

# Studies on Polymer Ignition and Development of a Relative Hazard Ranking Method

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## Synopsis

The argument is presented that a primary determinant for polymer ignition is the rate of heat input during thermal decomposition. An experimental protocol is described in which a conventional thermogravimetric analyzer is used to monitor the behavior of polymeric solids brought to ignition by exposure to preheated air. The data obtained are used to establish the minimum heating rate required for ignition and the initial decomposition temperature at that critical rate. These two properties are then combined to give a numerical ranking value which seems to be a reasonable indicator of a material's ignitability hazard potential. Data for a variety of polymers and mixed systems are presented.

## INTRODUCTION AND BACKGROUND

It is generally understood that a solid polymer exposed to heated air will not ignite unless it undergoes some form of partial or complete decomposition. Ignition (defined as initiation of self-sustaining flaming combustion for an observable time) occurs as a result of exothermic reactions between volatile decomposition products and oxygen. This has been demonstrated in a number of ways, most simply perhaps by the experiments of Summerfield's group<sup>1</sup>: when heated air was passed at a high rate over a polymeric solid, ignition was observed only at a downstream location remote from the solid. Ablative loss of material was observed at the upstream surface of the solid but no flame or other evidence of ignition.

However, the fact that ignition requires decomposition does not mean that decomposition guarantees ignition. This can be demonstrated with almost any organic polymer by heating it in air slowly (in most cases at  $<100^{\circ}\text{C}/\text{min}$ ). For many polymers this will result in partial or even complete thermal decomposition without any observable flaming. Exothermic processes may occur but not autoignition. Such observations have led to the idea that at least one critical requirement for autoignition is that the rate of thermal decomposition (that is, the rate of production of combustible gases) must reach a certain minimum value. This in turn requires a critical energy input rate to the polymer.<sup>2</sup>

Several investigators have published observations which support this concept. In 1948, Banford et al. reported that the ignition and continued burning of wood is controlled by the rate of combustible gas evolution.<sup>3</sup> The piloted ignition of cotton has been reported to require a minimum radiative energy input of  $1.25\text{ W}/\text{cm}^2$ .<sup>4</sup> Using appropriate physical constants for cotton, this corresponds to a heating rate of about  $2000^{\circ}\text{C}/\text{min}$ . Autoignition experiments on paper and cotton by Collins and Wendlandt<sup>5</sup> did not produce ignition at heating rates below  $50^{\circ}\text{C}/\text{min}$ .

These earlier studies had one defect in common: the heating rates of the solid polymer were considered to be constant up to the moment of ignition, which is very unlikely under any circumstances. This paper is concerned in part with refining the concept, for it is the rate of heating *during* thermal decomposition that is a specific determinant for autoignition. How to establish this critical rate and use it as a relative measure of ignitability is the main theme of this work.

The effect of large changes in heating rate on the "decomposition temperature" of a polymer has been predicted by Farré-Rius and Guiochon<sup>6</sup> and demonstrated by Wolf and co-workers.<sup>7</sup> The second group found that a characteristic pyrolysis temperature  $T_p$ , defined as the temperature when a fraction  $1/e$  (37%) of the sample remained, increased significantly with heating rate. Examples of this effect are given in Table I and Figure 1, the latter based on data obtained in our laboratory. The elevated  $T_p$  values can be explained by the fact that at high heating rates energy can be absorbed as sensible heat during thermal decomposition because it is coming in faster than it can be used for polymer decomposition processes.

A consequence of high energy input rate could be that less probable decomposition mechanisms (those with higher activation energies) may occur under such conditions. The influence of heating rate on the composition of polymer pyrolysis products has been studied by a few investigators. Martin and Ramstad<sup>8</sup> reported that at low heating rates the pyrolysis products of cellulose consisted mostly of CO and CO<sub>2</sub>, while at high heating rates the volatile product was considerably richer in hydrocarbons. The ability to alter the pyrolysis decomposition product mix by changes in heating rate is apparently being exploited in petroleum refining. An improved naphtha cracking process<sup>9</sup> uses higher heating rates (i.e., higher furnace temperatures and shorter residence times) to obtain greater yields of desirable higher molecular weight hydrocarbons with lower yields of methane. Recently, Durbetaki<sup>10</sup> has reported studies in which the ignitability of the volatile pyrolysis products from a polymer was found to be dependent on the rate of heating.

