Pyrolysis Kinetics of Nylon 6-6, Phenolic Resin, and Their Composites

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SUMMARY

A multistep kinetic process is postulated to describe the pyrolysis of nylon 6-6, phenolic CTL-91LD (a phenolic novalac resin), and their composites. Kinetic coefficients are derived from thermogravimetric analysis data (TGA) at heating rates varying from 3-60°C/min for each component. Three correlation techniques are used to obtain consistent coefficients. A two-step kinetic equation is derived to describe the phenolic pyrolysis and a single-step kinetic equation is found to adequately represent nylon 6-6 pyrolysis. These equations are then combined to obtain an overall pyrolysis rate equation for the composite.

The derived rate equations for the individual components and the 1:1 composite are verified by comparing them with TGA data taken at rates of sample temperature rise varying from 3-100°C/min. Predictions are made for isothermal pyrolysis of a 1:1 composite. Weight-loss data for the nylon-phenolic composite, during both isothermal pyrolysis and pyrolysis at programmed rates of temperature rise, are accurately correlated by the multistep pyrolysis rate equation.

INTRODUCTION

The simultaneous depolymerization of a composite containing a thermo-setting resin and a thermoplastic fiber is difficult to formulate analytically. When heated, each polymer depolymerizes by a characteristic kinetic process in converting the condensed phase to solid and gaseous products. In order to accurately describe the response of such a composite material to hyperthermal environments, a detailed kinetic model is required which predicts weight loss under a variety of polymer heating conditions.

In previous studies, pyrolysis of nylon, phenolic, and their composites has been characterized by single-step kinetic processes [1-3, 7]. Agreement between the single-step kinetic theory and TGA data for phenolic and for nylon-phenolic composites is less than satisfactory, and the validity of extrapolating this theory to conditions far removed from laboratory conditions is questionable. For these reasons, a detailed kinetic study of nylon, phenolic, and a 1:1 weight-ratio nylon-phenolic composite was undertaken. The purpose of this study was to derive a rate equation and appropriate kinetic coefficients for use in solution of the transient thermal-response problem for nylon-phenolic composites. The particular constituents considered were du Pont nylon 6-6 fabric and CTL-91LD phenolic resin. These materials were believed to be representative of the nylons and phenolics to be used in the ablative environments of interest.

EXPERIMENTAL

Materials

Elemental composition and heat of combustion were determined for the nylon 6-6, phenolic CTL-91LD, and their 1:1 composite. Table 1 lists the elemental compositions for each component and two composites of the components. The mass fractions of phenolic and nylon in both composites were the same, but one composite had chopped nylon fibers and the other composite had a nylon fabric layup. Processing of both composites was the same.

These materials were obtained from production lots. The objective was to use materials representative of actual end use items. TGA and elemental analysis of a number of different batches showed no significant variation between lots, as long as the standard processing procedure was used. Samples were stored in a desiccator for at least 24 hr before TGA's were run.

Table 1. Composition of Heat Shield

Elemental composition wt%	Nylon 6-6 fabric	Phenolic CTL-91 LD resin	Chopped	1:1 Composite Laminated	Calculated[a]
C	62.8	75.7	70.4	69.8	70.0
H	9.5	6.4	7.8	7.8	8.1
O	14.9	17.5	15.3	15.7	15.4
N	12.8	0.4	6.5	6.7	6.5
Heat of formation at 298°K in cal/g	-784	-612	-711		

aCalculations assumed a 1:1 weight ratio of nylon and phenolic.

Table 1 gives heats of formation for each material. Heats of combustion were measured using a Parr Bomb calorimeter. Heats of formation were calculated based on the elemental compositions shown in Table 1.

Measurement Methods

Following is a description of the instrument and procedures used to obtain TGA data for the kinetics analysis.

An American Instrument Company thermograv was used for the thermogravimetric measurements. A schematic diagram of the instrument is shown in Fig. 1. The weight loss (or gained) by the sample moves the armature in or out of the transducer's magnetic field causing changes in the field strength which, after suitable amplification and modulation, is registered on the Y axis of the recorder. The sample thermocouple, located in the well adjacent to the sample, provides a continuous reading of material temperature. A timing device, electromechanically connecting heater and recorder, indicates time marks at 1-, 5-, and 20-min intervals. The furnace can be programmed to give sample temperature rates of 3, 6, 9, 12, 15, and 18°C/min, with a maximum rate of about 25°C/min. The temperature range is from 0 to 1000°C with selective ranges within this limit (for example, 0-500°C, 200-500°C, etc.). There is a variable time scale with intervals of 0-50, 0-100, 0-200, and 0-400 min for isothermal experiments. Measurements can be performed in various atmospheres or in vacuum.

Operational procedure was as follows: A sample (250 mg) was prepared in block form and placed in the center of the sample holder. After assembling sample holder, rod support, and spring, the zero point was adjusted by addition of tare weights, and the recorder pen was set to proper temperature position on the graph. The quartz well was then centered about the sample holder and clamped into position. A selected gas flow was established and the temperature program adjusted for a preselected rise rate and end point. After several minutes of flushing with gas, the recorder was readjusted electronically for the difference between air and gas buoyancy. During initial temperature rise, the gain control of the recorder was adjusted to compensate for temperature-induced fluctuations. After the preset temperature was reached, the instrument was shut off and allowed to cool, and the residue was weighed to check recorder weight-loss readings (method of [4]).
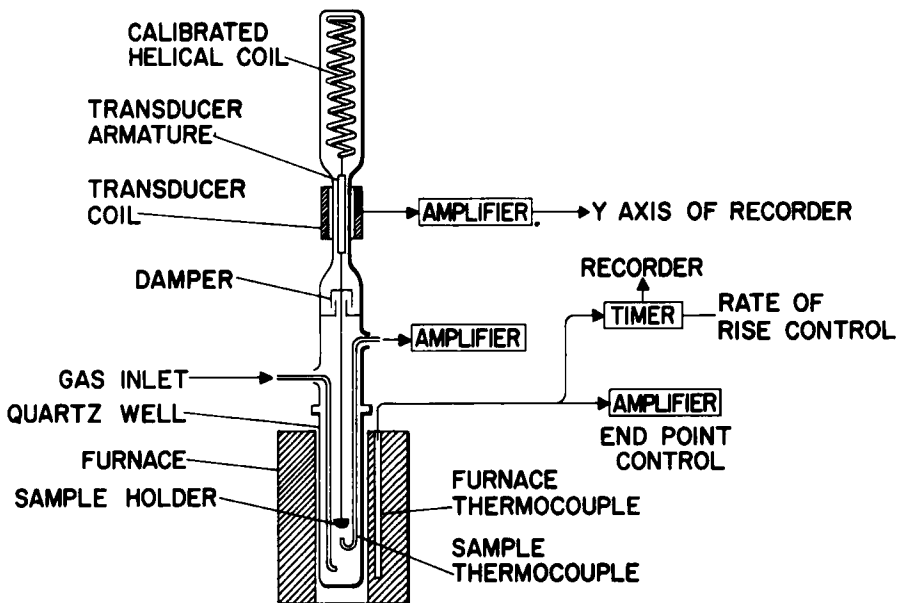
Fig. 1. Thermogravimetric analysis apparatus.

