

# Flammability Limits of Some Polymer Pyrolysate–Air Mixtures\*

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## Synopsis

Several textile fabrics have been heated in a closed cell and the flammability limits of the gaseous products produced determined. In addition the energy released on combustion of these gaseous products has been measured in order to obtain an indication of the heat feedback capabilities of the fabric. Comparison of the data obtained was made in order to provide an indication of the flash fire potential of the materials and their contribution to a potential fire hazard situation.

## INTRODUCTION

One of the fundamental concepts of combustion is that in order for a polymer to burn it must be converted into gaseous products, and be present with air in the correct proportions. The proportions of gaseous fuel to air which are combustible are defined as the flammability limits for that particular fuel. The existence of such intrinsic flammability limits for a fuel/air system is still the subject of much debate; however, practical limits do exist, although they are dependent upon the experimental equipment used in their determination. Coward and Jones<sup>1</sup> and Zabetakis<sup>2</sup> have published the flammability limits of a whole spectrum of gases and vapors in air and other oxidizing atmospheres. Unfortunately, when it comes to the flammability limits of the gaseous products produced during the pyrolysis and thermal decomposition of polymeric materials, few data are available. Such data are of fundamental importance in determining the potential flammability hazard of a polymeric material. Since most organic materials produce gaseous combustible products on heating, it is likely for these materials to be capable of ignition and combustion when mixed with air in the correct proportions and exposed to a suitable ignition source. For ignition to occur the concentration of pyrolysate in air must be above its lower flammability limit and below its upper flammability limit. It should be noted, however, that because of starting with solid materials rather than gases and vapors, the pyrolysate being examined is greatly dependent upon such factors as type of heating and heating rate in addition to equipment type and size.

This approach of measuring the flammability limits of pyrolysate–air mixtures of thermally degraded polymeric materials is not entirely new since several workers have devised equipment to measure the flash fire potential of the products of the thermal degradation of polymeric materials. Brown and Comford<sup>3</sup> studied the flash fire potential of a variety of polyurethane foams in order to better assess the fire hazard posed by these materials in aircraft fires. Hilado and Cumming<sup>4</sup> meanwhile have devised a method for determining flash-fire

\* Issued as NRCC # 20773.

propensities as a screening test for polymers in general<sup>5</sup> and cushioning materials in particular.<sup>6</sup> Fewell,<sup>7</sup> on the other hand, has measured the flash-fire propensity of materials of "improved fire resistance" using a modification of Brown and Comeford's<sup>3</sup> apparatus. Using a different approach, Durbetaki et al.<sup>8</sup> have studied the ignition characteristics of combustible gases generated from polymeric materials by measuring the minimum self-ignition temperature for pyrolysate-air mixtures generated from the pyrolysis of polymeric materials under various heating conditions.

In the work reported here the flammability limits of pyrolysate gases generated from several fabrics were determined in an attempt to obtain a better understanding of the potential fire hazard these materials might pose in an actual fire situation. In view of the importance of reflecting the temperatures and heating rates encountered in "real fires" an infrared heating system was employed. This system was found to give reproducible heating rates enabling meaningful comparisons to be made between the different fabrics studied.

## EXPERIMENTAL

### Materials

The materials selected for this study were all undyed textile fabrics obtained from a variety of commercial sources, and are described in Table I.

### Apparatus and Procedure

The experiments were carried out using the apparatus designed and built to measure the gas phase combustion characteristics of flame retarded polyesters.<sup>9</sup> Essentially the major components of the test apparatus are: (i) a closed insulated metal reaction vessel 165 mL in volume fitted with a mica window, (ii) an external infrared spot heater focused through the mica window on the sample contained in a crucible in the reaction vessel, (iii) instrumentation to generate the spark for ignition, and (iv) instrumentation to measure and monitor the temperature and pressure during heating and subsequent combustion if it occurred.

TABLE I  
Fabric Samples Tested

Fiber composition	Type	Weight (g/m <sup>2</sup> )
Cotton	100% Bleached sheeting	176
Polyester	Spun woven fabric	127
50/50C/P <sup>a</sup>	Bleached and mercerized sheeting	175
Viscose	Spun challis	124
Acetate	Tricot	141
Wool	Worsted Flannel	193
Silk	Degummed Crepe	75
Nylon 6	Filament Tricot	90
Nomex	Twill	200
Acrylic	Plain weave Acrilan type 16	210
Modacrylic	Verel A greige	198
Polypropylene	Woven fabric	153

<sup>a</sup> 50/50 Cotton/polyester blend.

