearization Technique for Determining Kinetic Parameters

Burningham and Seader[15] developed a quasilinearization technique for analyzing TGA data. Based on an assumed general kinetic model of a form of Eq. (1), their method determines the kinetic parameters by a least-squares optimization procedure to fit best the experimental data. An improved version of the quasilinearization technique was used in the study reported here to obtain the kinetic parameters for the high heating rate data.

The quasilinearization method utilizes experimental data directly and, thereby, avoids inaccurate data handling procedures, such as graphical data analysis and slope measurements. The method is iterative in nature and requires an initial set of assumed values for the kinetic parameters. As reported by Burningham and Seader, the two primary difficulties encountered in applying the method were 1) the lack of guarantee of convergence, and 2) the necessity of constraining the values of the order of reaction n. The technique of data perturbation as reported by Donnelly and Quon[16] was successfully applied in this study to the quasilinearization technique to overcome both difficulties. The following is a brief description of the improved quasilinearization method.

A modification of Eq. (1) was used in the form

$$-\frac{\mathrm{d}W}{\mathrm{d}t}=AW^{n}\exp-\frac{E}{RT} \tag{2}$$

where $W=(w-w_r)/w_0$. First, the problem of determining the kinetic parameters A, E, and n is transformed to one of determining the initial conditions for a set of differential equations in time that includes Eq. (2) subject to the initial condition

$$W(0)=1-(w_r/w_0) \tag{3}$$

and

$$\frac{\mathrm{d}A}{\mathrm{d}t}=0,\ A(0)=A_0 \tag{4}$$

$$\frac{\mathrm{d}E}{\mathrm{d}t}=0,\ E(0)=E_0 \tag{5}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t}=0,\ n(0)=n_0 \tag{6}$$

where T is a known function of time.

The problem now is to solve Eqs. (3-6) simultaneously to minimize the least-squares error. To do this, the equations are linearized by a Taylor's series expansion truncated after the first derivative to give the following recursive equations in terms of iteration $i+1$:

$$\begin{aligned}\frac{\mathrm{d}W^{i+1}}{\mathrm{d}t}=-\Big[&A^{i}e^{-E^{i}/RT}(W^{i})^{n^{i}}+n^{i}A^{i}e^{-E^{i}/RT}(W^{i})^{n^{i}-1}\\&\times(W^{i+1}-W^{i})+e^{-E^{i}/RT}(W^{i})^{n^{i}}(A^{i+1}-A^{i})-\frac{A^{i}}{RT}e^{-E^{i}/RT}\\&\times(W^{i})^{n^{i}}(E^{i+1}-E^{i})+A^{i}e^{-E^{i}/RT}\ln W^{i}(W^{i})^{n^{i}}(n^{i+1}-n^{i})\Big]\end{aligned} \tag{7}$$

$$\frac{\mathrm{d}A^{i+1}}{\mathrm{d}t}=0 \tag{8}$$

$$\frac{\mathrm{d}E^{i+1}}{\mathrm{d}t}=0 \tag{9}$$

$$\frac{\mathrm{d}n^{i+1}}{\mathrm{d}t}=0 \tag{10}$$

The iterative procedure is initiated by assuming values of A^{o}, E^{o}, and n^{o} and solving Eq. (2) by the Runge-Kutta numerical procedure for $W^{o}(t)$. Equations (7-10) then are solved for successive values of i by the well-known procedure of forming a particular and homogeneous solution.

The solution of Eq. (7) can now be represented in the form

$$W^{i+1}(t)=p^{i+1}(t)+\alpha_1^{i+1}h_1^{i+1}+\alpha_2^{i+1}h_2^{i+1}(t)+\alpha_3^{i+1}h_e^{i+1}(t) \tag{11}$$

where α_1^{i+1} are constants to be determined. Thus,

$$\begin{aligned}\frac{\mathrm{d}p^{i+1}}{\mathrm{d}t}=-\Big[&A^{i}e^{-E^{i}/RT}n^{i}(W^{i})^{n^{i}-1}(p^{i+1}-W^{i})\\&+(W^{i})^{n^{i}}A^{i}e^{-E^{i}/RT}(-1/RT)(-E^{i})\\&+A^{i}e^{-E^{i}/RT}(W^{i})^{n^{i}}\ln(W^{i})(-n^{i})\Big]\end{aligned} \tag{12}$$