THEORY AND ANALYSIS

The pyrolysis of a material to char and gases may be described by the following reaction scheme:

$$w_0 \rightarrow w_g + w_c \tag{1}$$

For an irreversible reaction the rate of disappearance of w_0 is given by

$$-\frac{d(w/w_0)}{d\theta} = k_f f\left(\frac{w - w_c}{w_0}\right) \tag{2}$$

with the following definitions:

$$f\left(\frac{w - w_c}{w_0}\right) = \left(\frac{w - w_c}{w_0}\right)^n \tag{3}$$

$$k_f = k_0 e^{-E/RT} \tag{4}$$

where w is the weight of condensed material; w_0, the initial weight of condensed material; w_c, the weight of condensed material retained as char; θ, the time; k_f, the Arrhenius rate coefficient (sec^{-1}); k_0, the specific reaction constant (sec^{-1}); E, the Arrhenius activation energy (cal/g-mole); R, the universal gas constant (cal/g-mole-^{0}K); n, the reaction order.

The final rate equation then takes the form

$$\frac{d(w/w_0)}{d\theta} = -k_0 e^{-E/RT} \left(\frac{w - w_c}{w_0}\right)^n \tag{5}$$

TGA gives the weight of material pyrolyzed versus temperature for a pyrolysis carried out at a fixed rate of sample temperature rise. Thus

$$dT/d\theta = C \tag{6}$$

Substituting Eq. (6) into Eq. (5) gives

$$\frac{d(w/w_0)}{dT} = -\frac{k_0}{C} e^{-E/RT} \left(\frac{w - w_c}{w_0}\right)^n \tag{7}$$

TGA data for nylon and phenolic at C = 3 and 18°C/min are shown in Figs. 2-5. Figure 6 shows a TGA run for the nylon-phenolic composite at C = 3°C/min. From data in Figs. 2-5, the rate of weight loss with respect to temperature was determined for each material. Figure 7 shows plots of temperature rate of weight loss (normalized to initial sample weight) versus temperature for phenolic and nylon.

The plot shows two maximums in rate of weight loss for phenolic, indicating that pyrolysis of the phenolic takes place in two major reactions. The rate equation for the two-step phenolic reaction takes the form

$$\left[\frac{d(w/w_0)}{dT}\right]_P = \left[\frac{d(w_I/w_0)}{dT}\right]_I + \left[\frac{d(w_{II}/w_0)}{dT}\right]_{II} \tag{8}$$
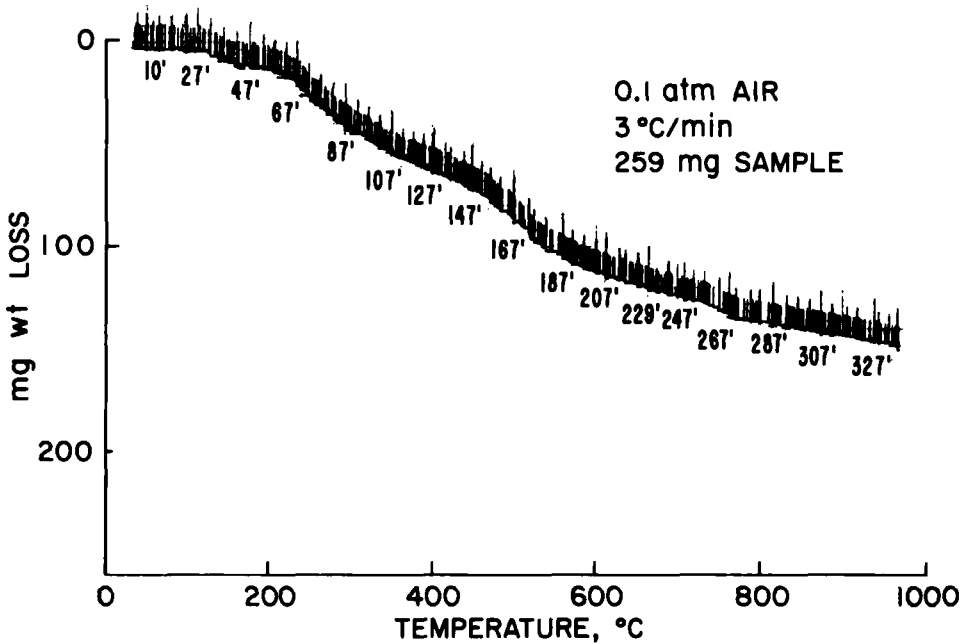
Fig. 2. TGA rate data: phenolic 91LD resin (3°C/min).

Rate equations for reactions I and II are both assumed to be defined by Eq. (5). Then Eq. (8) becomes

$$\frac{d(w/w_0)}{dT} = -\left[\frac{k_{0I}}{C} e^{-E_I/RT} \left(\frac{w_I - w_{cI}}{w_{0I}}\right)^{n_I} + \frac{k_{0II}}{C} e^{-E_{II}/RT} \left(\frac{w_{II} - w_{cII}}{w_{0II}}\right)^{n_{II}}\right] \quad (9)$$

For Eq. (9) to be true, the following identities must hold:

$$\frac{w}{w_0} = \frac{w_I}{w_0} + \frac{w_{II}}{w_0} \quad (10)$$

$$1 = \frac{w_{0I}}{w_0} + \frac{w_{0II}}{w_0} \quad (11)$$

The weight fractions w_{0I}/w_0 and w_{0II}/w_0 are weight fractions of the virgin plastic taking part in each reaction; similarly, w_{cI}/w_0 and w_{cII}/w_0 are the
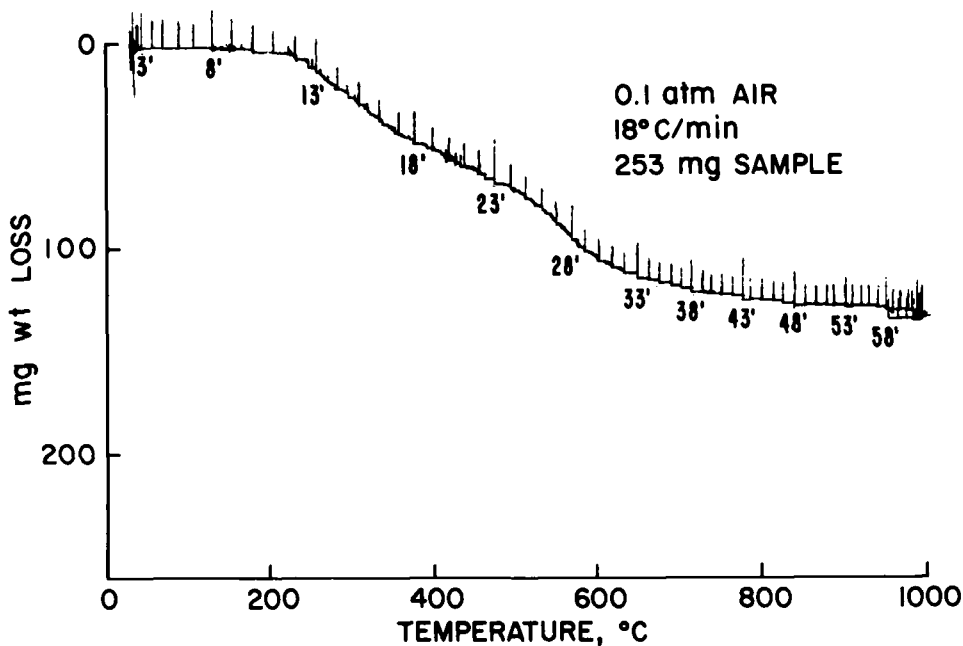
Fig. 3. TGA rate data: phenolic 91LD resin (18°C/min).