The determinations were carried out using 200-mg samples of fabric weighed out accurately into a preweighed crucible. After the sample was loaded into the reaction vessel, the heater was switched on employing 80 V, which gave a radiative heat flux at the sample of  $13.27 \text{ W/cm}^2$ . Every 30 s a spark was discharged at the electrodes and the pressure and temperature readings were noted. A sudden increase in these readings indicated that a combustible explosion had occurred, i.e., a pyrolysate-air mixture within the flammability limits had been obtained. Following such an indication the lamp was immediately switched off, and the cooled sample removed and reweighed to determine the percentage weight loss corresponding to the explosion. Further samples were subjected to different exposure times in order that a full range of weight losses could be obtained, sufficient that the flammability limits could be determined.

## RESULTS AND DISCUSSION

Because of the nature of the infrared spot heater employed, the actual sample temperature and air temperature within the reaction vessel are not necessarily the same. This arises because the heat flux generated by the lamp is focused towards a point which is arranged to coincide with the actual sample position. Figure 1 shows the actual temperatures monitored by the equipment thermocouple (air) and a thermocouple positioned in the sample position during a blank run.

The production of the pyrolysate gases in the flammability limit experiments is dependent not only on the thermal stability of the material under consideration but also on the heating rate. In these experiments since only one set of heating conditions was employed the generation of pyrolysate was time-dependent upon

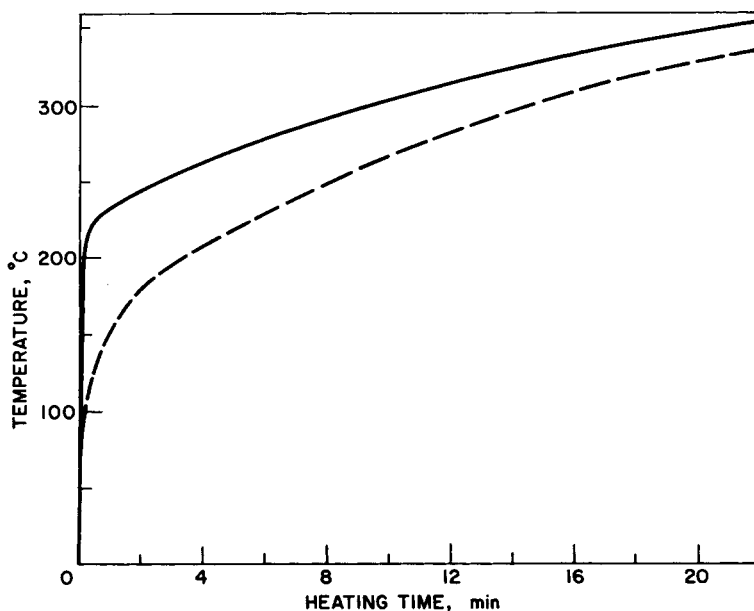


Fig. 1. Sample temperature (—) and air temperature (---) inside reaction vessel during a typical experiment.

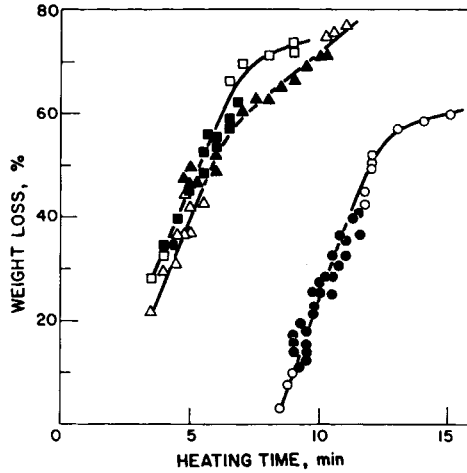


Fig. 2. Percentage weight loss on heating for cotton ( $\square$ ); polyester ( $\circ$ ); and 50/50 cotton/polyester ( $\triangle$ ) fabrics with combustible mixtures denoted  $\blacksquare$ ,  $\bullet$ , and  $\blacktriangle$ .

