

## The Autoignition of Polymers

BERNARD MILLER, J. RONALD MARTIN, and CHARLES H. MEISER, JR., *Textile Research Institute, Princeton, New Jersey 08540*

### Synopsis

A consistent and relatively simple method is presented for studying the unpiloted ignition of polymeric materials in contact with hot air. The ignition behavior of a particular polymer as determined by its bulk properties may be characterized by the relationship between sample mass and ignition time at constant area for a series of furnace temperatures. Extrapolation of this linear relationship at a given furnace temperature to zero mass results in an intrinsic ignition time which represents the rate of the ignition process when the time required to heat the sample to its decomposition temperature has been eliminated, i.e., the sample is brought to its decomposition temperature instantaneously. The temperature dependence of this intrinsic ignition time shows an Arrhenius relationship with an apparent activation energy of 8-10 kcal/mole for all but one material investigated. This indicates that the mechanism controlling the kinetics of such an ignition process is a physical one, most likely the diffusion of combustible gaseous products into the heated air surrounding the sample.

### INTRODUCTION

Autoignition is defined as the generation of flaming combustion resulting from placing a material in contact with heated air in the absence of any spark or flame. This unpiloted ignition is dependent on convective heat transfer from the heated air and must be differentiated from unpiloted ignition by conductive heat transfer or radiant heating and piloted ignition via flame impingement. As a research tool, ignition by radiant heating is not attractive if one requires results obtained from identical radiation sources (an obvious complication when attempting to correlate data obtained at different laboratories). Ignition by flame impingement or contact with a heated surface is even more difficult to reproduce. On the other hand, ignition by convective heat transfer is a highly reproducible phenomenon which has significant bearing both on the nature of flammability hazard and the technology of material disposal through incineration.

To date, most ignition studies have dealt with attempts to measure an ignition temperature characteristic of a particular material. A number of approaches to this problem have been reported and reviewed.<sup>1</sup> Direct measurement of the temperature at the igniting surface of an organic solid poses a number of serious problems. A temperature sensor must be placed in good contact with the surface, this contact must be maintained during heating, and the sensor should not significantly affect the ignition process.

For studies on most materials, these requirements are beyond the capabilities of present-day techniques. Direct measurement of the ignition temperature of wood has been attempted<sup>2</sup>; the results are claimed to be in error by no more than 20°C. A similar but yet indirect attempt to measure the surface ignition temperature for blackened  $\alpha$ -cellulose has been reported in which the surface temperature under thermal radiation was obtained by extrapolation of the internal temperature profile.<sup>3</sup> This procedure yielded a wide variation in results—as much as 300°C.

Noncontact methods of temperature measurement (i.e., radiation detectors) have also been employed to measure surface temperature in ignition studies.<sup>4-9</sup> Ignition temperatures measured by this method vary widely. It would seem that the effect of color changes inherent in the decomposition reactions would add considerable complication to the measurement of surface temperature by these techniques.

Estimation of surface ignition temperatures of cellulose by calculation from heat transfer models has also been attempted.<sup>10</sup> The reliability of such calculations is, of course, limited by the extent to which the mathematical model adequately depicts the real physical situation.

In light of the complications arising from attempts to measure a surface ignition temperature, many workers have undertaken a more pragmatic approach to the problem in which ignition is effected through contact with a solid surface or gas of known temperature, such as a hot plate,<sup>11</sup> a Calrod-type heater,<sup>12</sup> fused inorganic material in a hot-air oven,<sup>13</sup> and hot air in a furnace.<sup>14,15</sup> Inherent in the attempts to assign minimum ignition temperatures from these studies is the assumption that the sample, when it ignites, is at the same temperature as the heating surface or hot air. In addition, these methods do not take into account any time-dependent effects. Such effects have in fact been observed in that the long-term (up to 10 sec) and instantaneous (less than 1 sec) ignition temperatures for a material may vary by as much as 100°C.<sup>13</sup>

In the work reported here, we have avoided the concept of a discrete ignition temperature, believing that ignition represents a series of path-dependent events which cannot be completely described by a single ignition temperature. Instead, a kinetic study of ignition has been undertaken in which the time to ignition has been measured under completely reproducible conditions. These studies appear to provide new and fundamental information on the nature of ignition and the expectation that such information can eventually be of use in the more applied areas of flammability and disposability.