weight fractions of reacting virgin plastic remaining in the solid state at the
completion of each reaction. When reaction I has gone to completion, the
weight pyrolyzed will be the initial weight considered in the reaction w_{oI}
less the weight of partially reacted solid w_{cI}. By extrapolating the data for
reaction I in Fig. 7 to zero at T_2, and graphically integrating from T_0 to
T_2, the weight fraction pyrolyzed can be obtained as

$$\frac{w_{oI} - w_{cI}}{w_0} = \int_{T_0}^{T_2} \frac{d(w/w_0)}{dT} \, dT = \frac{\Delta w}{w_0} = 0.25 \tag{12}$$

The corresponding calculation for reaction II (using Fig. 7) is

$$\frac{w_{oII} - w_{cII}}{w_0} = \int_{T_1}^{T_3} \frac{d(w/w_0)}{dT} \, dT = \frac{\Delta w}{w_0} = 0.25 \tag{13}$$
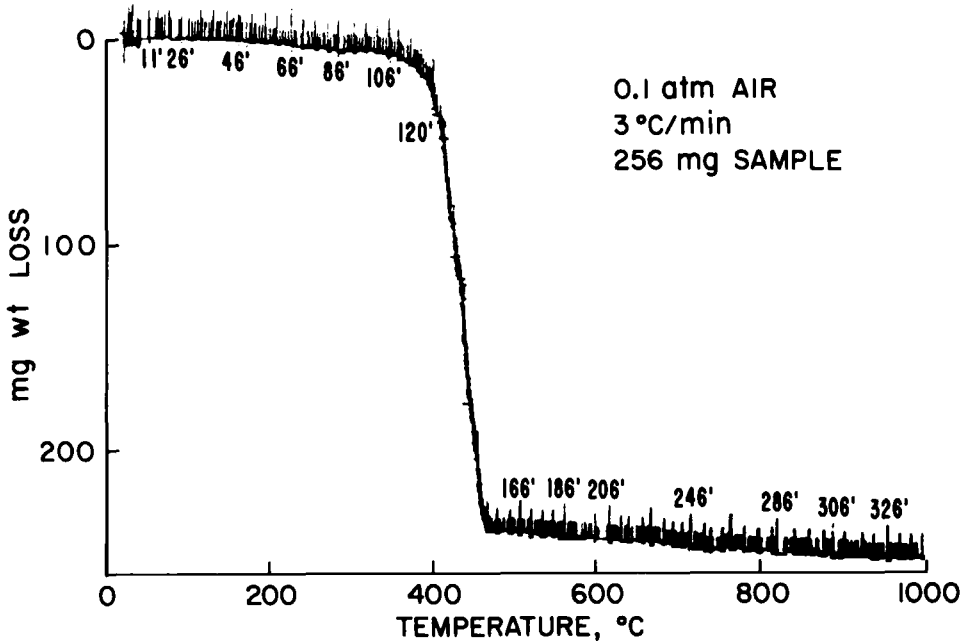
Fig. 4. TGA rate data: nylon 6-6 fabric (3°C/min).

Based on TGA and high-temperature pyrolysis data, the char weight-fraction adopted is 0.50. Then from Eqs. (11), (12), and (13) the following values are obtained:

$$w_{0II}/w_0 = 0.25 + 0.5 = 0.75$$

$$w_{0I}/w_0 = 1 - 0.75 = 0.25$$

$$w_{cI}/w_0 = 0.25 - 0.25 = 0$$

The kinetic coefficients, E, k_0, and n, are determined for each reaction. These parameters can be found using the following three correlation methods:
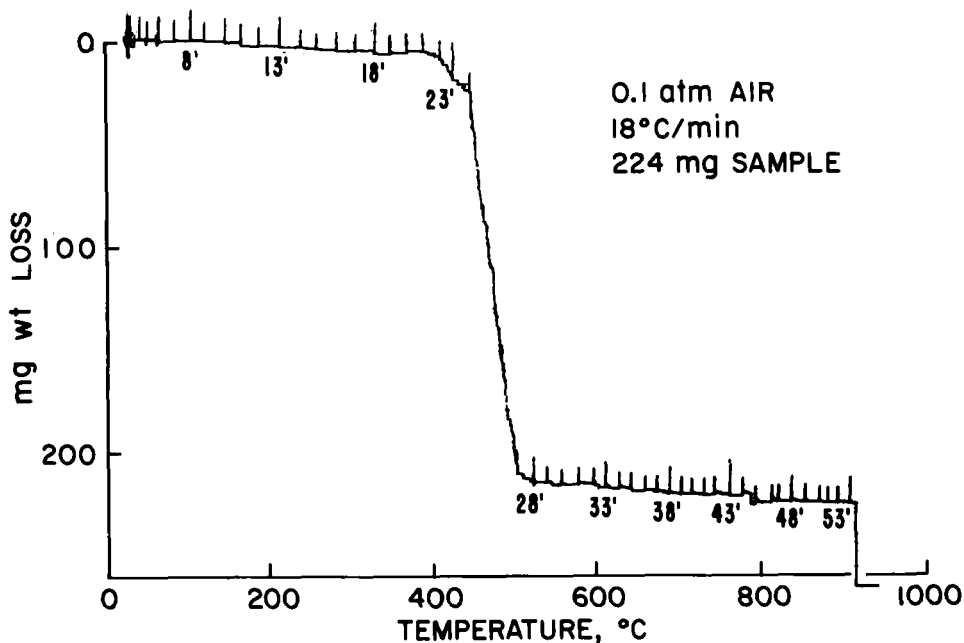
Fig. 5. TGA rate data: nylon 6-6 fabric (18°C/min).