the heating period and is different for each fabric studied. The weight losses (pyrolysate formation) for each of the materials studied as a function of heating time are therefore summarized in Figures 2-5. Also indicated in these graphs are the tests which gave combustible pyrolysate-air mixtures enabling the flammability limits to be determined. However, by plotting the observed pressure increase arising from the ignition of the pyrolysate as a function of total percentage weight loss, the flammability limits of each system studied which gave combustible pyrolysates can be clearly defined (Figs. 6-9). These figures can therefore be interpreted to give valuable information on the burning characteristics and the associated fire hazard. Since it is commonly accepted that for

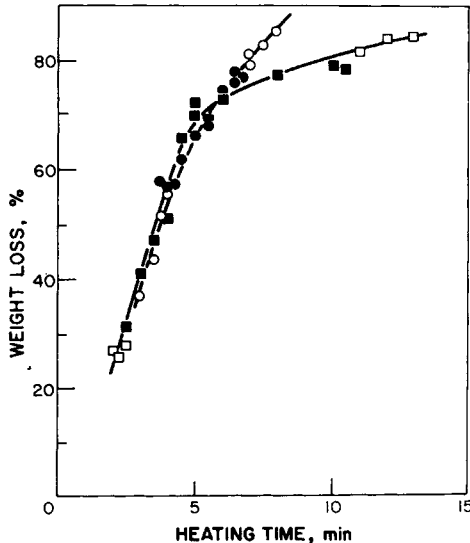


Fig. 3. Percentage weight loss on heating for viscose ( $\circ$ ) and acetate ( $\square$ ) fabrics with combustible mixtures denoted  $\bullet$  and  $\blacksquare$ .

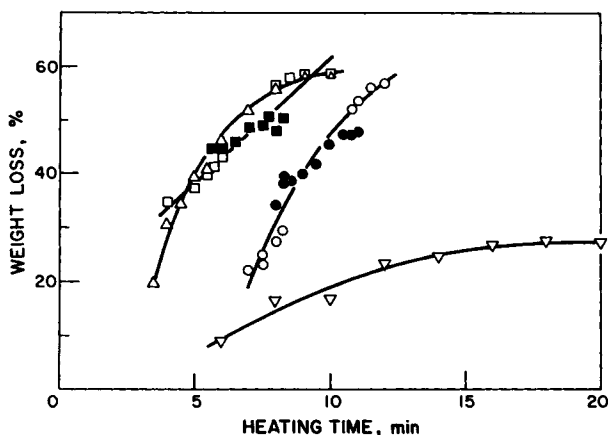


Fig. 4. Percentage weight loss on heating for nylon (O), wool (□), silk (Δ), and Nomex (▽) fabrics with combustible mixtures denoted ● and ■.

a given material there is a minimum pyrolysate/air ratio required for ignition, it follows that the measured lower flammability limit is a measure of the ignitability of the material, but one which has also to be balanced with the decomposition rate. Meanwhile, a material with a large flammability range between the lower and upper flammability limits represents a material capable of producing a fuel combustible over a wide range of fire conditions and represents a greater fire hazard than a material with a relatively narrow flammability range. The magnitude of the pressure rise on combustion is also a useful indication of the energy being released on combustion and is, therefore, capable of providing information on the potential heat feedback during the burning of the polymer. Ideally, for a material to represent a low potential fire hazard, it should have a high lower flammability limit, a small flammability range, and low pressure rise on ignition. These values for the fabrics studied in this investigation are listed in Table II along with the minimum heating time to obtain ignition at the lower flammability limit.

However, it should be noted that while the heating technique employed in this

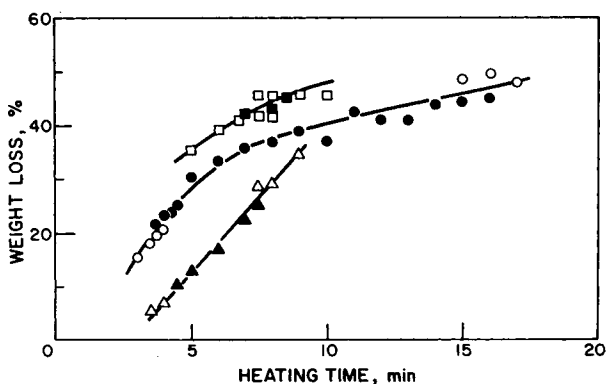


Fig. 5. Percentage weight loss on heating for acrylic (O) modacrylic (□) and polypropylene (Δ) fabrics with combustible samples denoted ●, ■, and ▲.