## EXPERIMENTAL

### Apparatus

The experimental apparatus designed for studying autoignition is shown schematically in Figure 1. The essential features of the apparatus are:

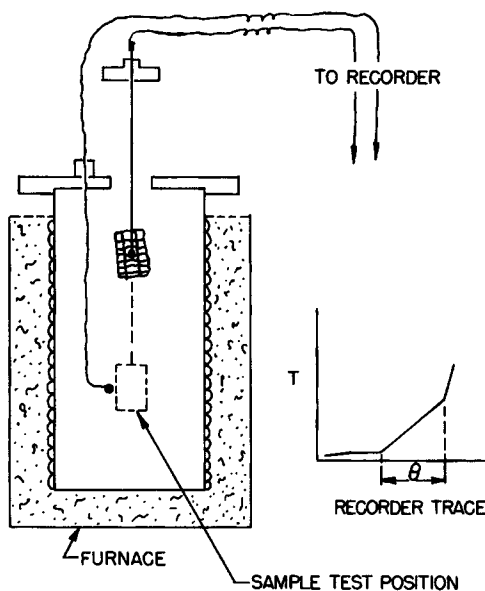


Fig. 1. Apparatus for autoignition studies.

1. A vertical, cylindrical, ceramic furnace ( $2\frac{1}{4}$  in. in diameter and 10 in. deep) surrounded by electrical heating coils. The temperature of the air in the furnace is controlled by adjusting the power to the heating elements.

2. One stationary thermocouple mounted to measure the temperature of the air in the oven. This thermocouple is at a point in the oven near to where the sample is placed.

3. A removable sample holder consisting of a ceramic tube (6 in. long) at the end of which are attached two prongs onto which the sample is impaled. A thermocouple is stationed between the sample prongs near the sample but not touching it. This thermocouple does not measure the sample temperature.

4. A strip chart recorder which is used to monitor the output of the thermocouple on the sample holder. From this trace of thermocouple output versus time, two inflection points can be clearly identified, one corresponding to the beginning of heating at the time the sample is placed in the oven, and the other to the moment of ignition. The time lapse between these two points represents the ignition time  $\theta$ . A typical readout of the strip chart recorder is included in Figure 1.

### Samples

Samples used in these autoignition studies were single and multiple layers (1 in.  $\times$   $\frac{1}{2}$  in.) of the material to be investigated. For work with thermoplastic materials, the sample was stapled onto a wire screen of the same size. This serves to preserve the geometric integrity of the sample

during the melting process which precedes ignition. The wire screen functions as an inert heat sink which acts in direct competition with the sample and lengthens the time to ignition. This effect is discussed below in greater detail. Initially, samples of thermoplastic materials were prepared by melting the fabric onto the wire screen with a hot plate. This resulted in uncontrolled thermal degradation of the material, affecting ignition times in a nonsystematic manner.

At first, nonthermoplastic materials (single layers or multiple layers sewn together) were impaled directly onto the two prongs of the sample holder. In order to be able to compare both thermoplastic and nonthermoplastic materials on the same basis, all materials were eventually run in contact with the same wire screen backing.

### Procedure

Samples (1 in.  $\times$   $\frac{1}{2}$  in.) are attached to a wire screen of the same size with two staples parallel to the long side of the sample. The sample is impaled onto the two prongs of the sample holder, and the thermocouple is positioned close to the sample but not touching it. The furnace temperature is adjusted to the desired level, and the sample is then placed into the furnace by dropping the sample holder into position. The time required to place the sample into position is of the order of a fraction of a second, short enough to give a sharp inflection point on the recorder which measures the output of the thermocouple on the sample holder as a function of time. The moment of ignition is represented by a second inflection point in the recorder output when the combustion reaction(s) abruptly increase (flaming). The time between these two inflection points is termed the ignition time  $\theta$ , measured in seconds.

Each reported experimental value represents a mean average of five to ten independent determinations of  $\theta$ , with a standard deviation, generally, of 0.5 sec and a mean coefficient of variation of 5% or less.