Method 1 is that of Freeman and Carrol [5]; it gives both the activation energy, E, and reaction order, n. Taking logarithms of Eq. (7)

$$\log\left[-\frac{d(w/w_0)}{dT}\right] = \log\frac{k_0}{C} - \left(\frac{E}{RT}\right)\log e + n \log\left(\frac{w-w_c}{w_0}\right) \quad (14)$$

and finite differences of Eq. (14), gives

$$\Delta\log\left[-\frac{d(w/w_0)}{dT}\right] = \Delta\log\frac{k_0}{C} - \Delta\left(\frac{E}{RT}\right)\log e + n \,\Delta \log\left(\frac{w-w_c}{w_0}\right) \quad (15)$$

For constant C and k_0

$$\Delta\log k_0/C = 0 \quad (16)$$

Combining Eqs. (15) and (16) and assuming E and n constant

$$\frac{\Delta\log\left[-d(w/w_0)/dT\right]}{\Delta\log\left[(w-w_c)/w_0\right]} = -\frac{E}{R}\left\{\frac{\Delta(1/T)}{\Delta\log\left[(w-w_c)/w_0\right]}\right\}\log e + n \quad (17)$$
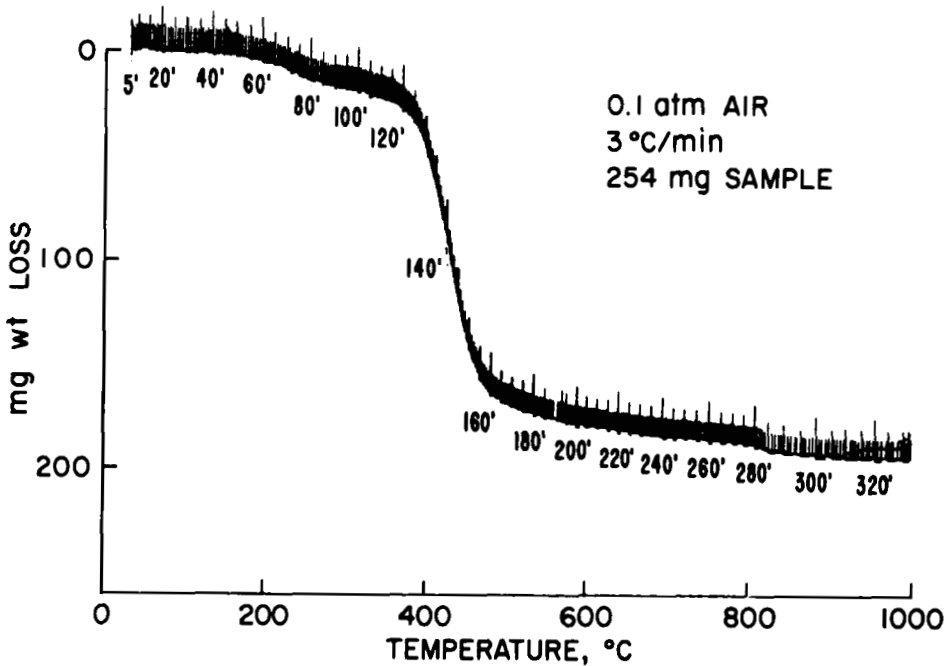
Fig. 6. TGA rate data: 1:1 resin-fabric weight ratio composite (3°C/min).

A plot of the left side of Eq. (17) versus the bracketed term on the right side gives $-(E/R)$ log e as slope and n as the intercept. Plots of this equation for the two phenolic reactions are shown in Fig. 8.

Method 2 gives the reaction order n independently. For a pyrolysis reaction carried out at two rates of temperature rise C_a and C_b, Eq. (7) may be evaluated for each rate of temperature rise. As in the first method, activation energy E, specific rate constant k_0, and reaction order n are assumed constant. A ratio of Eq. (7) evaluated for C_a to Eq. (7) evaluated for C_b is then

$$\frac{[d(w/w_0)/dT]_a}{[d(w/w_0)/dT]_b} = \frac{k_0 \exp(-E/RT_a)}{k_0 \exp(-E/RT)} \frac{[(w-w_c)/w_0]_a^{n/C_a}}{[(w-w_c)/w_0]_b^{n/C_b}} \quad (18)$$
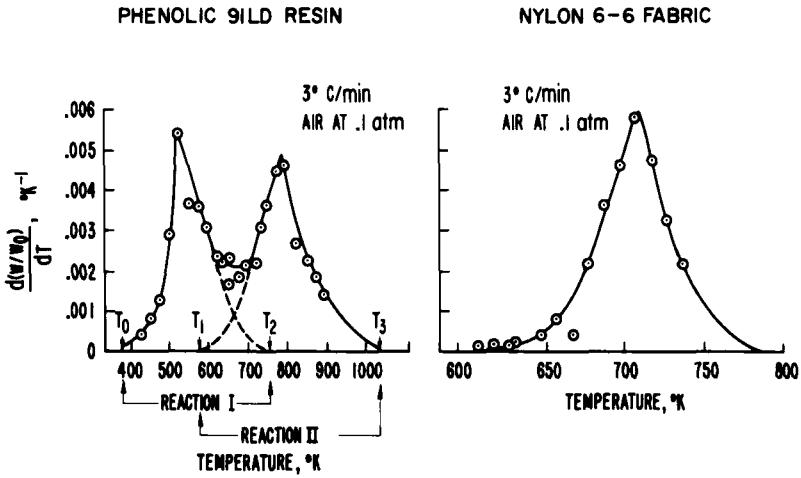
Fig. 7. Derivative TGA plot: phenolic 91LD resin (3°C/min), nylon 6-6 fabric (3°C/min).
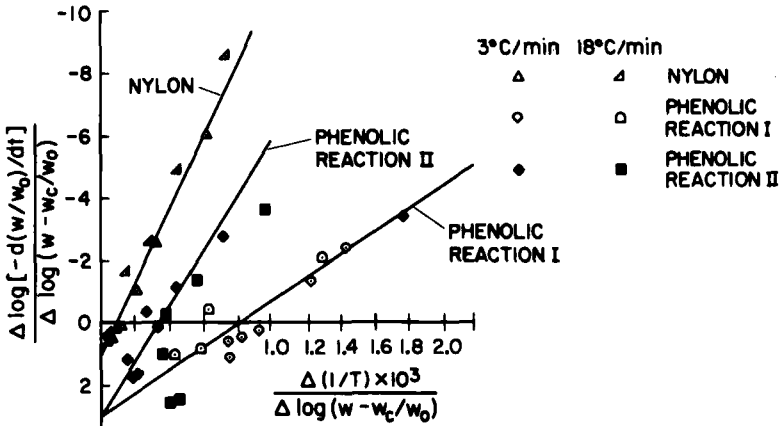
Fig. 8. Second derivative plot [Eq. (17)] used to determine reaction order and activation energy.

