PYROLYSIS AND IGNITION OF POLYMERS UNDER APPROXIMATED FIRE CONDITIONS

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Pyrolysis rates and ignition temperatures of several polymers were determined in a special apparatus in which it was possible to simulate the surface exposure and sample heating rates (1 to 100°K/sec) to be expected under actual fire conditions. Sample pyrolysis occurred in air at a known, uniform temperature; and a direct measure of the ignition temperature was obtained. The rate of mass loss from samples was obtained at high, constant temperatures; and these data were described in terms of global but physically feasible mechanisms. These global descriptions were used to predict mass-loss-temperature relationships for heating at constant rates of temperature rise, and the predictions were compared to experimental measurements. The descriptions of pyrolysis were used to interpret the ignition data and to show that piloted ignition occurred when a combustible mixture is generated in the gas boundary layer at the exposed surface of the sample.

Introduction

The ignition and burning properties of polymeric materials should be determined by their oxidative pyrolysis properties. However, examples of quantitative confirmation of this assertion are seldom found in the literature. Because of the complexity of this type of process, quantitative comparisons of pyrolysis and combustion experiments seem to require that tests be performed under similar conditions in nearly identical apparatuses. Such conditions have seldom been achieved in prior research, and few conventional laboratory test devices are really capable of simulating conditions of interest in combustion.

The most convenient, conventional technique for evaluation of the pyrolysis of materials is by thermal gravimetric analysis (TGA) employing automated systems for mass-loss determination and temperature programming.[1,2,3] The determinations of mass-loss rates from samples at constant temperature or at predetermined heating rates can be obtained with high precision under well-defined conditions. The principal deficiency of the devices employed for such tests is that accuracy can only be assured at relatively low heating rates. Since the time to heat a sample to high temperature at these low rates is long relative to the decomposition times at these temperatures, the conventional devices are limited to low-temperature studies. Also, programmable heating rates are one to two order of magnitudes less than the heating rates encountered in many practical combustion situations. In many cases, predictions of constant heating rate pyrolysis characteristics of polymers from isothermal test data in the same TGA apparatus may not be accurate, which is an indication of the complexity of the process under consideration.[2] Because of the low heating rates normally employed in TGA tests, it is possible to obtain rather complete analysis of the evolved gases as a function of time. Such data yield useful qualitative results concerning the pyrolysis; but, again because of the complexity of the processes, it is seldom possible to use information concerning the evolved gas composition in quantitative comparisons.

The study described here was undertaken to evaluate the effects of large variations in heating rates on the pyrolysis and ignition in air of polymers. An experimental technique evolved which permitted tests under conditions which closely approached those likely encountered in a fire situation. It was possible to determine oxidative pyrolysis characteristics of selected polymers at both high temperatures and at high heating rates. In essentially the same apparatus, ignition tests were performed under closely defined conditions in which nearly direct measurements were made of the polymer sample temperature at the point of ignition. From the results of tests at high constant temperatures, a mechanistic description of the oxidative pyrolysis of three commercial polymers was developed which permitted direct comparison of predicted and measured ignition temperatures and of pyrolysis characteristics at high heating rates.

Apparatus

The experimental system was designed to heat thin polymer films at predetermined heat rates up to 200°K/sec for ignition studies and degradation tests and at heating rates of nearly 1000°K/sec to reach a preselected temperature for pyrolysis. Figure 1 is a sketch showing the essential features of the system. Films of polymer 25- to 125-μm thick were bounded to preoxidized strips of stainless steel. These strips were 25 μm thick, 12.5 mm wide and 50 mm long. The polymer sample was positioned on one side of the strip. The ends of the strip were clamped between electrodes; the strip and sample were then electrically heated under control of a feedback system. The length of the samples was varied according to the heating rate to insure uniform longitudinal temperature. The temperature on the side of the strip opposed to the sample side was measured by use of fast-response infrared thermometers. Calculations indicate that this measured temperature would be within 1 to 2 degrees K of the sample surface temperature under the conditions of tests reported here. For the pyrolysis tests shown in Fig. 1, the radiation shield was positioned 5 mm from the exposed surface of the sample.