### RESULTS

When the sample is placed into the furnace, it is heated by convective heat transfer from the hot air in the oven. During this heating process, the material melts, if it is a thermoplastic, and begins to decompose into gaseous products as it is heated above its decomposition temperature. Combustible decomposition products diffuse into the volume of air surrounding the sample and eventually reach an explosive concentration. The gases surrounding the sample will then ignite followed immediately by ignition of the sample itself. Ignition in the gaseous boundary layer rather than on the surface of the solid phase has been substantiated by ignition studies of a solid polymeric fuel in a hot-gas wind tunnel. Under suitable conditions, ignition was observed in the gaseous phase well downstream from the solid phase.<sup>16</sup>

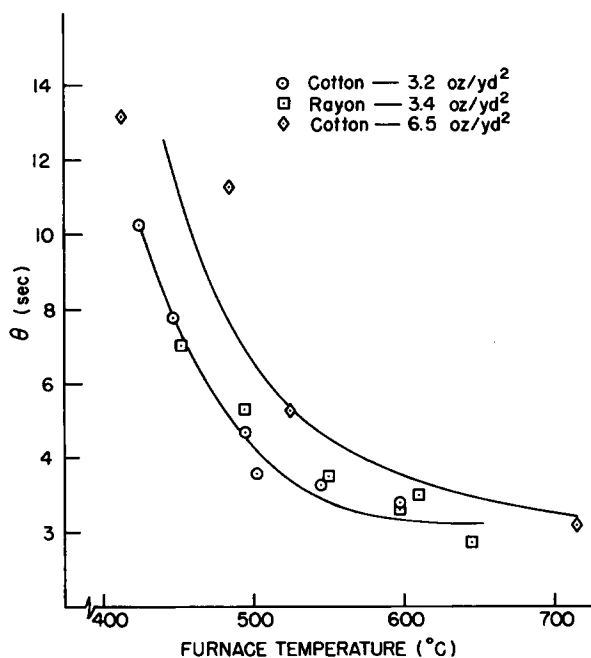


Fig. 2. Autoignition behavior of cellulosic fabrics.

The time required for ignition depends not on the *amount* of combustible gases produced but rather on the *rate* of production of these gases or the *rate* of their diffusion into the volume of air surrounding the sample. If the rate of production of these gases is small, the gases will be able to diffuse away from around the sample fast enough so that the critical concentration for explosion is never reached and no ignition is observed.

Figure 2 shows the relationship between ignition time and furnace temperature for single layers of rayon and cotton fabrics. The samples were impaled directly onto the sample holder without any wire screen. It is seen that the ignition time decreases in a nonlinear fashion with increasing furnace temperature. The temperature of the air in the furnace is a measure of the driving force for heat transfer to the sample and is therefore a controlling parameter for the rate of sample heating and in turn for the rate of degradation or the rate of production of combustible gases. Furnace air temperature has therefore been used as an independent variable in the studies reported here and has been varied over as wide a range as possible, i.e., over a temperature range where ignition occurs within a consistently measurable time interval.

In Figure 2, the points for cotton and rayon of approximately equal weight (3.2 and 3.4 oz/yd<sup>2</sup>, respectively) lie on the same curve; the points for the heavier weight cotton (6.5 oz/yd<sup>2</sup>) are shifted to higher furnace temperatures and longer ignition times. This effect of sample weight on the ignition time results from heat transfer considerations where the sample

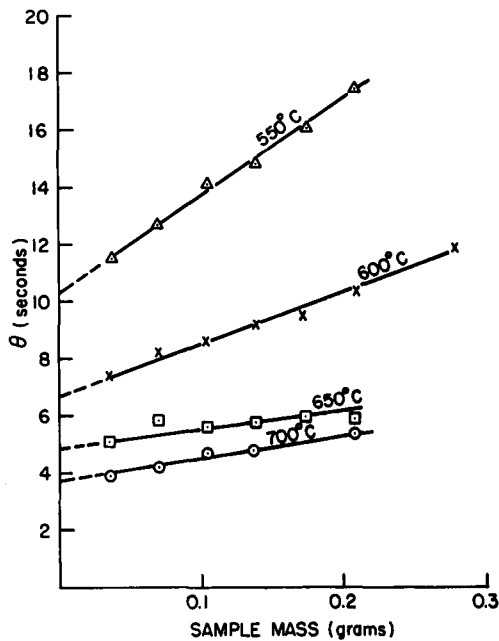


Fig. 3. Autoignition behavior of cotton fabric.

mass affects the heating rate of the sample. As will be shown, this mass effect can be eliminated by extrapolating experimental results to zero thickness, giving a direct comparison of materials exclusive of their bulk thermal properties.

The observed ignition time might also be expected to depend on the bulk surface area of the sample available for heat transfer. In these studies, bulk sample area was held constant by using samples of the same area, 1 in.  $\times$   $\frac{1}{2}$  in., assuming that sample thickness would make only a second-order contribution to the bulk surface area.