For $T_a = T_b$

$$\frac{C_a[d(w/w_0)/dT]_a}{C_b[d(w/w_0)/dT]_b} = \left\{\frac{[(w - w_c)/w_0]_a}{[(w - w_c)/w_0]_b}\right\}^n \qquad (19)$$

Taking logarithms of each side of Eq. (19) and substituting Eq. (6) gives

$$\log \left\{\frac{[d(w/w_0)/d\theta]_a}{[d(w/w_0)/d\theta]_b}\right\} = n \log \left\{\frac{[(w - w_c)/w_0]_a}{[(w - w_c)/w_0]_b}\right\} \qquad (20)$$

Equation (20) describes a straight line with intercept zero and slope n. Since the intercept is a constant, a line may be determined for every value of n. Figure 9 shows plots of these lines for n = 0.5, 1, 2, 3, 4, and 5. Data points for phenolic, calculated from Figs. 1 and 2, are also plotted.
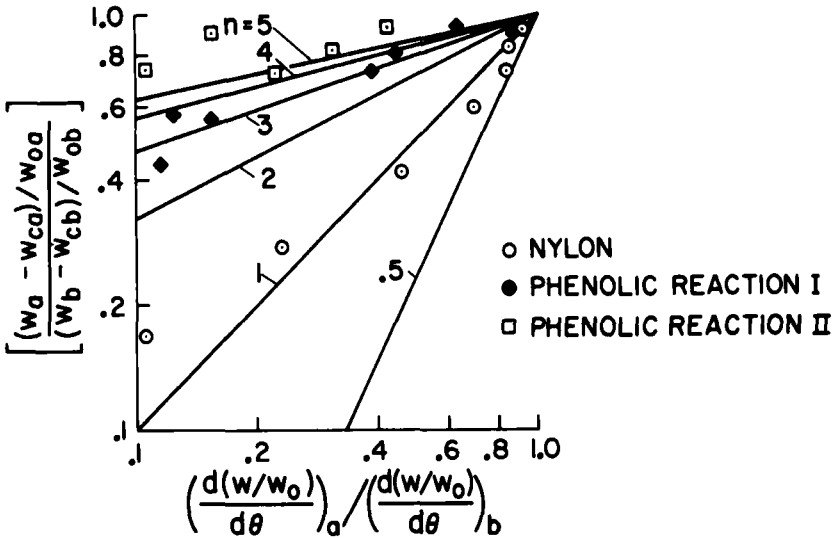

Fig. 9. Rate equation ratio plot [Eq. (20)] used to determine reaction order.

Method 3 is based on the Arrhenius relation. Equation (7) can be rearranged as

$$k_0 e^{-E/RT} = -\frac{d(w/w_0)}{dT}\left(\frac{w - w_c}{w_0}\right)^{-n}\frac{dT}{d\theta} \qquad (21)$$

The logarithm of Eq. (21) is

$$\log k_0 - \frac{E}{RT} \log e = \log \left[- \frac{d(w/w_0)}{dT} \left(\frac{w - w_c}{w_0} \right)^{-n} \frac{dT}{d\theta} \right] \qquad (22)$$

A plot of the right side of Eq. (22) versus 1/T gives - (E/R) log e as the slope and log k_0 as the intercept when E, k_0, and n are constant. In order to plot Eq. (22), the value of the reaction order n must be known. Methods 1 and 2 can be used to determine this parameter, since the reaction order is given by the intercept of the plot determined by Eq. (17) and as the slope of the plot determined by Eq. (20). Method 1 also gives the activation energy of the reaction. Unfortunately, it is difficult to accurately determine the slope of Eq. (17) from these data, as noted in Fig. 8. Therefore, the procedure used to calculate the kinetic coefficients for each reaction was to determine the best whole-number value of the reaction order from plots of Eqs. (17) and (20), and then to use this reaction order to plot the Arrhenius equation. The activation energy determined from the Arrhenius equation was then used to form a new plot of Eq. (17). Figures 8 and 10 show the results.
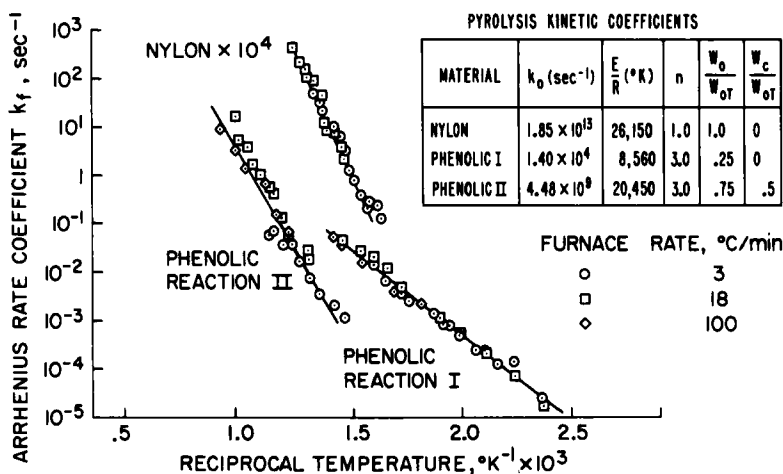

Fig. 10. Arrhenius correlation of TGA rate data.

A reaction order of 3 is indicated by both methods 1 and 2 for phenolic reaction I. Figures 8 and 10 show that, by using this order, both methods 1 and 3 give a consistent value of the activation energy, namely 17,000

cal/g-mole. The specific rate constant k_0 from Fig. 10 is 1.40×10^4 sec^{-1}. An important point to note is that the Arrhenius plot is a straight line and there is no regular deviation from linearity in the temperature range shown. If an incorrect reaction order had been chosen, different rate coefficients would be determined from TGA data for each rate of temperature rise. The fact that the data fit a single straight-line Arrhenius plot for the nearly two-orders-of-magnitude range in rates of temperature rise indicates that the analysis is essentially valid.

The reaction order indicated for reaction II by method 1 was 3, and by method 2 was greater than 5. Using a reaction order of 3, a linear Arrhenius plot is derived in Fig. 11. The higher value of the reaction order determined by method 2 was not used because a higher order would not give better correlation between experimental data and theoretical equations. As Figs. 7 and 9 show, the activation energy and specific rate constant are 40,700 cal/g-mole and $4.48 \times 10^9/sec^{-1}$, respectively.

The pyrolysis kinetics of nylon were analyzed in essentially the same manner as for phenolic. Since only one maximum occurs in the rate of weight loss versue temperature plot (Fig. 7), only one reaction is assumed to take place. Further, the char weight w_c in Eq. (5) is assumed to be zero. The rate equation then takes the form

$$\left[\frac{d(w/w_0)}{d\theta}\right]_N = -k_{0N} e^{-E_N/RT} \left(\frac{w}{w_0}\right)^n \tag{23}$$

Using the data from Figs. 4 and 5, Eqs. (17), (20), and (22) may be evaluated to determine the kinetic coefficients for nylon. Figures 8 and 9 show that the reaction order for nylon is 1. Figures 8 and 10 show that the value of the activation energy and specific rate constant are 52,600 cal/g-mole and $1.85 \times 10^{13}/sec$, respectively.