The pyrolysis chamber was fitted with a rapid-quench system through which cold gas was introduced across the sample surface to achieve cooling rates in excess of 1000°K/sec at high temperatures.

The chamber shown in Fig. 1 was mounted in a yoke which permitted movement to any desired surface orientation. In most tests, the sample surface was horizontal, facing upward as indicated by Fig. 1. The output signal from the temperature sensor was used as the control signal to a servo-system, which could be set to give the desired heating rate or temperature for a test. Mass-loss determinations were made by weighing the strips and samples before and after a test. Temperature calibrations were made with each strip before and after a test by noting the temperature at which a small quantity of zinc melted (692°K) when heating the strip at a rate of 2 K/sec. The accuracy of the temperature quoted here should be ±2°K for tests at constant temperature and about ±4°K for the dynamic tests. The fractional retention values presented are known to be about one part in one hundred. In these tests, the initial sample weights were 200 to 500 mg and were weighed to an accuracy of about ±0.02 mg. Further, details concerning the stainless strip preparation, sample bonding, control system, and experimental procedure are given in references 4 and 5.
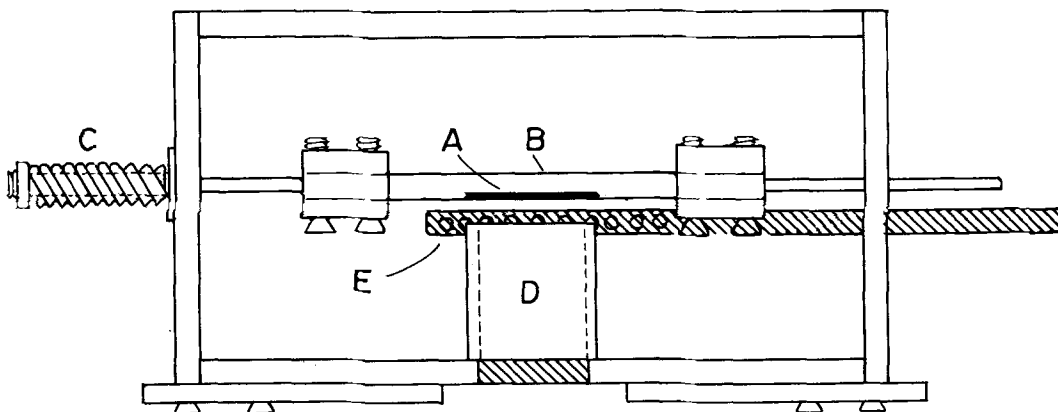

FIG. 1. A sections view of the 2.5 cm thick pyrolysis chamber used in the thermal degradation study of thin polymer films. Here, A is a stainless steel strip with polymer film bonded to the upper surface; B is a radiation shield strip; C is a spring to hold the strips in tension; D is a reentrant smoke shield tube; and E is a perforated tube for introducing cold quench gas.

Experimental Results

Preliminary ignition tests were made by use of a horizontal surface orientation with the sample on the top of the strip. The radiation shield shown in Fig. 1 was replaced by a 35-mm wide shield whose sides were bent to enclose the sample strip. The heated shield above the sample was used to direct pyrolysis gases through a slot cut in the center of the shield. The slot was parallel to the long dimension and positioned across the center of the sample. The mixture of air and pyrolysis gases which issued from the slot were passed through a tiny 1-mm-long pilot flame. Deflagration initiated by the pilot flame quickly propagated through the slot to produce rapid burning across all of the sample surface. Ignition was detected by monitoring the signal from a 5-μm thick thermocouple which was positioned between the sample surface and the shield. In these tests 125-μm thick samples were employed, and the sample temperature at the ignition time was determined as a function of heating rates.