TABLE II  
Summary of Flammability Limit Results

Fiber composition	Heating time (min)	Flammability limits (% wt loss)		Flammability range (% wt loss)	Max pressure on ignition (kPa)
		Lower	Upper		
Cotton	4.00	33.6 ± 1.0	64.0 ± 2.0	30.4	254
Polyester	9.00	10.4 ± 1.3	41.6 ± 0.7	31.2	247
50/50 C/P <sup>a</sup>	4.75	46.7 ± 0.9	73.1 ± 2.1	26.4	241
Viscose	3.75	56.2 ± 0.6	77.1 ± 0.6	20.9	212
Acetate	2.50	29.2 ± 2.0	80.1 ± 1.1	50.9	316
Wool	5.75	43.4 ± 0.4	53.4 ± 3.0	10.0	124
Silk	—	—	—	—	—
Nylon 6	8.00	31.8 ± 2.2	49.5 ± 2.3	17.7	184
Nomex	—	—	—	—	—
Acrylic	3.75	21.1 ± 0.7	46.5 ± 1.7	25.4	345
Modacrylic	7.00	41.5 ± 0.4	45.2 ± 0.3	3.7	62
Polypropylene	4.50	8.5 ± 1.8	26.6 ± 1.6	18.1	>350

<sup>a</sup> 50/50 cotton/polyester blend.

study was selected to reflect the temperatures and heating rates encountered during the burning process, the types and magnitude of fires can vary enormously. Consequently, the chemical composition of the pyrolysates generated in this study are representative of only one set of test conditions, and changes in the testing conditions and exposure are likely to cause changes in pyrolysate composition and hence the flammability limits. For example, studies in our laboratory<sup>10</sup> have shown that for poly(ethylene terephthalate) the composition and concentration of thermal decomposition products is dependent upon the

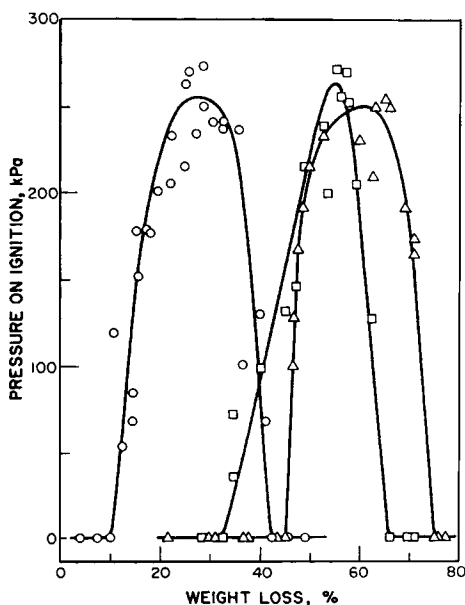


Fig. 6. Pressure rise on ignition as a function of percentage weight loss on heating for cotton ( $\square$ ), polyester ( $\circ$ ), and 50/50 cotton/polyester blend ( $\triangle$ ).

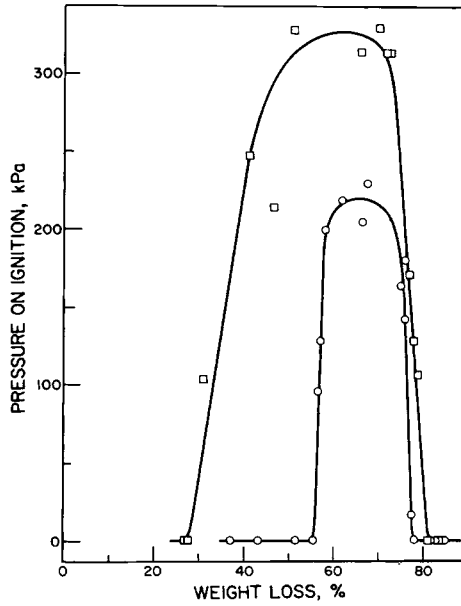


Fig. 7. Pressure rise on ignition as a function of percentage weight loss on heating for viscose (O) and acetate (□) fabrics.

decomposition temperature. Hence, in the case of this polymer, the chemical composition of the pyrolysate-air mixture will be dependant upon the thermal exposure. The results presented in Table II were all determined under the same test condition, and hence it is possible to make comparisons of different polymeric materials with respect to their performance under these specific test conditions.