CORRELATION OF EXPERIMENTAL DATA AND THEORY

The equations derived in the previous section should now fit the data from which they were derived. In order to calculate TGA curves from the theoretical equations, the integrals of these equations must be determined. Equation (7) may be rearranged as

$$\frac{d(w/w_0)}{[(w - w_c)/w_0]^n} = -\frac{k_0}{C} e^{-E/RT} dT \tag{24}$$
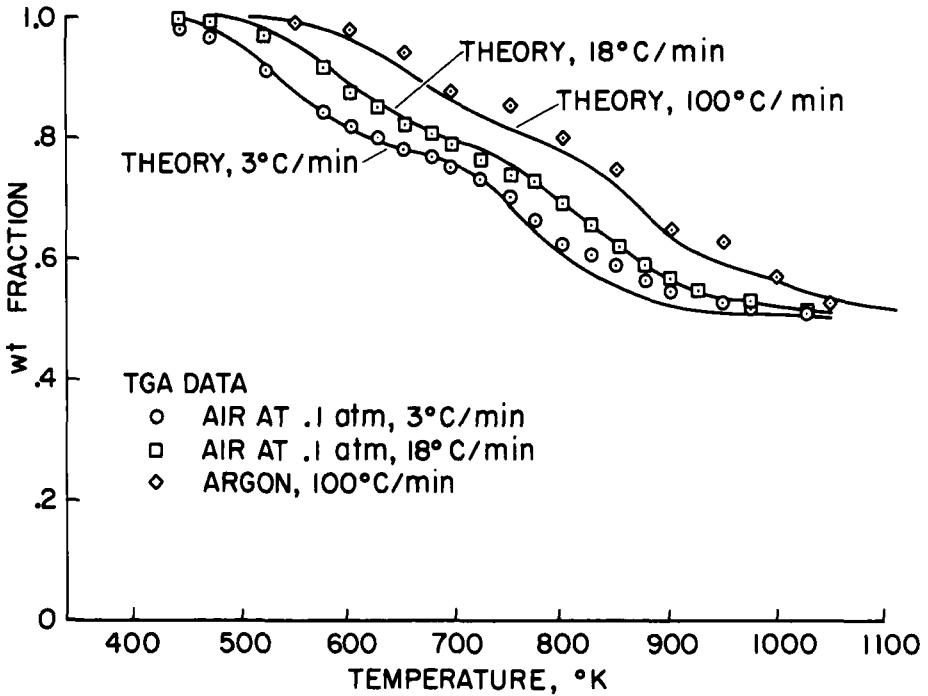
Fig. 11. Comparison of theory and TGA rate data: phenolic 91LD resin.

The left side of Eq. (24) may be integrated by standard methods. For $n = 1$

$$\int_{w_0/w_1}^{w/w_0} \frac{d(w/w_0)}{[(w - w_c)/w_0]^n} = \ln\left[\frac{(w - w_c)/w_0}{(w_0 - w_c)/w_0}\right] \tag{25}$$

and for $n \neq 1$

$$\int_{w_0/w_1}^{w/w_0} \frac{d(w/w_0)}{[(w - w_c)/w_0]^n} = \frac{1}{1 - n}\left[\left(\frac{w - w_c}{w_0}\right)^{1-n} - \left(\frac{w_0 - w_c}{w_0}\right)^{1-n}\right]^{1/1-n} \tag{26}$$

The integration of the right side of Eq. (24) with respect to temperature is somewhat more complicated. Let

$$X = -\frac{E}{RT}; \quad \mu = \frac{T}{T_a}; \quad d\mu = \frac{dT}{T_a} \tag{27}$$

where T_a is the upper limit of integration. Then

$$-\frac{k_0}{C} \int_0^{T_a} e^{-E/RT} dT = -\frac{k_0 T_a}{C} \int_0^1 e^{-X/\mu} d\mu \qquad (28)$$

The term

$$\int_0^1 e^{-X/\mu} d\mu$$

was calculated for values of X varying from 0 to 10 in Ref. [6] and from 10 to 50 in Ref. [9].

Equation (23) may now be integrated, using Eqs. (26) and (28) to describe the weight loss of nylon as a function of temperature for a constant rate of temperature rise:

$$\frac{w}{w_0} = 10^{-\left[(k_0/C)T_a \int e^{-X/\mu} d\mu\right]} \qquad (29)$$

Similarly, Eq. (9) may be integrated, using Eqs. (25) and (28), to predict the weight loss of phenolic:

$$\frac{w}{w_0} = \left[\frac{(n_I - 1)k_{0I}T_a \int_0^1 e^{-X/\mu} d\mu}{C} + \left(\frac{w_{0I} - w_{cI}}{w_{0I}}\right)^{1-n_I}\right]^{1/1-n_I} + \left(\frac{w_{cI} + w_{cII}}{w_0}\right)$$

$$+ \left[\frac{(n_{II} - 1)k_{0II}T_a \int_0^1 e^{-X/\mu} d\mu}{C} + \left(\frac{w_{0II} - w_{cII}}{w_{0II}}\right)^{1-n_{II}}\right]^{1/1-n_{II}} \qquad (30)$$

Figures 12 and 13 show these equations plotted against experimental data.

The correlation between the phenolic data and Eq. (30) shown in Fig. 11 illustrates the advantages of assuming a two-step depolymerization. Only the two-step process can account for both the early and later part of the degradation process. Other analyses have treated either the early degradation period [3] or the later degradation period [1], or have used a one-step rate equation for the whole process. Friedman [1] pointed out that both periods had to be treated to completely describe pyrolysis. Parker and Winkler also indicate that a multistep rate process [10] is required. Using the two-step method, Eq. (30) can be used to predict the entire pyrolysis
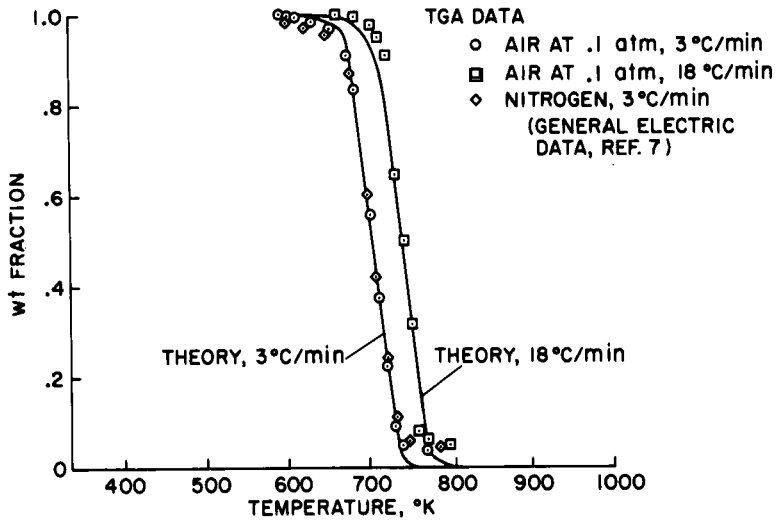
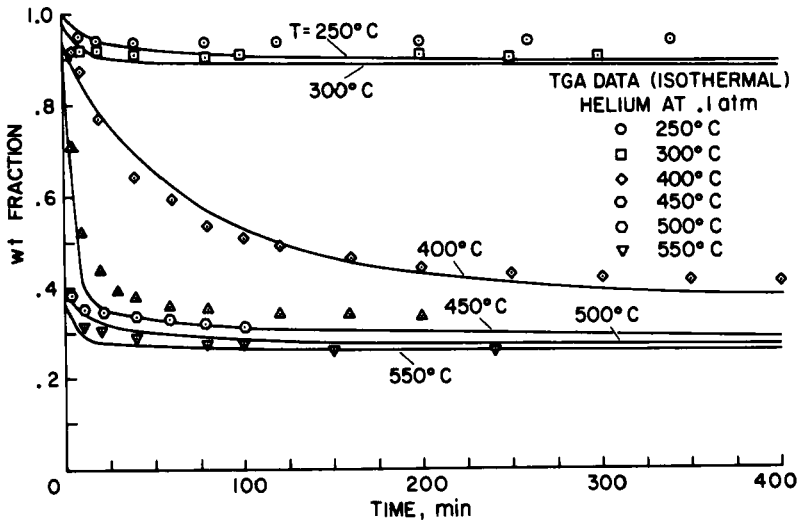Fig. 12. Comparison of theory and TGA rate data: nylon 6-6 fabric.