In this paper we will describe means for determining two critical ignition criteria: (1) the minimum heating rate, at the beginning of thermal decomposition, which will produce ignition, and (2) the initial decomposition temperature of the solid phase at this heating rate. The work has been done with fabric or yarn samples, which have such a high surface-to-volume ratio that they can be heated uniformly, especially by hot gases.

TABLE I  
Pyrolysis Decomposition Temperatures for Polystyrene<sup>7</sup>

Heating rate (°C/min)	$T_p^a$ (°C)
22	320
$17 \times 10^2$	370
$32 \times 10^3$	420
$54 \times 10^4$	475
$70 \times 10^6$	580

<sup>a</sup> Temperature at which 37% remains.

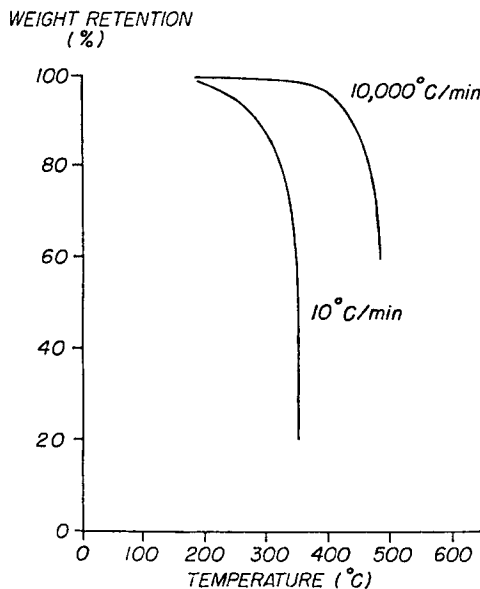


Fig. 1. Increase of major decomposition temperature with heating rate for cotton.

## EXPERIMENTAL

Previous experimental studies on polymer autoignition have established that reproducible ignition delay times could be obtained by thrusting a small sample of polymer into a heated air environment.<sup>11</sup> With the apparatus used for these earlier studies, however, it was not possible to determine effective heating rates or weight losses. Therefore, it was decided to employ a DuPont 951 Thermogravimetric Analyzer both to produce the heated air and to monitor sample temperature and weight up to the moment of ignition. This instrument was especially suitable for autoignition studies because the sample holder is mounted on rails so that it can be moved into the heated furnace very quickly. (It would have been better, however, if the furnace were movable and the sample holder stationary.)

In all experiments the heated air was brought to a fixed temperature, and then the sample, premounted on the weighing arm of the analyzer, was moved quickly into the heated zone. With the rails greased, it was possible to accomplish this injection consistently in less than 1 s. The readout controls of the analyzer were set so that sample weight and temperature were recorded, both as a function of time. Under these conditions the temperature-sensing thermocouple is able to give a close approximation of the surface temperature of the sample and a good measurement of the heating rate. This was established by extensive testing using temperature-sensitive paints placed on equivalent samples; more details of this procedure and calibration can be found in a previous publication.<sup>12</sup>

Each ignition experiment produced a set of responses such as that shown in Figure 2. The abrupt discontinuity in the temperature-time plot indicates the moment of ignition. This transition point was clearly indicated with nearly all materials; for temperature resistant polymers such as Nomex® and PBI, the