Figure 2 shows typical results for four commercial polymers. With the exception of the Nylon results at low temperatures where severe bubbling was noted, the functional dependence of the piloted ignition temperatures on the heating rate is consistent for the polymers; the ignition temperature is highest at low heating rates and approaches a limiting value at high rates. At very high rates, the apparent ignition temperature increases as a result
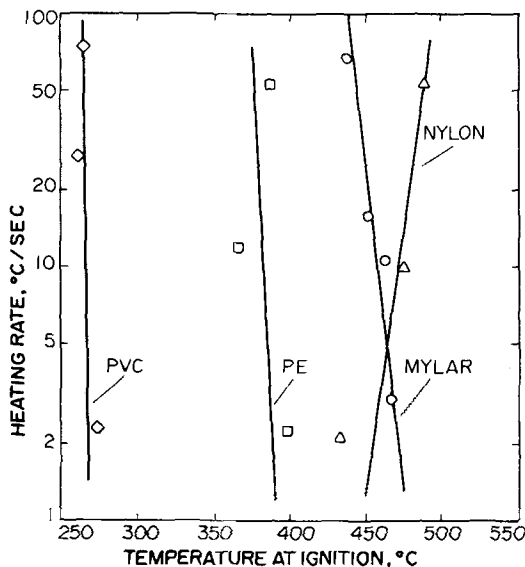

Fig. 2. Measured temperatures at the ignition time are shown as a function of heating rate for commercial polymers in the form of 125-μm thick films. These films were with horizontal surface facing upward. The lines are drawn only as guides.

of apparatus limitations. These results are consistent with the hypothesis that ignition occurs at a fixed-combustibility limit in the gas phase, and this hypothesis will be discussed later. Because this apparatus heated the sample in a cold gas environment with no possible hot spots to trigger spontaneous ignition, ignition of samples in the absence of the pilot flame was only rarely observed.

These ignition results indicated the direction for the primary effort of this study. If a nearly obvious expectation is true; i.e., one only has to generate a gas at the lower combustion limit, only two factors are important in polymer ignition and possibly for the related phenomenon of flamespread. The first of these factors is the ignition environment such as the nature of the sample heating, the ambient gas composition, and the gas dynamics near the surface, etc. This factor is not really a property of the material. The second factor is the nature of the oxidative pyrolysis of the material. It is thus necessary to adequately define the ignition conditions and to accurately characterize the pyrolysis kinetics of the material of interest. In the test discussed below, both of these requirements were met.

Samples of three commercially available polymer films were studied by heating rapidly to temperatures of 600 to 750°K and following the rate of mass loss at constant temperature. Films of 25-μm thick Mylar, a medium-density polyethylene, and 50-μm thick Nylon-66 were pyrolyzed in ambient air (0.85 atms). It was found that more reproducible results were obtained by use of thin films to avoid problems associated with bubbling in 125- to 200-μm thick films. The constant-temperature pyrolysis results indicated a complex mechanism for the gasification. Figure 3 shows typical results of such tests for the Nylon and Mylar films in air as fractional mass retention as a function of time at a constant temperature of 475°C. Tests in nitrogen showed significantly less mass loss at the same time and temperature. Such data were differenced to obtain fractional rates of mass loss as a function of time. In order to obtain consistent accuracy in the differenced data, tests not separated significantly in time were averaged; and the averaged points are indicated in Fig. 3. Figure 4 shows the result of such a procedure for Mylar tests at 475 and 400°C. The pattern of the fractional rate of mass loss noted for all Nylon and Mylar tests were similar to the results shown in Fig. 4. The rate initially decreased rapidly, went through a minimum followed by a maximum, and then decreased again with time. When these results are presented as the rate as a function of total mass fraction retained for the Nylon and Mylar, it appears that the initial decomposition rate was of a very high apparent order in the range of 8 to 12; and the final decomposition reaction was of an apparent order of 2 to 4. The polyethlene pyrolysis was initially an apparent zero-order reaction of low
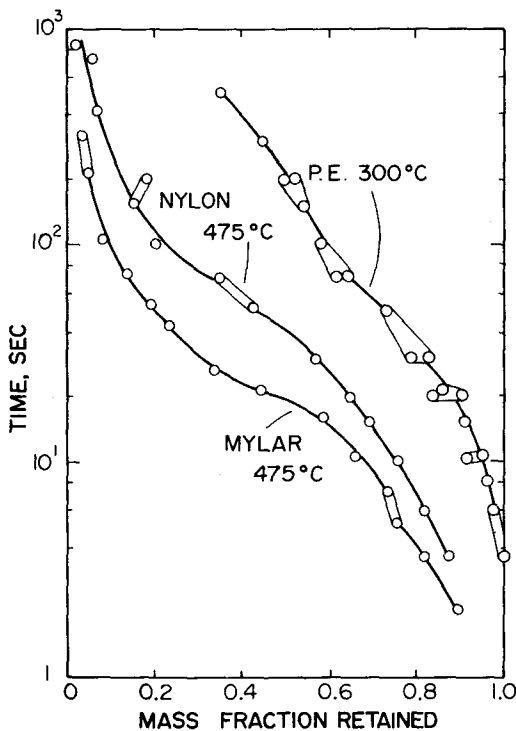
FIG. 3. Typical mass-loss results at constant temperatures for Mylar, Nylon and Polyethylene films are shown here. All data are shown; the connected points were averaged to obtain rates of mass loss as a function of time from the increments of mass loss and time. The lines are shown only to help connect the points; the data analysis was based on the incremental values.