Fig. 13. Comparison of theory and TGA rate data: 1:1 resin-fabric weight
ratio composite (isothermal).

process within the limits of experimental accuracy. Of particular note is the correspondence between the theory and data for the weight versus temperature plots between 350 and 600°C. No previous analysis has achieved similar success in this region. It is also noteworthy that the theory fits TGA data for nearly a two-orders-of-magnitude variation in rate of temperature rise, a much larger range than has been attempted in earlier analyses.

Correlation between the theory for nylon, Eq. (29), and TGA data is quite satisfactory, as noted in Fig. 13. The correlation shows that a one-step kinetic process is sufficient to describe the pyrolysis data for nylon. This is consistent with earlier analyses [2]. Figure 12 also shows data obtained by Doyle [7] for nylon, plotted against Eq. (29). The good agreement demonstrated indicates that the analysis for nylon 6-6 is valid.

If the assumption that the pyrolysis kinetics of nylon and phenolic are independent of each other is correct for the composite, the kinetics of a composite of nylon and phenolic should be described as the sum of Eqs. (9) and (23):

$$\left(\frac{d(w/w_0)}{d\theta}\right)_{comp} = \Gamma\left(\frac{d(w/w_0)}{d\theta}\right)_P + (1-\Gamma)\left(\frac{d(w/w_0)}{d\theta}\right)_N \qquad (31)$$

Integration of Eq. (31) with respect to time gives

$$\left(\frac{w}{w_0}\right)_{comp} = \Gamma\left\{\left[(n_I-1)k_{0I}10^{-E_I/2.3\,RT}\;\theta + \left(\frac{w_{0I}-w_{cI}}{w_{0I}}\right)^{1-n_I}\right]^{1/1-n_{II}}\right.$$

$$+ \left[(n_{II}-1)\,k_{0II}10^{-E_{II}/RT}\;\theta + \left(\frac{w_{0II}-w_{cII}}{w_{0II}}\right)^{1-n_{II}}\right]^{1/1-n_{II}}$$

$$\left. + \left(\frac{w_{cI}+w_{cII}}{w_{0I}+w_{0II}}\right)\right\} + (1-\Gamma)\,10^{-\left[\dfrac{k_{0N}e^{-E_N/RT}\theta}{2.3}\right]} \qquad (32)$$

For a 1:1 weight ratio composite of nylon and phenolic, $\Gamma = 0.50$.

This equation should predict the weight pyrolyzed versus time data for isothermal degradation of a 1:1 composite. Figure 13 shows a comparison of isothermal pyrolysis data and the predicted results. This correlation is a severe test of the theoretical equations. First, the data were not used in any way in the derivation of the equations. Second, these data are for isothermal pyrolysis while the equations were derived from nonisothermal pyrolysis data. Predictions are within 5% of the experimentally determined degradation in all cases, indicating the validity of the individual equations and of the assumption that the pyrolysis kinetics of the components are independent of each other in the composite. This conclusion agrees with the results of Parker and Winkler [10]. Of particular interest is the fact that these equations predict very closely the pyrolysis at 523 and 573°K and yet also predict very accurately the pyrolysis at 673°K. If a two-step reaction for phenolic is not used, the initial pyrolysis at the low temperatures cannot easily be accounted for.

When Eq. (31) is integrated with respect to temperature for $dT/d\theta = C$,

$$\left(\frac{w}{w_0}\right)_{comp} = \Gamma\left(\frac{w}{w_0}\right)_P + (1 - \Gamma)\left(\frac{w}{w_0}\right)_N \tag{33}$$

Here, $(w/w_0)_N$ and $(w/w_0)_P$ are defined by Eqs. (29) and (30), respectively. Equation (33) should predict the weight versus temperature data for a composite degraded at a fixed rate of temperature rise. Figure 14 shows TGA data and theoretical predictions for the composite, at three rates of temperature rise: 3, 18, and 60°C/min. These three plots illustrate changes in the TGA as the rate of temperature rise increases. When the rate of temperature rise is 3°C/min, a definite decrease in the weight versus temperature curve occurs between 450 and 600°K during which about 10% of the total material is pyrolyzed. This same weight decrease appears to a somewhat lesser extent when rate of temperature rise is 18°C/min starting and ending at higher temperatures. When the rate of temperature rise is 60°C/min, the initial weight decrease nearly disappears. Without using a multistep kinetic process, this phenomenon cannot be described mathematically. Using the sum of the two-step phenolic equation and the one-step nylon equation, one sees that this shift in initial weight loss is primarily due to the low activation energy of the first phenolic reaction. As the rate of temperature rise increases, the temperature at which phenolic reaction I takes place shifts much more quickly to higher temperature than in either the nylon or the second phenolic
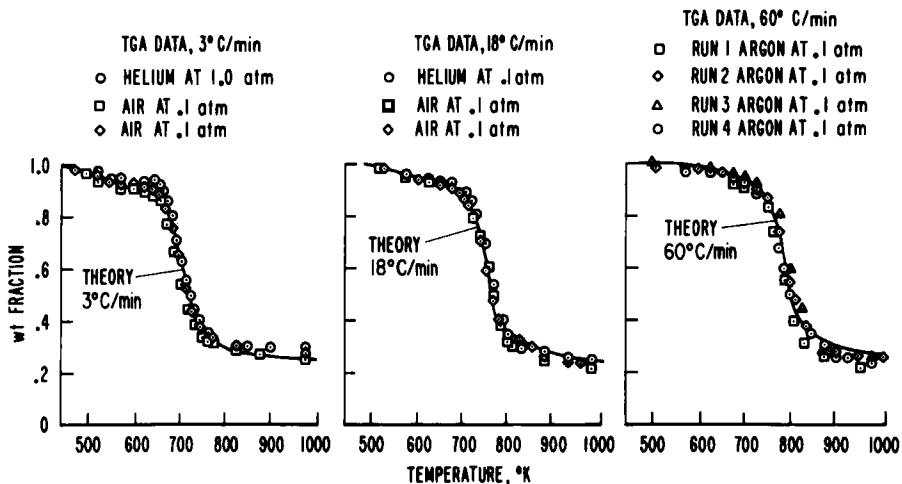
Fig. 14. Comparison of theory and TGA rate data: 1:1 resin-fabric weight ratio composite.

reaction. As this shift occurs, the first phenolic reaction is superimposed on the second phenolic and nylon reactions and is therefore no longer visible as a separate step in the TGA. The comparison described above illustrates the good correlation that can be obtained between TGA data and the multi-step pyrolysis theory.