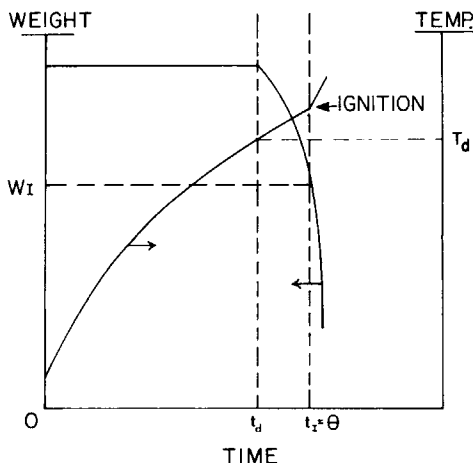


Fig. 2. Typical responses in autoignition studies using the DuPont Thermogravimetric Analyzer.

ignition point was pinpointed better by means of a derivative plot of heating rate vs. time. In all cases at least five replications were carried out, and ignition times could be obtained to  $\pm 0.5$  s. Other information obtained from data such as that in Figure 2 are the initial decomposition time  $t_d$ , the initial decomposition temperature  $T_d$ , and the fraction of polymer volatilized up to the moment of ignition. This preignition weight loss is usually a minor fraction of the original material and decreases as the air temperature is increased.<sup>12</sup>

### DETERMINATION OF A CRITICAL HEATING RATE

Although ignition time increases systematically with decreasing air temperature, the probability of ignition is reduced, so that it is difficult by trial and error to determine the minimum air temperature that will still cause ignition. (This approach is the basis of the Setchkin ASTM method for ascertaining a so-called "ignition temperature" for polymers.<sup>13</sup> Even when this limiting temperature can be determined, it is fundamentally incorrect to assume that it is the surface temperature of the solid.) A more precise method has been used to establish this critical air temperature. Ignition time data for a fixed amount of sample are obtained at several air temperatures, and the reciprocal of ignition time ( $1/\theta$ ) is plotted vs. air temperature. This produces a linear relationship which can be extrapolated to infinite ignition time ( $1/\theta = 0$ ) and thus identifies the air temperature below which there is zero probability of ignition  $(T_\infty)_c$ .

Figure 3 shows this extrapolation for three mass levels of polyester. The finding that the  $(T_\infty)_c$  value is apparently independent of sample size over the ranges indicated can be explained if the ignition process is understood to consist of two sequential steps: (1) heating the polymer up to its initial decomposition temperature and (2) decomposition of the polymer to produce a mixture of combustible gases which must diffuse and ignite. The contributions of these two processes to the observed ignition time are illustrated in Figure 4, which shows hypothetical plots of sample temperature and extent of decomposition

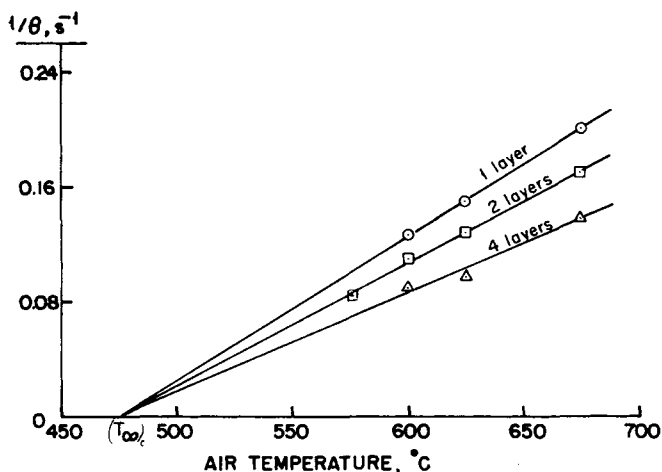


Fig. 3. Extrapolation of  $1/\theta$  vs. air temperature to obtain  $(T_{\infty})_c$ .

vs. time with sample mass as a parameter.<sup>2</sup> Latent heat processes (e.g., melting or volatilization of water) are not considered significant perturbations at high heating rates and are lumped in with sensible heating effects. Below the initial decomposition temperature  $T_d$ , sample temperature increases with time in a decaying exponential manner until decomposition is initiated. Above  $T_d$ , sample temperature still increases exponentially but at a slightly different rate because of absorption (or generation) of heat caused by decomposition processes. Once the initial decomposition temperature has been exceeded, the rate of decomposition increases with time in an accelerating exponential manner (as a result of increasing sample temperature) up to the moment of ignition.