activation energy with the final reaction of about order 2. A different global mechanism was found to describe the decomposition of each material over the range of temperatures for which the reactions could be studied. For the sake of brevity, only the Mylar results will be discussed here.

The mechanism of global reaction found to describe the Mylar pyrolysis in air was of the form

$$P_1 \xrightarrow{k_1} P_2 + G_1 \qquad (1)$$

$$P_2 \xrightarrow{k_2} P_3 \qquad (2)$$

$$P_3 \xrightarrow{k_3} P_4 + G_2 \qquad (3)$$

$$P_4 \xrightarrow{k_4} G_3 \qquad (4)$$

where, P_1 is the original polymer, and P_2, P_3, and P_4 are intermediate solid or liquid products and G_1, G_2, and G_3 are gaseous materials which represent the loss of mass from the sample. The fraction of

the mass of P_1 which is retained by P_2 is f_1, and the fraction of the mass of P_3 which is retained by P_4 is f_2. The values of the first-order rate constants (k_1, k_2, k_3, and k_4) were determined at each temperature by a pattern search involving a least-squares fit of the rate of mass-loss data as a function of time to the prediction of the mechanism.

Constant values for $f_1 = 0.7$ and $f_2 = 0.3$ were assumed to apply to all temperatures, and the values of the rate constants were found to be insensitive to small variations in these values. Figure 5 shows a comparison between the experimental fractional decomposition rates and values calculated from the optimum set of rate constants as a function of reaction time. Except for not predicting the magnitude of the intermediate maximum in the rate, the calculations essentially reproduce the data. Although several proposed global mechanisms were evaluated in an effort to describe these data and the set represented by Eqs. (1) through (4) best served this purpose, it is possible that other mechanisms would produce a better description. Because of the inaccuracies in the data, a more complex set would likely not be justified. The mechanism outlined above is
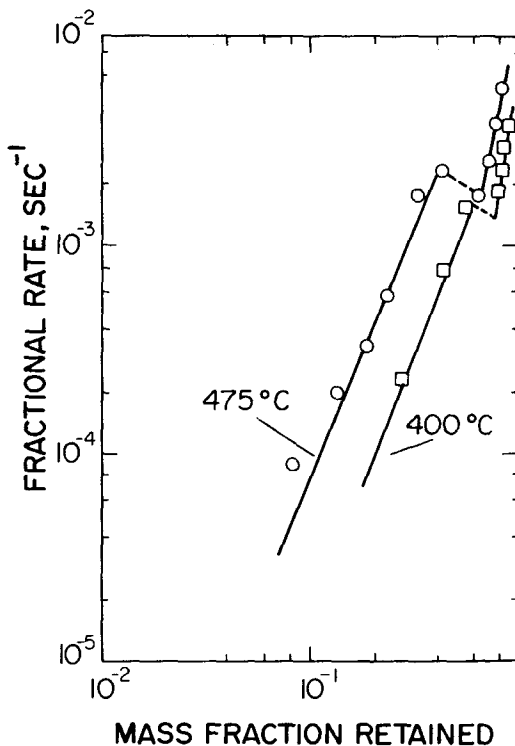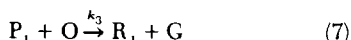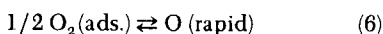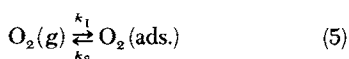