The thermal properties, heat transfer characteristics, and chemical degradative properties of the polymers themselves will also affect the ignition properties. These factors would be constant for a particular material and represent lumped material parameters which differentiate the ignition behavior of one material from another.

Figure 3 shows the ignition times for samples of cotton fabric studied as a function of mass at a series of temperatures. The mass of the samples was adjusted by using multilayers of fabric. For each temperature, the relationship between sample mass and ignition time is linear over the range investigated. The extrapolated intercept of this line with the  $\theta$  axis is termed the intrinsic ignition time,  $\theta_0$ . The theoretical interpretation of such an intrinsic ignition time is discussed below in greater detail. For the moment, let it be sufficient to say that intuitively this extrapolation represents an empirical means of eliminating the effect of thickness on the

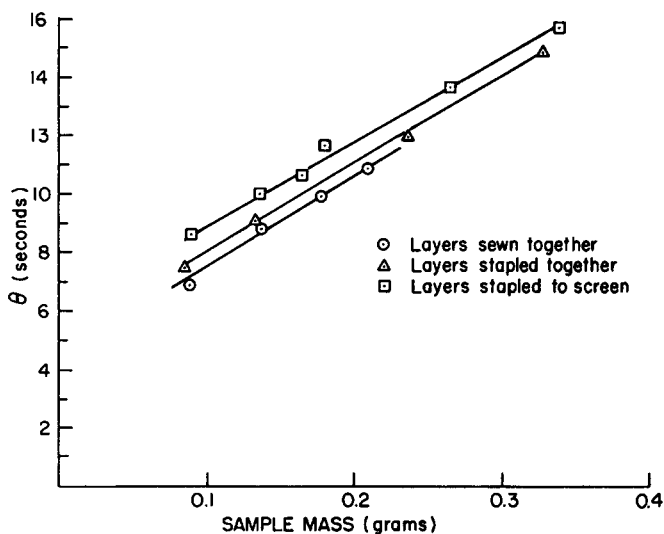


Fig. 4. Effect of competing heat sinks on autoignition behavior (furnace temperature 544°C).

ignition time so that different materials can be compared on a common basis.

The use of wire screens in contact with the sample has been postulated as introducing an inert heat sink which would act in direct competition with the sample and serve only to lengthen the time to ignition. The effect of such additional heat sinks on the autoignition behavior of rayon is shown in Figure 4. These data show the ignition time-sample mass relationship at a single furnace temperature for multiple layers (0.8 to 3.4 g) of rayon (1) sewn together with cotton thread, (2) stapled with two metal staples weighing 0.0335 g each, and (3) stapled with two metal staples to a wire screen weighing 0.250 g. The latter two samples represent two extremes in weight for the inert heat sink in contact with the sample; the metal staples a small mass relative to that of the fabric and metal screens with staples a large mass approximately equal to that of the fabric. It can be seen that the addition of an inert heat sink to the sample does not alter the linearity or slope of the ignition time-sample mass relationship but serves only to shift it vertically to slightly higher ignition times.

The possible effect of fiber surface characteristics was investigated by comparing the autoignition behavior of two different forms of regenerated cellulose, namely, rayon fabric and cellophane. The autoignition times were obtained using multilayered samples stapled together; no screens were used in order to avoid the possibility that they would mask any small differences which might exist between the two materials. The results in Figure 5 show identical ignition times for both materials, indicating that autoignition behavior is controlled by the bulk rather than by the surface characteristics of the samples. If this were not so, it would be unlikely

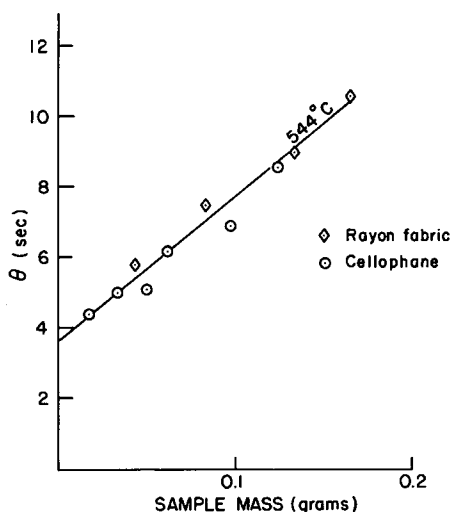


Fig. 5. Autoignition behavior of regenerated cellulose; comparative behavior of a film and fabric (furnace temperature 544°C).

that thermoplastic and nonthermoplastic materials could be compared at all.