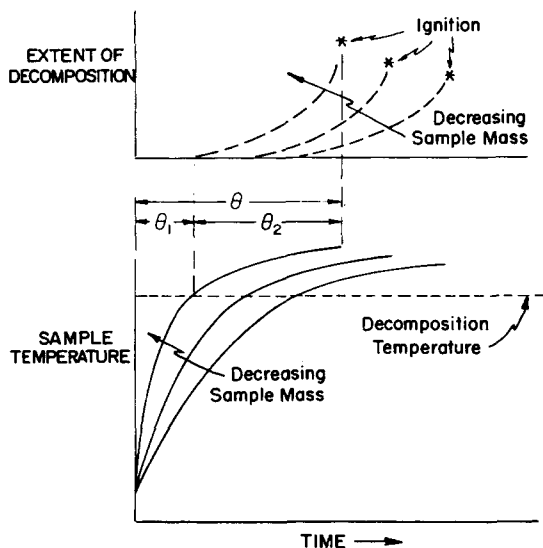


Fig. 4. Hypothetical plots of the variation of sample temperature and extent of decomposition with time at several values of sample mass.

As illustrated in Figure 5, the total time of ignition,  $\theta$ , should consist of two parts:  $\theta_1$ , the time required to heat the sample to its initial decomposition temperature, and  $\theta_2$ , the remaining time required for a sufficient amount of combustible decomposition product gases to form, diffuse from the sample, reach an explosive concentration level while in contact with oxygen, and ignite. From heat transfer considerations,  $\theta_1$  would be expected to increase linearly with sample mass if there were no significant influence of bulk thermal conductivity (i.e., if the sample were thermally thin). Studies of heat transfer through fabrics have shown this to be a valid assumption for such materials.<sup>14</sup> On the other hand,  $\theta_2$  should be practically independent of sample mass and should increase exponentially with decreasing temperature. Values for  $\theta_1$  and  $\theta_2$  have been obtained for many different polymers by means of simple autoignition time measurements,<sup>11</sup> and analysis of such data shows that  $\theta_2$  increases much more rapidly than  $\theta_1$  as  $T_\infty \rightarrow (T_\infty)_c$ . This is illustrated in Figure 5. In consequence, since  $\theta_2$  is mass-independent, ignition times near the limiting air temperature become essentially mass independent as seen in Figure 3. Therefore, there is really no need to obtain data for multiple layers in order to establish  $(T_\infty)_c$ , and in most cases only single-layer samples were used.

The value of  $(T_\infty)_c$  under these experimental conditions appears to be a characteristic polymer property, not influenced significantly by fabric or fiber

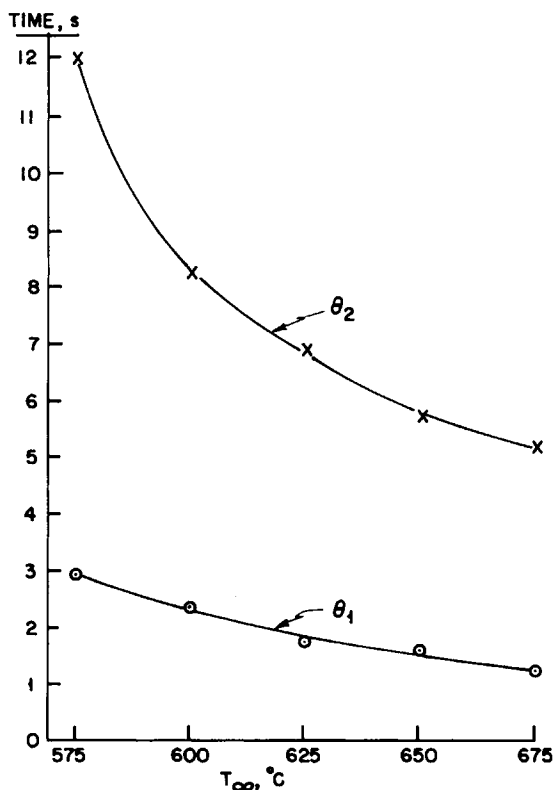


Fig. 5. Temperature dependence of the time to initial decomposition,  $\theta_1$ , and the remaining time to ignition,  $\theta_2$ , for polyester.