One very important advantage of the multistep theory over the single-step theory is its versatility. When a single-step kinetic theory is used, every time the weight fractions of components are changed new kinetic constants must be derived. Using the multistep theory one simply changes the value of Γ to account for a change in weight fraction. The following paragraph illustrates how useful this can be.

Figure 15 compares the theoretical equations with TGA data for a material obtained from a satellite-vehicle entry heat shield. The nylon-phenolic material (produced by General Electric) is supposed to be similar in weight ratio to the material in the present study. However, TGA data indicate that only 20% char remains after pyrolysis of the heat shield material. Elemental analysis indicates that the material is richer in hydrogen than the 1:1 composite studied herein. Both of these pieces of information would infer that the material has a higher ratio of nylon to phenolic than 1:1. Since no appreciable char is left after pyrolysis of nylon, all the char remaining after pyrolysis of this composite must be due to phenolic. Since
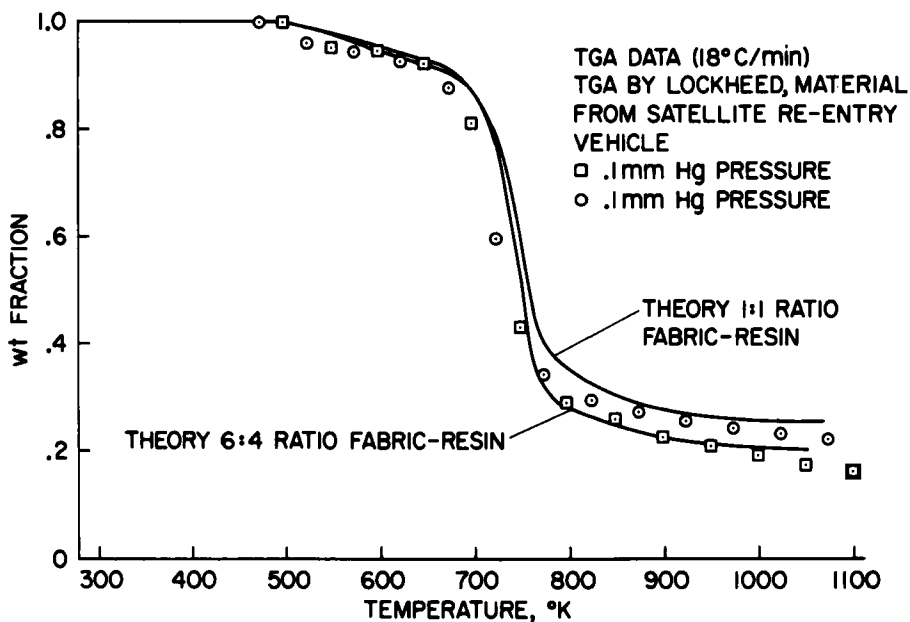
Fig. 15. Comparison of theory and TGA rate data: General Electric nylon-
phenolic (18°C/min).

the phenolic yields 50% char when pyrolyzed, the satellite heat shield
material must be a 6:4 weight-ratio composite of nylon and phenolic if the
components are the same as those considered in this analysis.

   In Fig. 15 the theory for both a 1:1 mass ratio and a 6:4 mass ratio of
nylon to phenolic is shown. As the figure illustrates, the 6:4 weight ratio
theory fits these data quite well, particularly in the low-temperature region.

   Doyle [7] published a TGA for the General Electric nylon-phenolic
composite material. His data are shown in Fig. 16. These data again show
only 20% char. No weight ratios of nylon to phenolic were published with
the data, but similarity between TGA's of the satellite vehicle material and
Doyle's TGA indicates that they are of the same material. A comparison of
Doyle's data and the 6:4 weight-ratio theory indicates good agreement. The
fit is particularly good for the early degradation, once again supporting the
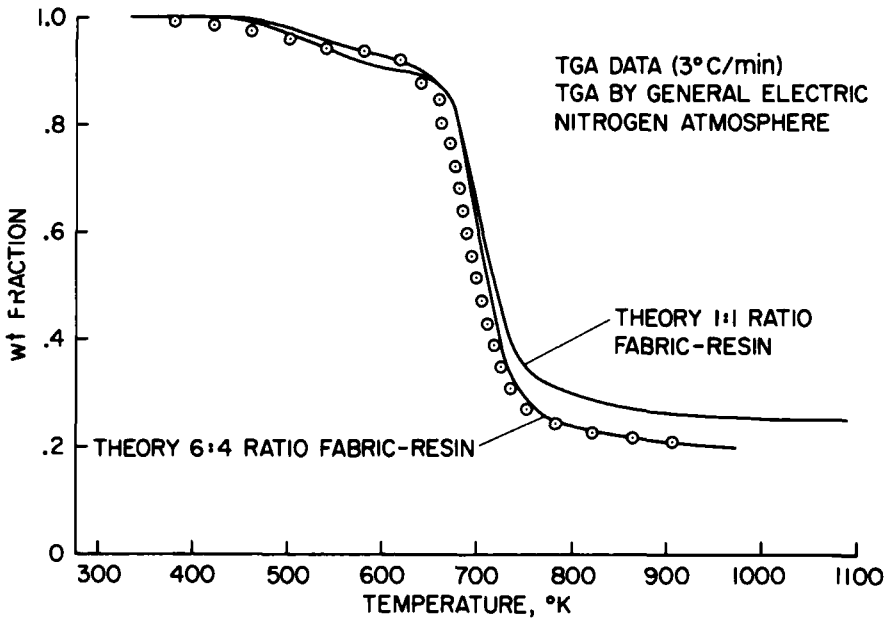multistep pyrolysis theory.

Fig. 16. Comparison of theory and TGA rate data: General Electric nylon-phenolic (3°C/min).

CONCLUSIONS

Agreement between TGA data for the composite and rate equations derived from nylon TGA's and phenolic TGA's individually indicates that the method of analysis is essentially valid. The ability of the rate equations to predict a large range of data from several investigations demonstrates their versatility.

ACKNOWLEDGMENTS

This work was done as part of the Lockheed Missile and Space Company's Polaris Advanced Materials Program.

NOMENCLATURE

E	Arrhenius activation energy, cal/g-mole
k_f	Arrhenius rate coefficient, sec^{-1}
k_0	specific reaction constant, sec^{-1}
n	reaction order
R	universal gas constant, cal/g-mole-°K
w	weight
θ	time
Γ	weight fraction of nylon-phenolic composite

Subscripts

a, b	denoting different rates of temperature rise
c	char
comp	composition
g	gas
N	nylon
o	initial condition
P	phenolic
pyr	pyrolysis
S	solid plastic
I, II	phenolic reactions I and II, respectively

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