Autoignition data have been obtained for multiple-layered samples of other materials. Figures 6 through 11 show the relationship between sample mass and ignition time at a number of temperatures for fabrics of poly(ethylene terephthalate) (Dacron), polyacrylonitrile (Orlon), polypropylene, cellulose acetate, Nomex, and nylon 66. Over the mass range investigated, all the materials display a linear relationship between sample mass and ignition time. The data for each temperature have been extrapolated to zero mass to give an intrinsic ignition time,  $\theta_0$ .

It is of interest to note that the data for Orlon at all but the lowest temperature investigated (525°C) show an ignition time independent of sample mass over the mass range investigated. All other materials investigated show a decreasing dependence of ignition time on sample mass with increasing temperature.

The temperature dependence of the intrinsic ignition time is shown in Figure 12 in the form of an Arrhenius plot ( $\log 1/\theta_0$  versus  $1/T$ ) for all the materials investigated. The relationship is consistently linear with an apparent activation energy (obtained from the slopes) corresponding to 8–10 kcal/mole for all materials investigated, except Nomex, which shows an activation energy of 17 kcal/mole. These low activation energies coupled with the fact that the same activation energy is obtained for nearly all chemical species investigated suggest that the ignition phenomenon is controlled by physical processes (heat or mass transfer) which would be associated with such a low activation energy. The activation energy is derived using the temperature of the air in the oven and therefore probably represents the kinetics in the gas phase where diffusion of combustible



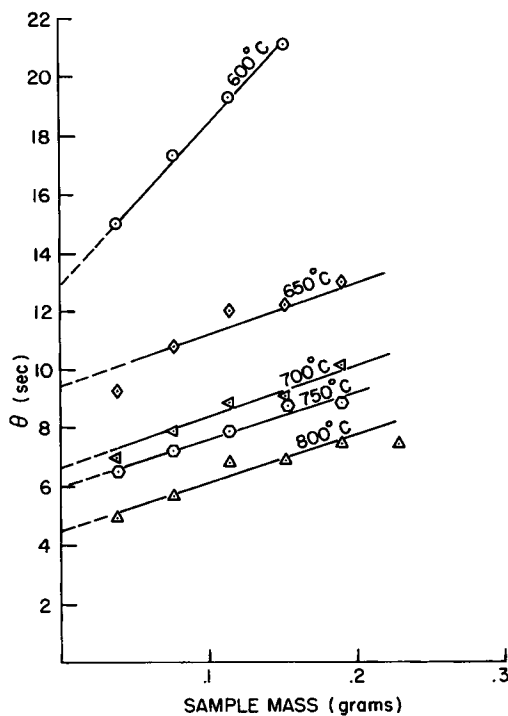


Fig. 6. Autoignition behavior of poly(ethylene terephthalate) fabric (Dacron).

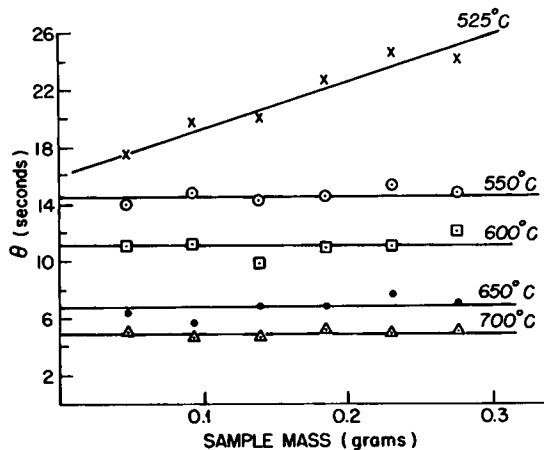


Fig. 7. Autoignition behavior of polyacrylonitrile fabric (Orlon).

gases from the sample would be expected to be important. For purposes of comparing the materials investigated, the intrinsic ignition times for different temperatures are tabulated in Table I.