and $p^{i+1}(0)=W(0)$. Also,

$$\begin{aligned}\frac{\mathrm{d}h_1^{i+1}}{\mathrm{d}t}=-\Big[&A^{i}e^{-E^{i}/RT}n^{i}(W^{i})^{n^{i}-1}(h_1^{i+1})\\&+(W^{i})^{n^{i}}e^{-E^{i}/RT}(A^{i+1})+(W^{i})^{n^{i}}A^{i}e^{-E^{i}/RT}\\&\times(-1/RT)(E^{i+1})+A^{i}e^{-E^{i}/RT}(W^{i})^{n^{i}}\ln(W^{i})(n^{i+1})\Big]\end{aligned} \tag{13}$$

The following convenient values of initial conditions are chosen: $h_1^{i+1}(0)=0$, $A^{i+1}(0)=1$, $E^{i+1}(0)=0$, and $n^{i+1}(0)=0$.

Similarly,

$$\frac{dh_2^{i+1}}{dt} = -\Big[A^i e^{-E^i/RT} n^i (W^i)^{n^i-1} (h_2^{i+1})$$

$$+ (W^i)^{n^i} e^{-E^i/RT} (A^{i+1}) + (W^i)^{n^i} A^i e^{-E^i/RT}$$

$$\times (-1/RT)(E^{i+1}) + A^i e^{-E^i/RT} (W^i)^{n^i} \ln(W^i)(n^{i+1})\Big] \quad (14)$$

with $h_2^{i+1}(0)=0$, $A^{i+1}(0)=0$, $E^{i+1}(0)=1$, and $n^{i+1}(0)=0$. Also,

$$\frac{dh_3^{i+1}}{dt} = -\Big[A^i e^{-E/RT} n^i (W^i)^{n^i-1} (h_3^{i+1})$$

$$+ (W^i)^{n^i} e^{-E^i/RT} (A^{i+1}) + (W^i)^{n^i} A^i e^{-E^i/RT}$$

$$\times (-1/RT)(E^{i+1}) + A^i e^{-E^i/RT} (W^i)^{n^i} \ln(W^i)(n^{i+1})\Big] \quad (15)$$

with $h_3^{i+1}(0)=0$, $A^{i+1}(0)=0$, $E^{i+1}(0)=0$, $n^{i+1}(0)=1$.

Equations (12-15) are also solved by the Runge-Kutta method. The constants α_j^{i+1} are determined for each iteration such that the objective function Q is minimized:

$$Q = \sum_{j=1}^{k} \left[W^{i+1}(t_j) - W_{j,\text{data}}\right]^2 \quad (16)$$

where $W^{i+1}(t_j)$ are the computed points, and $W_{j,\text{data}}$ are the corresponding data points for the particular times. Sets of data at different heating rates may be considered simultaneously.

The objective function may be written as

$$Q = \sum_{j=1}^{k} \Big[p^{i+1}(t_j) + \alpha_1^{i+1} h_1^{i+1}(t_j) + \alpha_2^{i+1} h_2^{i+1}(t_j)$$

$$+ \alpha_3^{i+1} h_3^{i+1}(t_j) - W_{j,\text{data}}\Big]^2 \quad (17)$$

For a minimum Q,

$$\frac{\partial Q}{\partial \alpha_1^{i+1}} = \frac{\partial Q}{\partial \alpha_2^{i+1}} = \frac{\partial Q}{\partial \alpha_3^{i+1}} = 0 \quad (18)$$

The linear equations generated by Eq. (18) are solved simultaneously for α_1^{i+1}, α_2^{i+1}, and α_3^{i+1} using experimental values of $W_{j,\text{data}}$ and the computed values of p^{i+1}, h_1^{i+1}, h_2^{i+1}, and h_3^{i+1} at t_j. The resulting α values are related to the next set of kinetic parameters as follows:

$$\alpha_1^{i+1} = A^{i+1}, \; \alpha_2^{i+1} = E^{i+1}, \; \alpha_3^{i+1} = n^{i+1}$$