The results obtained with the cotton, polyester, and cotton/polyester blend

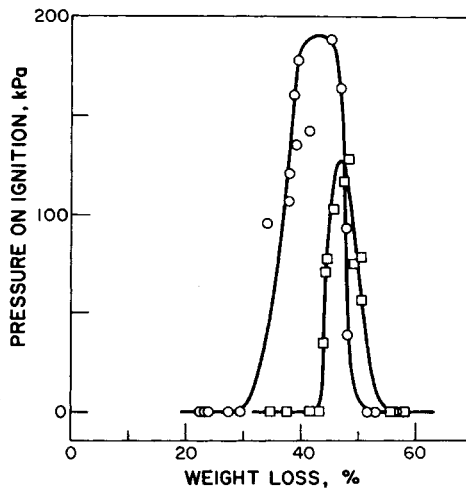


Fig. 8. Pressure rise on ignition as function of percentage weight loss on heating for nylon (O) and wool (□) fabrics.

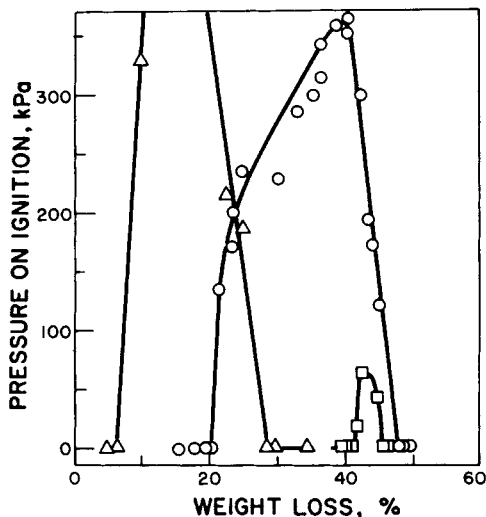


Fig. 9. Pressure rise on ignition as a function of percentage weight loss on heating for acrylic (O), modacrylic (□) and polypropylene (Δ) fabrics.

are summarized in Figures 2 and 6. The cotton sample was observed to give a flammable pyrolysate-air mixture in a relatively short time span, but the lower limit was quite high, i.e., one third of the cellulose had to pyrolyze before a flammable composition was obtained. The pyrolysate was then flammable for the next 30.4% weight loss until too rich a pyrolysate mixture was obtained. In terms of energy released on ignition, the magnitude of the pressure increase on ignition would indicate that, although the value was on the high side, it was not as high as the acrylic or polypropylene samples.

Considering next the thermoplastic polyester, it is interesting to note that this polymer has a very small lower flammability limit, indicating ease of ignition since only a relatively small weight loss of 10.4% will give a flammable pyrolysate-air mixture in our experimental equipment. However, in comparison to the cellulosic sample a larger amount of heat energy has to be fed into the system (i.e., longer heating period) before ignition is obtained. Interestingly, the delay in weight loss observed with the polyester is associated with the initiation processes since the actual rates of weight loss for the polyester and cotton are very similar (i.e., approximately equal slopes in Fig. 2). In terms of actual flammability range and energy release on ignition, the cotton and polyester are very similar.

In view of the behavior of the individual materials, cotton and polyester, it would have been reasonable to assume that the 50/50 cotton/polyester blend would have fallen somewhere between the behavior of the individual materials. Examination of Figures 2 and 6 indicates that this does not occur. Although the time delayed onset for obtaining a flammable mixture is to be expected, in view of the greater stability of the polyester, the observed high lower flammability limit of 46.7% is totally unexpected. This is even more surprising in view of studies made with blended cotton/polyester fabrics which have revealed these blends to be more flammable than the individual components.<sup>11</sup>

The thermal stability curves (Fig. 3) for the two other cellulosic fibres studied (viscose and acetate) appear very similar. However, the acetate has a smaller



lower flammability limit than does the viscose, which, consequently, is reached sooner than that for the viscose. The acetate not only has a small lower limit, but also a high upper limit which means that the pyrolysate gases produced are flammable over a very wide range of pyrolysate-air mixture. The flammability range for the acetate is larger than that for any of the other fibres studied in this investigation. The energy released on ignition (Fig. 7) is also high, being larger than for any of the other cellulosics. In contrast the viscose has the highest lower flammability limit of all the fibers considered, which implies that a large percentage of the material would have to be pyrolyzed in order to obtain a flammable gas mixture. This would suggest that, in terms of ignitability, it should be the most difficult to ignite. However, it should be emphasized that decomposition rate must also be considered, and viscose has a low thermal stability under fire conditions and as such reaches its lower flammability limit after only 3.75 min.