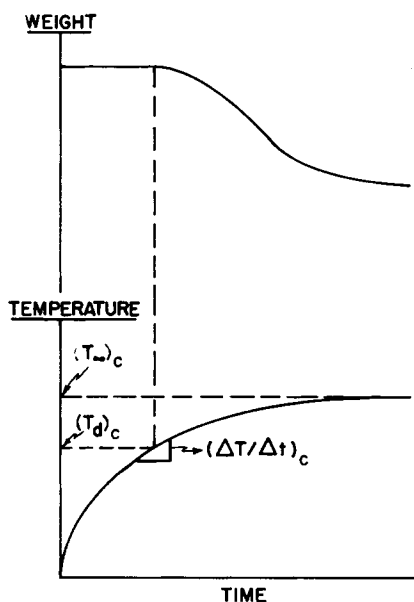


Fig. 6. Determination of critical heating rate  $(\Delta T/\Delta t)_c$  and critical decomposition temperature  $(T_d)_c$  from weight-time and temperature-time data. Oven temperature =  $(T_\infty)_c$ .

physical characteristics. For example, the same value of  $(T_\infty)_c$  was obtained for polyester fabric samples from three sources, which differed in weight, construction, finish, and manufacturing history.

The critical air temperature  $(T_\infty)_c$  defines the limiting case for ignition under a specific set of physical conditions. For example, if the size of the heated enclosure were changed, a different  $(T_\infty)_c$  would result. To determine a more general criterion, it is necessary to measure the critical heating rate under these conditions, that is, the rate of heating at which the polymer starts to decompose. To do this, a fresh sample of the polymer is inserted as before into the thermogravimetric analyzer oven preheated to  $(T_\infty)_c$ , and sample temperature and weight are recorded once again as a function of time. (Ignition will not occur, since its probability at  $(T_\infty)_c$  is essentially zero.) Figure 6 illustrates how the critical heating rate  $(\Delta T/\Delta t)_c$  and the decomposition temperature  $(T_d)_c$  are determined from this experiment.

Table II summarizes the critical ignition data for a variety of single-component polymeric materials. Also included are initial decomposition temperatures obtained with two slower linear programmed heating rates.

### RELATIVE IGNITION HAZARD RANKING

It is obvious that a material's resistance to accidental ignition will depend on its initial decomposition temperature as well as on its critical heating rate. The data in Table II show that these two properties do not operate in tandem; high critical heating rates do not necessarily go along with high  $(T_d)_c$  values. Figure 7 is a rectilinear plot of these two criteria, and, while it would appear that the two are not interdependent, there is a consistent and logical subgrouping of the

TABLE II  
Ignition Data for Single-Component Materials

	$(\Delta T/\Delta t)_c$ (°C/min)	$(T_\infty)_c$ (°C)	$(T_d)_c$ (°C)	$(T_d)_{100^\circ\text{C}/\text{min}}$ (°C)	$(T_d)_{20^\circ\text{C}/\text{min}}$ (°C)
Wool	3379	590	357	245	220
Kynol®	2087	575	455	450	400
Kermel®	1709	625	525	460	425
Arnel®	1478	463	340	320	300
Acrylic	1284	520	408	355	315
Polypropylene	933	494	410	405	375
Rayon	806	403	320	280	260
Nylon 66	802	507	430	405	370
Cotton	780	425	338	305	285
Nomex®	734	600	545	445	405
PBI	522	700	644	645	600
Polyester	419	480	427	395	385
Acetate	412	379	331	280	260
Vinylon	383	465	400	345	325

collection. If one imagines a common origin [ $(\Delta T/\Delta t)_c = 0$ ,  $(T_d)_c = 25^\circ\text{C}$ ], it is possible to classify subgroups according to their average distance from this origin. In this manner, those polymers that are known from experience to be easily ignited (rayon, cotton, etc.) are located close to the origin, while materials