FIG. 4. Fractional rate of mass loss ($1/M_o\,dM/dt$) for 25-μm thick Mylar films at two temperatures. Here M_o is the initial film mass, M is the mass at any time, t.

roughly representative of the likely decomposition processes which are described by more complex relationships.[6,7] The first reaction models the initial depolymerization process to yield an intermediate molecular weight material. The accumulation of this intermediate and its subsequent decomposition gives the possibility for a minimum and maximum in the rate with time. The final reaction is likely the oxidation of residual char by atmospheric oxygen.

The Nylon mechanism was a four, first-order set similar to those shown above except that a parallel decomposition reaction to P_4 of P_1 was indicated by the data; and the reaction of the intermediate P_2 to P_4 was assumed to yield both a solid and gaseous product. A really satisfactory description of the polyethylene pyrolysis was not found for which unambiguous values of the rate constants could be found. A simplified mechanism was finally used to describe the polyethylene data, but the agreement between description and experiment was not as good as the results shown in Fig. 5. The polyethylene set was as follows:

$$O_2(g) \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_2 \text{(ads.)} \qquad (5)$$

$$1/2\, O_2\text{(ads.)} \rightleftarrows O \text{ (rapid)} \qquad (6)$$

$$P_1 + O \overset{k_3}{\rightarrow} R_1 + G \qquad (7)$$

Here, the first reactions represent an equilibrium between gaseous oxygen and adsorbed oxygen in the polymer. The equilibrium between O_2 (ads.) and
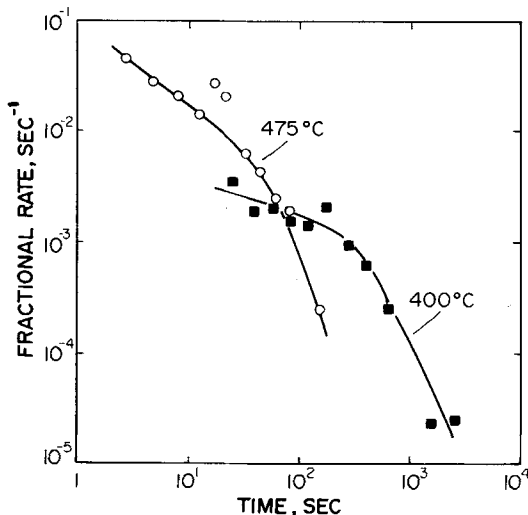

FIG. 5. A comparison of the experimental fractional rates of mass loss of Mylar with the results of calculations based on the Mylar mechanism indicated by Eqs. (1) through (4).

reactive species "O" was assumed to be very rapid, and the initial polymer species P_1 reacts to produce an unreactive species R_1. For temperatures below 375°C, R_1 was experimentally found to be about 0.2 times the initial mass of P_1. At high temperatures, further reaction of R_1 apparently occurs. This polyethylene mechanism gives an initial "zero"-order reaction and roughly describes the data after the transition to a higher-order reaction. The predicted transition between the two classes of reactions is much more gradual than was experimentally observed.

Each of the rate constants for the proposed mechanisms was determined at each temperature for which data were obtained. Table I gives the values for the Mylar mechanism. These rate constants were then plotted as shown in Fig. 6 as Arrhenius plots, and the activation energies and pre-exponential factors for each reaction were determined. When calculating the activation energies, some unequal weighing of the data was employed since the low-temperature tests gave better descriptions of the first reaction, and the high-temperature tests resulted in more reliable rate constants for the final reaction. The lines shown in Fig. 6 were calculated from the values for each reaction which are shown in Table I. The kinetic constants shown in Table I represent global reactions, and their values should not be interpreted in terms of elementary reactions. It is of interest to note that the activation energies for the initial and final Nylon reactions were essentially the same as for the corresponding Mylar reactions being 36200 and 71500 cal/g mole, respectively.