It is interesting to note that in Figure 12 the data for thermoplastic materials (with the exception of cellulose acetate) are clustered together

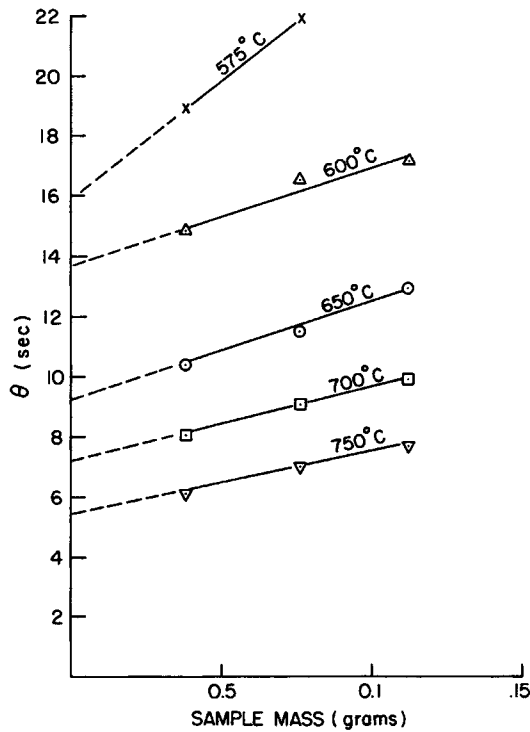


Fig. 8. Autoignition behavior of polypropylene fabric.

TABLE I  
Intrinsic Ignition Times\*

	Intrinsic ignition time, sec						
	500°C	550°C	600°C	650°C	700°C	750°C	800°C
Cellulose acetate	12.6	8.1	7.0	4.9	(3.9)	(3.45)	—
Cotton	(15.6)	10.3	6.7	4.85	3.7	(2.75)	—
Polyacrylonitrile	(22.2)	14.6	11.2	6.8	5.0	(3.95)	—
Polypropylene	(25.6)	(18.2)	13.7	9.2	7.2	5.4	—
Poly(ethylene terephthalate)	(25.6)	(17.5)	12.9	9.5	7.4	6.0	4.5
Nylon 66	(33.3)	(22.8)	15.6	11.45	8.7	6.4	—
Nomex	(80.0)	(41.7)	(22.2)	12.5	8.0	4.8	3.5

\* Numbers in parentheses represent extrapolated values.

and shifted to longer ignition times with respect to the other materials. The data for the two cellulosic materials are also clustered together. The distinct behavior of polyacrylonitrile may be a consequence of its exothermic heat of decomposition. The behavior of Nomex is as yet unexplained.

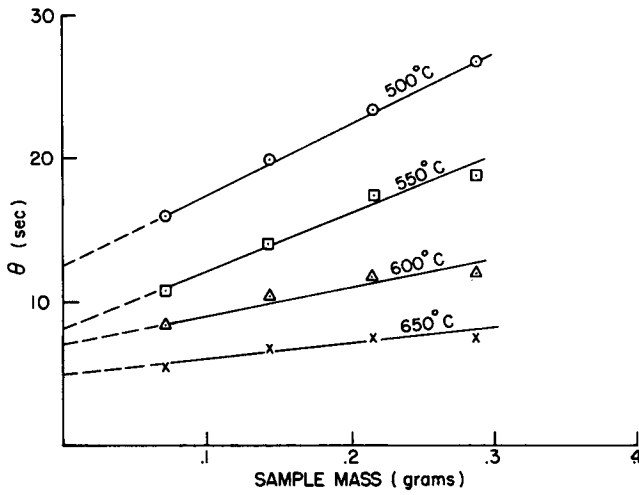


Fig. 9. Autoignition behavior of cellulose acetate fabric.

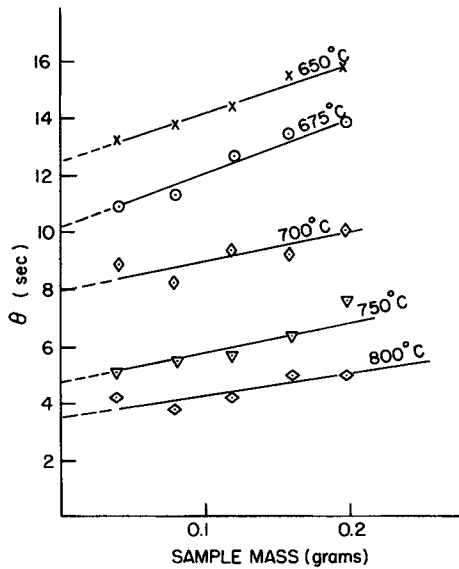


Fig. 10. Autoignition behavior of Nomex fabric.