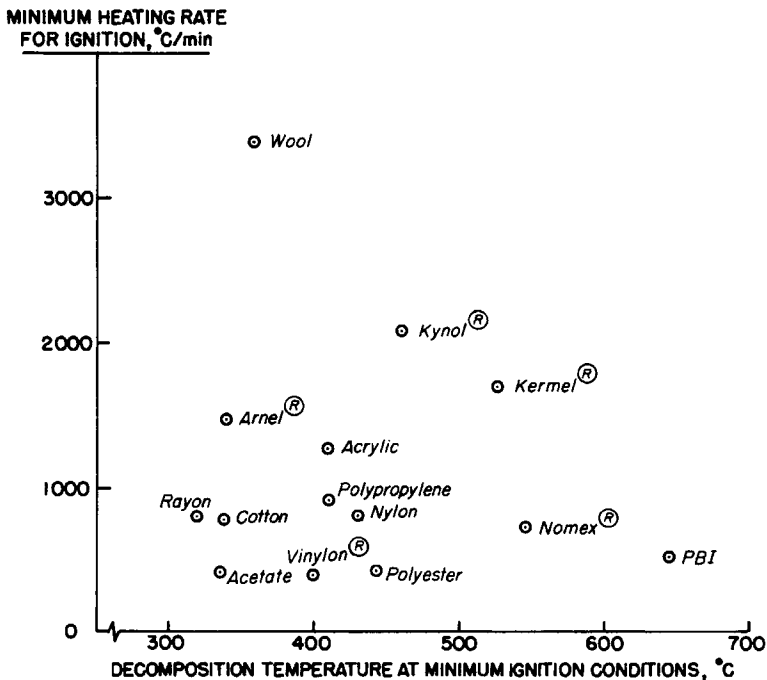


Fig. 7. Minimum heating rate for ignition plotted against decomposition temperature at this heating rate for a group of single-component fabrics.



TABLE III  
Values of  $[I]$  for the Materials in Table II

Acetate	196
Rayon	188
Cotton	180
Vynylon [poly(vinyl alcohol)]	162
Polyester	151
Arnel® (cellulose triacetate)	149
Polypropylene	147
Nylon 66	144
Acrylic	138
Nomex®	115
Kynol®	108
Kermel®	105
PBI	99
Wool	88

with the reputation for ignition resistance (wool, Nomex®, etc.) are much further away.

The above observation has led to the idea that a relative ignition hazard scale could be developed in terms of the distance of each plotted point from this origin. To eliminate the effect of scale arbitrariness, both quantities were converted into dimensionless ratios by dividing each result by the highest measured value, i.e., 3379°C/min for the rates and 644–25°C for  $(T_d)_c$ . The resultant pair of values for each material can then be used to calculate a length  $L$  of the vector from the origin to the plotted point, giving equal weight to each factor. That is,

$$L = \{[(\Delta T/\Delta t)_c/3379]^2 + [(T_{dc} - 25)/619]^2\}^{1/2}$$

An ignition probability function  $[I]$  is then defined as

$$[I] = 100/L$$

so that the magnitude of  $[I]$  will be directly related to relative hazard.

Table III contains the  $[I]$  values derived from the data in Table II. This function seems to give a reasonable ranking for all the materials studied, based on general experience. The cellulose (except for cellulose triacetate) have the

TABLE IV  
 $[I]$  Values for FR-Treated Cotton and Polyester

Cotton	180
Cotton + 2.5% DAP	224
Cotton + 8.1% DAP	223
Cotton + 4.6% Antiblaze 19®	201
Cotton + 8.4% Antiblaze 19®	197
PET	151
PET + 3.7% DAP	165
PET + 7.6% DAP	176
PET + 7.2% OBBP	171
PET + 16.1% OBBP	182
PET + 4.8% Antiblaze 19®	156
PET + 8.1% Antiblaze 19®	145