Of the two protein fibres examined only the wool was observed to produce flammable pyrolysate-air mixtures (Fig. 4). While both fibers gave similar weight loss curves indicating similar thermal stability, ignitions were only observed for the wool sample, and this was over a very small weight loss range of 43.4–53.4%. This narrow range and the low energy released on ignition (Fig. 8) would suggest that this material would not pose too great a hazard in a fire situation. Comparison of the behavior of the two polyamides, nylon 6 and Nomex clearly reveals the differences in thermal stability of the aliphatic and aromatic polyamides. Under the heating conditions employed in this study, a weight loss not greater than 27.5% was obtained with Nomex even when heated for periods greater than 20 min. Because of this thermal stability, insufficient pyrolysate was produced to obtain a flammable mixture in our experimental setup. Nylon 6, on the other hand, has a thermal stability between those of wool and Nomex in that an 8-min heating period was required to get a pyrolysate composition which was flammable, compared with only 5.75 min for wool and >20 min for Nomex. The actual flammability range for the nylon is, however, much larger and the energy release much greater (Fig. 8) for the nylon than for wool, indicating a potentially greater fire hazard for the former.

The acrylic fabric was observed to have a relative low thermal stability, providing a flammable pyrolysate-air mixture after only 3.75 min of heating. However, it will be noted that this material is a high-char-forming material in that its residue after 17 min heating is still greater than 50%. The lower flammability limit is also relatively small, indicating relative ease of ignition. Coupling these data with the magnitude of the energy released on ignition suggests that the acrylic represents a potentially hazardous material. Interestingly, the modacrylic can be seen (Fig. 5) to have a lower thermal stability than the corresponding acrylic; yet the lower flammability limit is significantly higher and the flammability range markedly reduced. These observations coupled with the small energy release on ignition (Fig. 9) clearly indicate the marked improvement in fire performance of the modacrylic polymer over that observed with the acrylic polymer.

The pronounced flammability of polypropylene is a generally recognized fact owing to its chemical similarity to liquid hydrocarbon fuels. It is not too surprising, therefore, to note that this material has a small lower flammability limit and high energy release on ignition, typical of hydrocarbon fuels.

In order to assess the relative ignitability of a material, it would be interesting

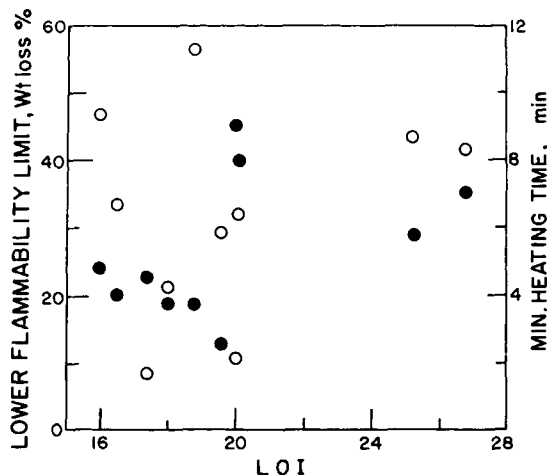


Fig. 10. Relationship between LOI and lower flammability limit (O) and minimum heating times for ignition (●) for several of the fabrics studied.

to compare the relevance of the lower flammability figure obtained in our study with actual ignition experiments. The limiting oxygen index (LOI) is one such technique which has been used extensively in comparing the flammability of polymeric materials. Comparison of LOI data with the lower flammability limit and the time to reach this limit are made in Figure 10. These data clearly indicates the lack of any correlation between LOI and the lower flammability limit as measured in our experimental setup. This result is to be expected since the flammability limit is only a measure of the flammability of the gases produced during polymer breakdown and does not consider the overall thermal stability of the polymer. Consequently, it is not too surprising to observe that a slightly better correlation is observed between the minimum heating time to obtain a flammable mixture and LOI (Fig. 10).

