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# High Throughput Flammability Characterization Using Gradient Heat Flux Fields

ABSTRACT: The quest for small-scale flammability tests useful for predicting large-scale fire test performance is an enduring undertaking. Often, this work is motivated by limited access to larger quantities of samples, in the case of materials development efforts, and by the slow turn-around and high cost of large scale flammability testing. Use of Cone calorimeter data such as heat release rate (HRR) and ignition data has been coupled with various models to attempt to predict the performance of materials in medium and large scale fire tests. In some instances this has been successful; however, the extensive amount of data that needs to be acquired has motivated the High Throughput (HT) Flammability program at the National Institute of Standards and Technology (NIST) to develop flammability characterization methods which significantly increase the rate of data generation. The goal is to keep pace with our sample preparation rate, which is a significant challenge since our capability to produce samples, either extruded rod, or gradient coatings, has developed to a rate of one sample per minute! The efforts described here are those specifically focused at developing HT flammability analysis methods. The method of evaluating the flammability of a sample at a variety of fluxes simultaneously involves use of a radiant panel to create a gradient heat flux field. Samples are ignited in the high flux region and burned until they self-extinguish. The local flux at this position is termed the minimum flux for flame spread (MFFS). The same general technique has also been accomplished on a smaller scale using the Cone calorimeter. Here MFFS and HRR can be measured concurrently.

KEYWORDS: flame spread, radiant panel, polymer, flammability

#### Introduction

The extensive amounts of data that need to be acquired to successfully predict fire safety using small-scale fire tests has motivated the High Throughput Flammability program at NIST to develop flammability characterization methods which significantly increase the rate of data generation. The goal is to keep pace with our sample preparation rate, which is a significant challenge since our capability to produce samples, either extruded rod, or gradient coatings, has developed to a rate of one sample per minute! The efforts described here are those specifically focused at developing High Throughput (HT) flammability analysis methods.

There are two general methods used in HT analysis; the first, invented in 1970 by Hanak at RCA, utilizes preparation and analysis of samples that contain a compositional gradient [1]. The other method, utilized by companies such as HTE, Avantium, and SYMYX, involves use of an array of discrete samples and automated testing of each individual sample. The gradient approach is used in the flammability studies here, but a gradient is created in the test conditions instead of in the sample composition [2].

This approach follows work by Lyon [3] and Quintiere [4]. Lyon has asserted that heat

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release rate (HRR) data taken at a variety of incident heat fluxes can yield a plot (HRR versus heat flux) whose intercept allows prediction of UL 94 behavior. Quintiere shows in his modeling of flame spread that a system can only be accurately modeled if the flammability is measured over a range of fluxes: ignition time, flame spread, and HRR versus heat flux all need to be determined [4].

Bundy and Ohlemiller have shown that, within a polymer-flame retardant system, Lyon's theory can be used as a guide to UL 94 behavior [5]. The plot of average heat release rate versus external irradiance (heat flux) for four different high impact polystyrene (HIPS) samples is shown in Fig. 1. Lyon asserts that the intercept of the best-fit line for these data is the HRR at zero external flux (HRR<sub>0</sub>), and that if this HRR<sub>0</sub> is below 100 kW/m<sup>2</sup> then the UL 94 rating will be V0. For the HIPS samples examined here, this appears to hold. The drawback to this approach is that it is time consuming. Cone calorimetry data must be taken several times at a minimum of three heat fluxes. Furthermore, the cone heater must be recalibrated with a flux gauge each time the flux is changed.

Apart from of the predictive value of this approach, characterization of the flammability performance of a material over a range of fluxes gives a more complete picture of the fire safety associated with the material.



FIG. 1—Average heat release rate (HRR, 60 s average) versus external irradiance (heat flux) for four HIPS formulations. The flame retardant (FR) in 2-HIPS was bromine/antimony oxide, 3-HIPS contained no FR, 9-HIPS contained bromine/antimony oxide, and 18-HIPS contained a non-halogen FR. The UL 94 rating for each formulation is indicated on the plot. The uncertainty in the HRR is  $\pm 5 \%$  ( $\sigma$ ).