As mentioned earlier, a serious drawback of the procedure described is the lack of guarantee of convergence. This is particularly evident unless the value of n is constrained. In this study, for material A, convergence was not obtained by the foregoing procedure when data at heating rates of 25, 170, 850, and 4200°C/min were considered simultaneously and when the initial set of parameters was assumed to be $A^o = 1.8 \times 10^{13}\text{min}^{-1}$, $n^o = 2.0$, and $E^o = 45{,}000$ cal/gm mole. However, by using the improved technique based on perturbing the experimental data points, rapid convergence was obtained.

The perturbation technique is based on the idea that, if the kinetic equation with the estimated parameters does not generate points within the convergence domain of the experimental data, then the generated points can be compared instead to a fictitious set of nearby experimental data points. The fictitious points are located at a fraction of the distance from the generated curve to the experimental data curve. During successive iterations, the fictitious data points are perturbed toward the actual experimental data in steps small enough that each successive application of the quasilinearization procedure converges. The solution is obtained when the fictitious and experimental data points coincide.

In this study, the successive sets of fictitious data points, $W_{j,\text{fict}}$, were obtained from the relation

$$W_{j,\text{fict}} = W^{i+1}(t_j) + \beta[W_{j,\text{data}} - W^{i+1}(t_j)]$$

where $0 \le \beta \le 1.0$.

With $\beta = 0.2$, it was found possible to converge experimental data for all materials. In some cases the initial assumed set of parameter values differed significantly from the converged values. In general, convergence was rapid. Generally, perturbation of data was not required for more than five iterations. By that iteration, the values of the kinetic parameters were such that the points computed from the kinetic equation were within the domain of convergence of the actual experimental data. The parameters where then adjusted further to satisfactory convergence tolerances with about five additional iterations.

Discussion of Results

The parameters in Eq. (2) were obtained for each of the three materials from the high heating rate data by use of the quasilinearization technique described above. For each material, experimental data at three or four heating rates were treated simultaneously. It should be noted that Eqs. (1) and (2) differ by the definition of W_1 and W, but the other parameters have the same meaning. For $n = 1$, the models are the same. Two pyrolysis models were used because of requirements of the TGA data analysis and the intended final use of these results. In the cases considered here, direct comparison between values of model parameters is meaningful.

It should be noted that the activation energy is the only parameter for which direct comparison can be made. Changes in the order of the reaction n only alter the shape of the tail-off to the high temperature asymptote, and the value of the pre-exponential factor would be changed as E is altered to produce coincidence with the TGA result at a fixed heating rate.

Table 2 includes the kinetic parameters for the various materials derived from application of the quasilinearization technique to the high-rate data. Figures 6-8 present comparisons of the high heating rate data to calculated curves based upon these parameters. The results shown in Fig. 6 were obtained by use of the quasilinearization technique applied to the data points. Essentially the same model parameters were obtained by use of points from the smooth curves drawn through the data. The results shown in Figs. 7 and 8 were

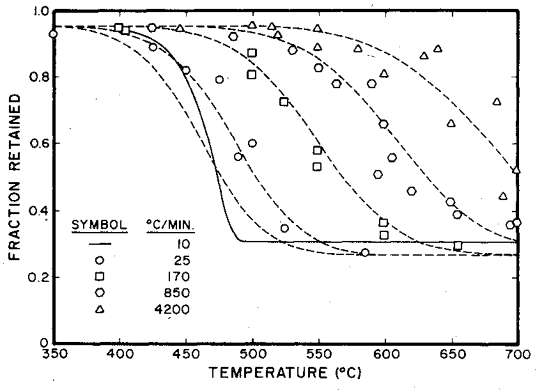

Fig. 6 Correlation of high heating rate data by quasilinearization method (dashed lines) for material A. The solid line is from the TGA tests at 10°C/min.