### DISCUSSION OF RESULTS

The dependence of ignition time on sample mass is interpreted in terms of two sequential controlling mechanisms in the autoignition process: (1) heating the material up to its decomposition temperature, and (2) the chemical degradation process that starts at the decomposition temperature and leads to the formation of combustible gases. The relative contributions of these two processes are presented in Figure 13 as hypothetical

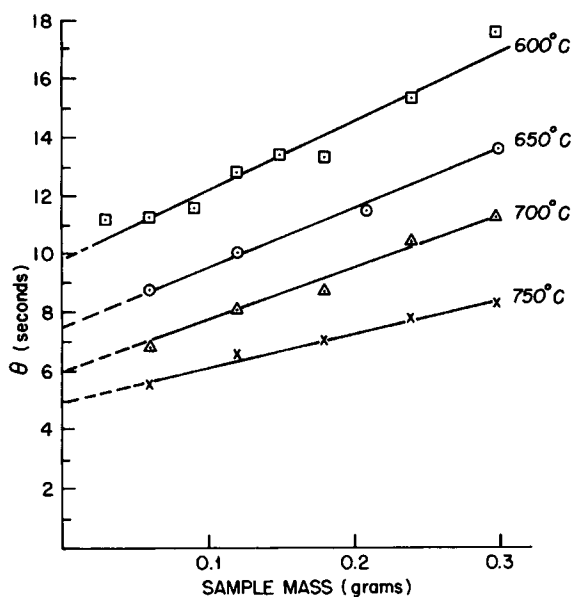
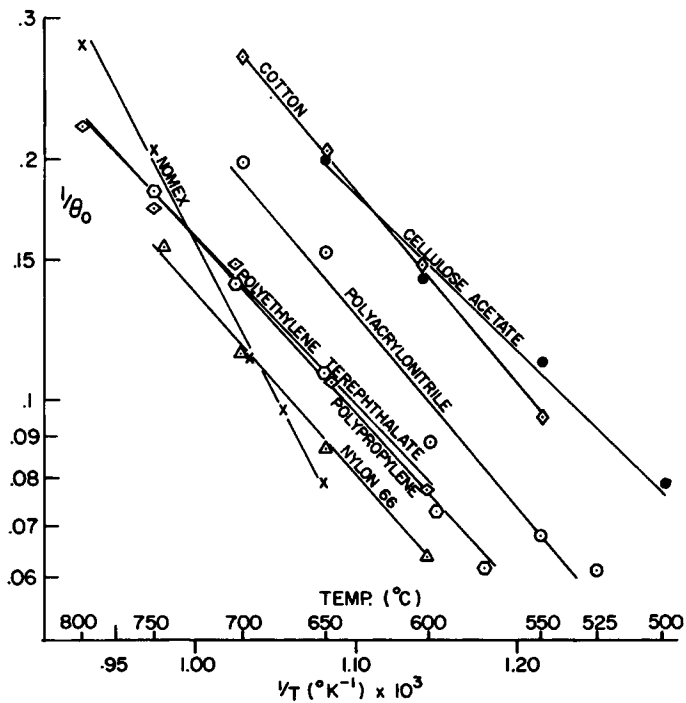


Fig. 11. Autoignition behavior of nylon 66 fabric.

Fig. 12. Arrhenius plots of intrinsic ignition time ( $\theta_0$ ) as a function of furnace air temperature.

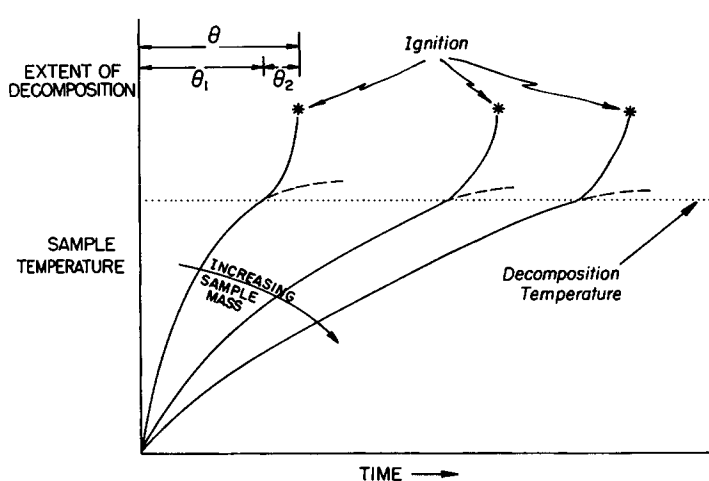


Fig. 13. Generalized hypothetical rate process analysis for autoignition.