TABLE V  
 $[I]$  Values for Mixed Systems

50% PET	(151)	} 171
50% Cotton	(180)	
45% PET	(151)	} 161
55% Acrylic	(138)	
55% PET	(151)	} 128
45% Wool	(88)	
45% Nylon	(144)	} 125
55% Wool	(88)	

highest  $[I]$  values, conventional thermoplastics such as polyester and nylon fall in the middle of the scale, and polymers developed especially for high temperature resistance (Nomex<sup>®</sup>, Kynol<sup>®</sup>, etc.) appear as least likely to ignite. The low ranking of wool is not implausible. In contrast, if one were to rank in terms of critical heating rate alone (as in Table II), it is obvious that certain polymers (PBI, Arnel<sup>®</sup>, etc.) are not in their expected places. Similarly, if we were to use only  $(T_d)_c$  values and ignore the critical heating rates, other erroneous rankings would result.

### MULTICOMPONENT SYSTEMS

Critical ignition data for cotton and polyester both treated with flame retardants have been obtained using the same experimental technique. The resultant  $[I]$  values are given in Table IV. It appears that the presence of phosphorus, either in the form of diammonium phosphate (DAP) or Antiblaze 19<sup>®</sup> (Mobil Chemical Co. nonhalogen additive), actually decreases the ignition resistance of cotton. This is not surprising, since phosphorus is known to lower the thermal decomposition temperature of cellulose and to shorten its ignition time. The  $[I]$  value for polyester fabric can also be increased somewhat by the addition of flame retardants, both phosphorus and halogen (octabromo biphenyl, OBBP) types, though the Antiblaze 19<sup>®</sup> seems to have no effect. These results reinforce the point that a flame retardant is not necessarily an ignition retardant; in fact, there is still no available evidence that any substance can, by chemical reaction, retard the ignition of a polymer.

Polymer blends are quite common, particularly in textile materials, and the question arises as to what would be the resultant ignitability of such mixtures. Table V shows results for four mixed systems. In three cases the  $[I]$  value for the blend falls between those of the individual components but is closer to the more ignitable one. The polyester-acrylic mixture, however, is more easily ignited than either of the two polymers.

In one sense the  $[I]$  function by itself, while apparently useful as a means for ranking materials in terms of ignition hazard, can obscure significant changes in the thermal decomposition behavior of a sample. The intermediate value of  $[I] = 171$  for the 50/50 polyester/cotton blend shown in Table V does not suggest that this blend behaves in any way that is much different from that of its parent

TABLE VI  
Critical Ignition Data for Cotton, Polyester, and a 50/50 Blend

	$(\Delta T/\Delta t)_c$ ( $^{\circ}\text{C}/\text{min}$ )	$(T_d)_c$ ( $^{\circ}\text{C}$ )	$[I]$
Cotton	780	338	180
PET	419	427	151
50/50	1152	320	171

polymers. However, the more detailed results in Table VI show that the blend has a much higher critical heating rate and a lower thermal decomposition temperature. Since the two factors compensate, the net effect on the  $[I]$  function is only minor.

### CLOSING COMMENTS

The methodology for establishing the critical heating rate during thermal decomposition of a polymeric solid that will bring about ignition seems to be precise and sensitive enough to register differences between typical polymeric materials. When combined with the critical initial decomposition temperature, the two criteria can be used to provide a relative ranking which gives a reasonable index of potential ignition hazard. The initial decomposition temperature of a polymer is not a fixed material property but is strongly dependent on the effective heating rate. This is evident when one compares the decomposition temperatures at low heating rates (included in Table II) with the  $(T_d)_c$  values obtained at the critical rate. This can be considered additional evidence that the idea that a polymer has a characteristic ignition temperature has no validity.

The  $[I]$  hazard function used in this work is based on the arbitrary assumption that the two criteria have equal weight in controlling whether or not a material will ignite under given conditions of energy input. It is possible and likely that further analysis will reveal that one of the two should be assigned more significance than the other. At this writing, however, we feel that the simple vector summation used here is adequate.

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