The mechanism characterized by tests at constant temperature was used to predict the mass-retention temperature relationship for the three polymers at various constant heating rates. The prediction was compared to experimentally determined results as a test of the mechanisms. Figure 7 shows this comparison. The agreement is surprisingly good since a large number of errors must be considered. The prediction of the mechanisms for the initial rates of mass loss, which was of greatest interest, was adequate for the purposes of this study.

Additional ignition tests were performed with the 25- to 50-μm thick films in a surface-vertical orientation at heating rates of 1, 10, and 100°K/sec. The radiation shield was removed, and the pilot flame was located above the strip in the gases rising in the thermal boundary layer. With this configuration, the gas dynamics are those of the heated, vertical flat plate, and the rate of gas flow past the upper edge of the strip can be estimated from the classical theory of free-convection heat transfer. The ignition tests showed that with the thin films, ignition could be achieved only at heating rates of 100°K/sec for the Nylon and the Mylar and at rates of 100 and 10°K/sec for the polyethylene. These results are consistent with the predictions of the pyrolysis

TABLE I

Kinetic constants for the four first-order reactions for mylar degradation
(Shown as Eqs. (1) through (4))

Reaction	Activation energy cal/g mole	Pre-exponential factor sec^{-1}
Eq. (1)	38,200	4.58×10^{10}
Eq. (2)	40,800	3.24×10^{11}
Eq. (3)	47,600	1.08×10^{13}
Eq. (4)	69,700	4.43×10^{18}

model. Figure 8 shows the predicted, fractional rates of gasification of Mylar from which the flow of pyrolysis gases into the thermal boundary layer was calculated at various heating rates. The measured ignition temperatures of Mylar at 100°K/sec was 755°K which corresponds to a fractional rate of mass loss from the sample of about 0.15 sec^{-1}. For the same sample size, at a heating rate of 10°K/sec, the maximum fractional gasification rate was predicted to be about 0.12 sec^{-1}, which was not high enough to produce a combustible mixture in the boundary layer. Essentially the same relationship between predicted gasification rates and ignition was observed for the Nylon films. The qualitative

effects noted in Fig. 2 are easily explained in terms of the type of results shown in Fig. 2, although, because of the differences in the size and configuration, qualitative predictions are not possible.

It was possible to calculate the mass fraction of pyrolysis gases in the boundary layer at the ignition time for heating rates of 100°K/sec. This mass fraction at ignition was about 0.1, 0.05, and 0.04 for Nylon, Mylar, and Polyethylene, respectively. For hydrocarbon gases, the mass fraction of fuel at the lower deflagration limit is 0.03 to 0.04 with the higher value applicable for heavier gases.[8,9] Since some of the pyrolysis gases are not combustible, the agreement here between the literature values of the combustible limit and a value calculated from the pyrolysis model and thermal boundary-layer theory is significant. It thus appears that if the oxidative pyrolysis of the polymer can be adequately described, and the environmental conditions roughly defined, the ignition process can be adequately treated in terms of values for the gas composition at the deflagration limit for hydrocarbons. Since in
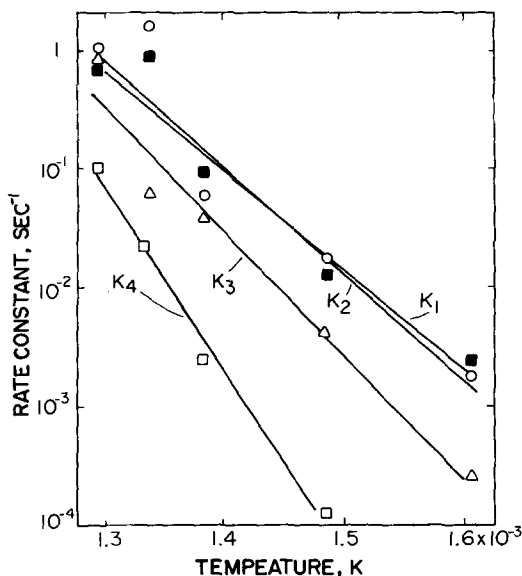