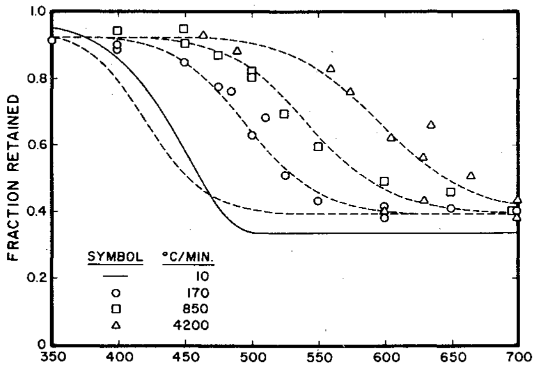

Fig. 7 Correlation of high heating rate data by quasilinearization method (dashed lines) for material B. The solid line is from the TGA tests at 10°C/min.

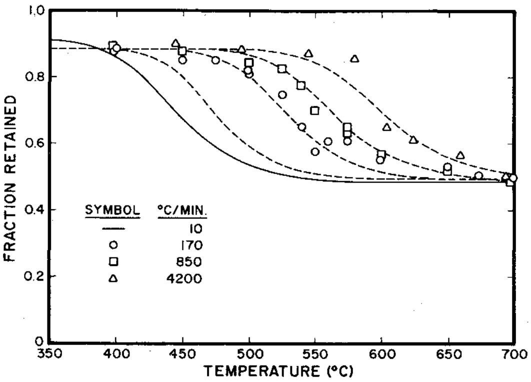

Fig. 8 Correlation of high heating rate data by quasilinearization method (dashed lines) for material C. The solid line is from the TGA tests at 10°C/min.

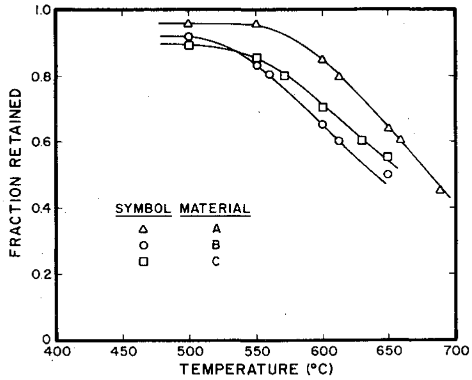

Fig. 9 A comparison of the mass retention of the three materials at the highest heating rate of 4200°C/min.

obtained using points at 5°C intervals from the curves at 170, 850, and 4200°C. In all cases, the agreement between calculation and measurement is excellent and is, in fact, well within the temperature measurement error bounds. Since the 4200°C/min data were thought to be the least accurate, a characterization which omitted these test results was made, and the kinetic parameters were only slightly changed and in this case, the agreement between calculation and observation was still good at the 4200°C/min rate.

Figures 6-8 present a reproduction of the TGA result at 10°C/min given as a dark, solid line on the left side. In general, the extrapolation of the quasilinearization results to this low heating rate yields reasonable agreement with the TGA result except for the "tail-off" region. It is suggested that the model parameters derived from data at several rates may be more useful for extrapolation than would be the parameters derived from very precise data at one heating rate.

Figure 9 is a comparison of the data for the three materials at the highest heating rate. It is of some interest to note that while the temperature of half-loss of the volatile material was increased from about 450°C at 10°C/min (Fig. 2) to about 650°C at 4200°C/min the relative thermal stability of the organic material in the A film remained higher than that of the other materials, while the apparent stability of the B and C materials reversed as the heating rate was increased.

Conclusion and Recommendations

A review of the data obtained during this program shows that reliable predictions of high heating rate pyrolysis phenomena cannot be made from data obtained in conventional low heating rate apparatus based upon our present understanding of the pyrolysis process. The predicted temperatures for half-mass loss may be lower, higher, or equal to the measured values; and there appears to be no way to predict which of these three cases will apply.

Extrapolation of pyrolysis data based upon results from a single heating test is not recommended. If extrapolation is required, the best procedure appears to be to base the extrapolation on data from tests at several heating rates covering as wide a range as possible. For the materials tested in this program, the pyrolysis model constants obtained by application of the quasilinearization technique to the high heating rate data and summarized in Table 2 are the best available values to be used for extrapolation to higher rates. Since these constants are for an experimental model, the wide variations in values of the parameter A have little physical significance. Serious errors in the predictions would not be expected for heating rates less than 10,000°C/min; however, there would be no justification for expecting to be able to predict material response from these results at much higher rates.