Textile fabric flammability was the subject of a detailed investigation under the sponsorship of a U.S. Government Industry Research Committee on Flammable Fabrics (GIRCFF).<sup>12</sup> In this study two parameters  $A$  and  $F$  were proposed for ranking fabrics with respect to their ease of ignition (or melting) under radiative and convective heating conditions. These parameters were defined by the following expressions:

$$A \equiv P\delta C(T_{im} - T_0)/\alpha \quad (\text{for radiative heating})$$

$$E \equiv P\delta C(T_{pim} - T_0)/(1 - T_{pim}/2T_f) \quad (\text{for convective heating})$$

when  $P$  = fabric reflectivity,  $\delta$  = fabric thickness (cm),  $C$  = specific heat (W-s/g°C),  $\alpha$  = absorptivity,  $T_{im}$  = self-ignition or melting temperature (°C),  $T_{pim}$  = pilot ignition on melting temperature (°C),  $T_f$  = flame temperature (°C),  $T_0$  = ambient temperature (°C)

Comparison of these values calculated using the data in the GIRCFF report with the lower flammability limits determined in this investigation are given in Figure 11. This comparison would indicate that the lower flammability limit is in fact a reasonable parameter for monitoring the "ease of ignition" of fabrics provided that due consideration is given to thermal stabilities.

Another important factor in the combustion of polymeric materials is the heat

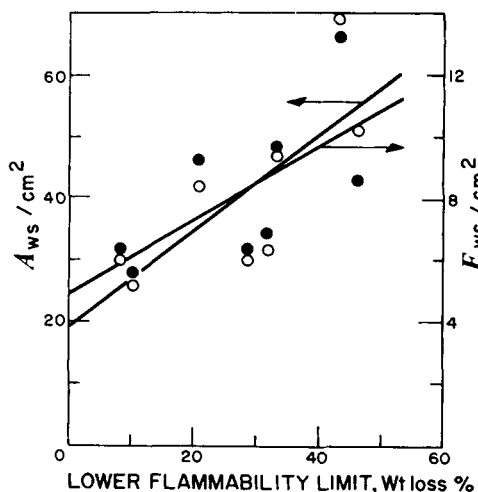


Fig. 11. Relationship between the lower flammability limits and the fabric ranking parameters characteristic of radiative A (O) and flaming E (●) ignition.

of combustion of the gaseous products formed on decomposition, or more specifically the heat released during the combustion process. This arises because the heat generated during the combustion process may be transferred back to the polymer causing further gaseous fuel production. In our experimental setup, we monitor the pressure rise associated with the ignition of the flammable gas-air mixture. The "larger" these explosions, the greater is the energy release for that particular mixture of combustible fuel gas. In Figure 12, we have compared the heat of combustion of the various polymers with maximum pressure rises on ignition. It will be noted there is no correlation between the specific heat of combustion of the polymers and the energy release on combustion. However, when the pressure rise on ignition is compared with the heat release values obtained by Yeh and contained in the GIRCFF report,<sup>12</sup> a very good correlation

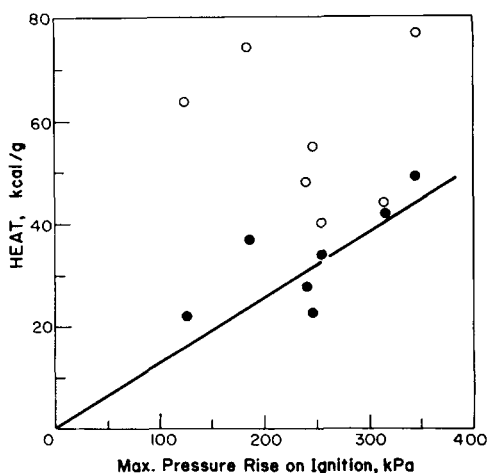


Fig. 12. Relationship between the maximum pressure rise on ignition and the heat of combustion (O) and the heat released in burning in air (●).

was obtained. This would confirm that the pressure rise is indeed a good measure of the actual heat output from the polymeric materials studied.

### CONCLUSION

An apparatus has been developed which can provide some fundamental information on the ignitability and combustibility of the gaseous fuels produced from polymeric materials during radiative thermal degradation. In addition to determining the possible flash fire potential of a material, it provides information on the energy release capability of the fuels produced. It is possible that the information obtained using this equipment will assist materials engineers in specifying organic materials for particular applications dependant upon potential fire risk. For example, a material which decomposes slowly to give fuel gases which have a high lower flammability limit, narrow flammability range, and small energy release on combustion are going to be safer from a fire hazard point of view than materials which have the opposite properties.

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Received June 8, 1982

Accepted July 22, 1982