FIG. 6. An Arrhenius plot is shown here of the rate constants for the Mylar pyrolysis mechanisms indicated by Eqs. (1) through (4). The circles, squares, triangles and squares are the experimental values of K_1, K_2, K_3 and K_4, respectively. The lines are least square fits with some weighting of the data as indicated in the text.
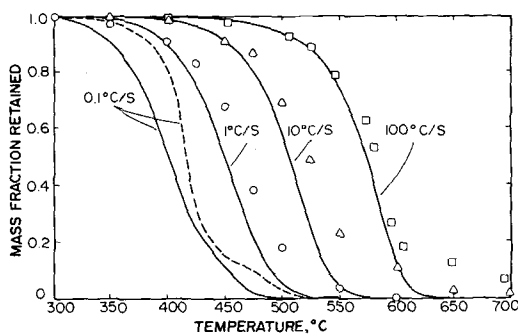

FIG. 7. A comparison is shown here between experiment and predicted (solid lines) constant heating rate data for Mylar thin films. The predictions were generated from the Mylar mechanism indicated by Eqs. (1) through (4). The dashed line was derived from tests run in a Mettler Model 1 Thermoanalyzer (TGA). The circles, triangles and squares are for heating rates of 1, 10 and 100°K/S.
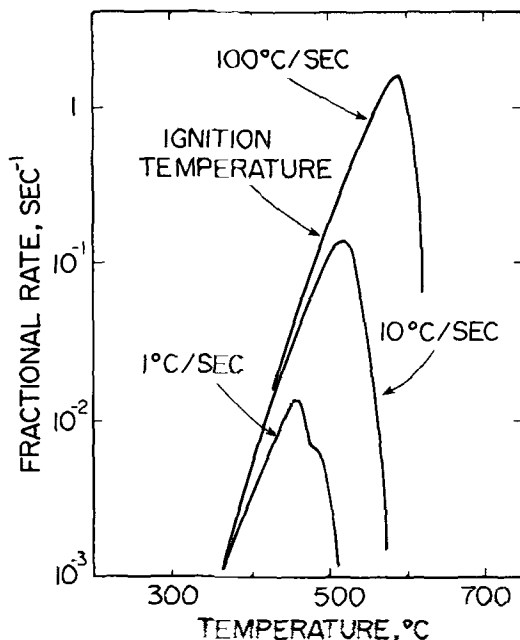
FIG. 8. Calculated fractional gasification rate for Mylar as a function of temperature at constant heating rates. The Mylar mechanism represented by Eqs. (1) through (4) was used. The measured ignition temperature for 25 μm thick films at 100°K/ sec is indicated. At 1 and 10°K/sec rates, ignition was not obtained with the 25 μm thick films.

practice the mass-loss rate is such a strong function of temperature, only an approximate description of the gas dynamics near the polymer surface is needed.

Conclusions

An experimental technique was developed for studying the oxidative thermal pyrolysis and piloted ignition of thin polymer films. This technique offered a definable environment for sample exposure at high heating rates matching those found in actual fire conditions. An analysis of the rate of mass-loss data obtained at constant temperature yielded a rate of mass-loss relationship which suggested very complex pyrolysis mechanisms. Pyrolysis results of Mylar and Nylon 66 at 400 to 500°C showed the rate of reaction initially decreasing as the film mass decreased, the rate then increasing to a maximum value after 10 to 20 percent mass loss, and then the rate of mass loss decreasing continuously until the film disappeared. For polyethylene at 350 to 425°C, a constant mass-loss rate was initially observed, and after a 10 to 20 percent mass loss, a rapidly decreasing rate of mass loss was measured. High apparent reaction orders from 2 to 12 were

also observed in all cases during the periods of decreasing rate.