Acknowledgment

The authors gratefully acknowledge the interest and suggestions of I. N. Einhorn, Director of the Flammability Research Center, University of Utah. This study was conducted under contract to Hercules Inc., Magna, Utah, subcontractors to Lockheed Missiles and Space Company, Inc., prime contractors for Navy's Trident I-C4 Missile.

References

[1] Daniels, T. C., *Thermal Analysis*, Wiley, New York, 1973, pp. 53-72.

[2] Einhorn, I. N., "The Chemistry of Fire Resistant Materials and Suppression," *Fire Research Abstracts and Reviews*, Vol. 13, No. 3, 1971, pp. 236-267.

[3] Friedman, H. L., "Kinetics of Thermal Degradation of Char-Forming Plastics from Thermogravimetry. Application to a Phenolic Plastic," *Journal of Polymer Science*, Pt. C, No. 6, 1964, pp. 183-195.

[4] April, G. C., Pike, R. W., and del Valle, E. G., "Modeling Reactive Gas Flow in the Char Layer of an Ablator," *AIAA Journal*, Vol. 9, June 1971, pp. 1113-1119.

[5] Inami, S. H., Rosser, W. N., and Wise, J., "Heat-Release Kinetics of Ammonium Perchlorate in the Presence of Catalysis and Fuels," *Combustion and Flame*, Vol. 12, 1968, pp. 41-50.

[6] Sammons, G. D., "Application of Differential Scanning Calorimetry to the Study of Solid Propellant Decomposition," *Third ICRPG Combustion Conference*, CPIA Publication No. 138, Feb. 1967.

[7] Waesche, R. H. W., "Research Investigation of the Decomposition of Composite Solid Propellants," United Aircraft Research Laboratories, East Hartford, Conn., Rept. H910476-36 under Contract No. NAS-481, Sept. 1969.

[8] Cheng, J. T., Ryan, N. W., and Baer, A. D., "Oxidative Decomposition of PBAA Polymer at High Heating Rates," *Twelfth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1969, pp. 525-532.

[9] Bouck, L. S., Baer, A. D., and Ryan, N. W., "Pyrolysis and Oxidation of Polymers at High Heating Rates," *Fourteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1973, pp. 1139-1149.

[10] Levy, R. L. and Fanter, D. L., "Measurement of Temperature Rise Times in Pyrolysis Gas Chromatography," *Analytical Chemistry*, Vol. 41, Sept. 1969, pp. 1465-1467.

[11] Wolf, C. J., Levy, R. L., and Fanter, D. L., "Determination of the True Decomposition Temperature in Pyrolysis Experiments," *Journal of Fire and Flammability*, Vol. 5, Jan. 1974, pp. 76-84.

[12] Barlow, A., Lehrle, R. S., Robb, J. C., and Sunderland, D., "Direct Examination of Polymer Degradation by Gas Chromatography II—Development of the Technique for Quantitative Kinetic Studies," *Polymer*, London, Vol. 8, 1967, pp. 523-527.

[13] Barlow, A., Lehrle, R. S., and Robb, J. C., *Techniques of Polymer Science*, Society of Chemical Industry, London Monograph #17, Gordon and Breach, New York, 1963, pp. 267-280.

[14] Mickelson, R. W. and Einhorn, I. N., "The Kinetics of Polymer Decomposition Through Thermogravimetric Analysis," *Thermochemica Acta*, Vol. 1, May 1970, pp. 147-158.

[15] Burningham, N. W. and Seader, J. D., "Determination of Kinetic Parameters for the Thermal Degradation of Polymers by the Quasilinearization Technique," *Thermochemica Acta*, Vol. 5, Nov. 1972, pp. 59-69.

[16] Donnely, J. K. and Quon, D., "Identification of Parameters in Systems of Ordinary Differential Equations Using Quasilinearization and Data Perturbation," *Canadian Journal of Chemical Engineering*, Vol. 48, Feb. 1970, pp. 114-119.