plots of sample temperature versus time (solid and broken lines) as well as the degree of chemical degradation versus time (solid line above the decomposition temperature), with sample mass as a parameter. Below the decomposition temperature, sample temperature increases with time in a decaying exponential manner until decomposition is initiated. Above the decomposition temperature, sample temperature still increases in a decaying exponential manner, but at a slightly slower rate because of the absorption of heat by endothermic degradation processes (except in the case of polyacrylonitrile). At the same time, above the decomposition temperature, the degree of degradation increases with time in an accelerated exponential manner (as the result of increasing sample temperature) up to the point of ignition.

As illustrated in Figure 13, the total time to ignition,  $\theta$ , should consist of two parts: the time required to heat the sample to its decomposition temperature,  $\theta_1$ , and the remaining time required for the concentration of combustible gases around the sample to reach an explosive level and ignite,  $\theta_2$ . From heat transfer considerations,  $\theta_1$  would be expected to increase linearly with sample mass in the absence of effects from bulk thermal conductivity which in model studies of similar systems have been shown to be insignificant.<sup>17</sup> The dependence of  $\theta_2$  on sample mass has been assumed to be insignificant compared to that of  $\theta_1$ . Thus, the linear extrapolation of the ignition time-sample mass relationship to zero mass eliminates  $\theta_1$  and results in an ignition time for a sample assumed to be instantaneously heated to its decomposition temperature. From this, it follows that at a given temperature,  $\theta_0$  may be assumed equal to  $\theta_2$ . The extrapolation to zero mass is also equivalent to eliminating any effect from the furnace wall so that the extrapolated intrinsic ignition time also represents the ignition time for a finite sample in an infinitely large furnace.

The work presented here deals only with the ignition behavior of single-component textile materials. Other studies currently in progress are concerned with the ignition behavior of flame-retardant materials and multicomponent systems in general.

### References

1. J. R. Welker, *J. Fire Flamm.*, **1**, 12 (1970).
2. R. Gardon, Fuel Research Laboratory, M.I.T., Tech. Report No. 3, 1953.
3. S. B. Martin and R. W. Ramstad, U.S. Naval Radiological Defense Laboratory, Tech. Report USNRDL-TR-353, NS 081-001, DASA-1142, 1959.
4. N. J. Alvares, U.S. Naval Radiological Defense Laboratory, Tech. Report USNRDL-TR-735, DASA-1467, 1964.
5. N. J. Alvares, U.S. Naval Radiological Defense Laboratory, Report No. WSCI 76-18, 1967.
6. W. K. Smith and L. E. Schilberg, Technical Note 40604-9, Naval Weapons Center, China Lake, California (June 20, 1969).
7. W. K. Smith and J. B. King, *J. Fire Flamm.*, **1**, 272 (1970).
8. A. N. Koohyar, J. R. Welker, and C. M. Sliepcevich, *Fire Technol.*, **4**, 221 (1968).
9. A. N. Koohyar, J. R. Welker, and C. M. Sliepcevich, *Fire Technol.*, **4**, 284 (1968).
10. D. L. Simms and M. Law, *Combust. Flame*, **11**, 377 (1967).
11. L. W. Sayers, *Text. Inst. Ind.*, **3**, 168 (1965).
12. W. D. Freeston, Jr., *J. Fire Flamm.*, **2**, 57 (1971).
13. J. Delmonte and M. A. Azam, *Mod. Plast.*, **20**, 88 (1943).
14. N. P. Setchkin, *J. Res. Nat. Bur. Stand.*, **43**, 591 (1949).
15. G. A. Patten, *Mod. Plast.*, **38**, 119 (1961).
16. T. Kashiwagi, B. W. MacDonald, H. Isoda, and M. Summerfield, Thirteenth International Symposium on Combustion, Salt Lake City, Utah, August 1970.
17. A. Alkidas, R. W. Hess, W. Wulff, and N. Zuber, Final Report for Government-Industry Research Committee on Fabric Flammability, Office of Flammable Fabrics, National Bureau of Standards, Washington, D.C., December 1971.

Received June 28, 1972