The rate-of-mass-loss data at constant temperature was described by means of sequences of global reactions. The observed high apparent reaction orders were explained by noting that only a fraction of the polymer mass would participate in each of the sequences of reactions. The rate parameters of the mechanism for each polymer were obtained with a pattern search technique that generated a "best" fit to the experimental rate-time data at each temperature. By use of the rate parameters from the several temperatures considered, the activation energies and pre-exponential factors of the reactions were calculated. Predictions were then made for results anticipated of constant heating tests at heating rates of 1°K/sec, 10°K/sec, and 100°K/sec by means of the overall rate expression of each reaction mechanism. The calculated constant heating-rate predictions described the actual experimental data, within an expected experimental error, for all three polymers.

Piloted ignition tests at 100°K/sec produced ignition temperatures of 754°K, 755°K, and 651°K for 25 to 50-μm thick Mylar, Nylon 66, and polyethylene films, respectively. For thicker films, the ignition temperatures increased slightly or remained the same as the heating rate decreased.

The sequential reaction mechanisms, in which the kinetic parameters were obtained from the pattern search, were used to calculate mass-loss rates as a function of temperature for different heating rates in order to explain the observed ignition results. The rate of gaseous product formation at the time of ignition was then determined from the rate-temperature plots at the experimentally observed ignition temperature. Presumably, combustible pyrolysis products entered the free-convective, thermal-boundary layer. The mass fraction of gaseous fuel generated by pyrolysis could be calculated from the knowledge of the film pyrolysis rate and the characteristics of the thermal boundary layer. These mass fractions correspond to the observed lower flammability limits of hydrocarbon vapors in air. Thus the piloted ignition was achieved by forming a combustible mixture in the gas, and most of the pyrolysis products were ignitable under the conditions of these tests.

It is concluded that from knowledge of gas dynamics near the polymer surface and a proper description of the pyrolysis mechanism, one can characterize the piloted-ignition process. Since both the nature of the polymer and the experimental configuration determine when a combustible mixture is achieved in the gas phase, the ignition temperatures reported here are not truly properties of the material. Nevertheless, since the rates of gasification are such strong functions of temperature, piloted-ignition temperatures measured in different systems should be similar and comparable.

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COMMENTS

D. J. Rasbash, University of Edinburgh, Scotland. When ignition took place, was it just a flash or did a flame stabilise on the vertical surface?

Also, did you estimate the mass flow rate of volatiles from the surface when ignition took place and if so, was it a constant for a given material?

Authors' Reply. High-speed movies showed that the flame propagated from the pilot flame, and a stable flame was then established over the surface of the polymer films. As indicated in the paper, the mass flux of volatiles from the surface was calculated by use of the pyrolysis models. In the case of the materials for which we obtained ignition data at different heating rates, the mass flux of volatiles at ignition was the same at the different heating rates.

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A. W. Benbow, The City University-London, England. Concerning the difference between your thermoanalytical and pyrolysis traces; I assume that the thickness of the samples was identical. Have you any information concerning the catalytic effects, if any, of the etched iron surface on the decomposition of the polymer.

Authors' Reply. The TGA tests were run with small sections of the same film of the same thickness material used in the high-heating-rate tests. We made a number of comparative tests in which the normal stainless steel strips, strips covered with platinum black, or platinum strips were used. Within the limits of accuracy of the measurements, the pyrolysis results were the same for all three types of strip surface. Apparently, at the high rates of heating and for the other conditions of these tests, catalytic effects were not significant.

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J. DeRis, Factory Mutual Research Corp., USA. You mention that ignition occurs at a certain critical mass flux for different materials and different heating rates. My question is what is the magnitude of the critical mass flux.

Authors' Reply. The critical mass fluxes observed corresponded to the values required to product a fuel concentration of about .05 weight fraction in the gas flow in the thermal boundary layer. This weight fraction was interpreted as the lean combustion limit. In the case of the Nylon 66, this weight fraction was higher than the other polymers, and this fact is explained by noting that much of the early weight loss of Nylon is water.

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G. H. Markstein, Factory Mutual Research Corp.,

USA. Could you comment on the process of char formation that is a prominent feature of oxidative pyrolysis with some polymers (e.g. nylon 66) but not with others (e.g. polyethylene) and on possible reasons for the different behavior of these polymers?

Authors' Reply. We did note that the Nylon 66 produced more char during pyrolysis than did the other polymers. The results generated in this study form no basis for speculating on the mechanism for this difference.