## Experimental<sup>2</sup>

## Extrusion

Homogeneous sample rods (4 mm  $\times$  1 m) were produced in our twin screw extruder (B&P, 19 mm diameter screw with a 25:1 length to diameter ratio, and feed rates: 2 kg/h–3 kg/h). A two-hole die produces two 4 mm round strands, which are cooled with an air-knife attached to the conveyor belt (see Fig. 2). Polystyrene (PS) containing ammonium polyphosphate (APP) and pentaerythritol (PER) was compounded in the B&P twin screw extruder at six loading levels as shown in Table 1. In all samples the mass ratio of APP to PER was 3:1. Temperatures in the extruder were: zone-1, 170°C; zone-2, 180°C; zone-3, 180°C; zone-4, 190°C; and screw speed was 10.5 rad/s (100 rpm). A portion of these formulations was pelletized and extruded with organo-clay (15A (MMT), Southern Clay Products, Gonzales, TX) so as to prepare formulations which also contained nano-dispersed organo-clay. The five different loading levels used are also shown in Table 1. This includes a set of nanocomposite only samples. All 42 members of the matrix were prepared as extruded rods for flammability testing. A set of polyethylene (Petrothene 206, Equistar) samples, in rod form, was also prepared via extrusion; one with magnesium hydroxide (mass fraction<sup>3</sup> 60 %) and a control sample with an inert filler CaCO<sub>3</sub> (mass fraction 60 %).



FIG. 2—Photo of the twin-screw extrusion facility.

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<sup>&</sup>lt;sup>3</sup> Mass fraction % is defined as: (mass of additive/mass of total formulation)  $\times$  100 %.

Mass fraction % of	Mass fraction % of organo-						
APP/PER $\downarrow$ (3:1)	$clay (15A) \rightarrow$	0	2	4	6	8	10
0							
5		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
10		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	
15		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$
20		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$
25		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$
30		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		

TABLE 1—42 member matrix of samples prepared using PS with APP/PER (3:1) and organo-clay 15A.

## Flammability Properties

The flammability properties of polymer samples were evaluated by measuring *minimum flux for flame spread* (MFFS, see Fig. 3) and  $t_{ign}$  (see Fig. 4) in a gradient heat flux environment in the radiant-panel device, like that shown in Fig. 5, or in the Cone calorimeter (see Fig. 6). The sample is lit at the high-flux end and allowed to burn until the sample self-extinguishes. The flux at that point is defined as the MFFS. The heat flux gradients were mapped using a flux gauge along the center-line where the sample lies. These gradients for both radiant sources are shown in Fig. 7. Additional mapping of the gradient, from the cone heater away from the center-line, showed that at a given distance, the center region of the gradient is homogeneous over a 3 cm wide area (data not shown). For the normal configuration of the Cone calorimeter, see [6].



FIG. 3—Schematic of the gradient flux experiment, where a homogeneous sample strip is exposed to a gradient in the heat flux intensity.



FIG. 4—Schematic of the gradient heat flux approach where ignition time,  $t_{ign}$ , of 3–4 samples is measured simultaneously at several incident fluxes for one material.



FIG. 5—NIST Radiant Panel apparatus.



FIG. 6—Cone heater and flame spread experimental set up.



FIG. 7—Flux gradients generated in the radiant panel apparatus and in the Cone calorimeter.

## **Results and Discussion**

## Minimum Flux for Flame Spread

For the purpose of measuring flammability at a variety of fluxes, nearly simultaneously and in a high throughput fashion, the radiant panel apparatus was used. A schematic of the experiment performed in the radiant panel is shown in Fig. 3. The radiant panel creates a gradient flux field, which is measured at several positions along the sample region, using a calibrated flux gauge. The flux map for the radiant panel is shown in Fig. 7 (top curve). Samples are ignited in the high flux region and burned until they self-extinguish. By using the flux map the local flux at the point of self-extinguishment can be determined. The local flux at this position is termed the *minimum flux for flame spread (MFFS)*. Previously, it has been shown that a MFFS of 13 kW/m<sup>2</sup>, or above, corresponds to a UL 94 rating of V-0. This was for flame retarded polyamide-6 with either of two FR-systems: organo-bromine/antimony trioxide or magnesium hydroxide [7]. Furthermore, in evaluating the flammability of rigid polyisocyanurate foams using this method, the MFFS was found to correlate with the flame spread index in the E-84 tunnel test [7].

This MFFS method was used to evaluate the flammability properties of a large matrix of flame retarded polystyrene (PS) samples. The purpose was to determine the efficiency of the high throughput methods and to evaluate the effectiveness of combining a standard intumescent flame retardant (ammonium polyphosphate (APP) and pentaerythritol (PER)) with a nanocomposite flame retardant (organo-clay, 15A).

The rapid rate at which the extruder produces samples (1-2 kg/h) allows several formulations (10 or more replicates) to be prepared per hour. The 4 mm extruded rods of the 42 formulations shown in Table 1 were prepared over a 3-day period. The MFFS of the PS formulations were determined over a 3-day period also, using the methods described above (see Experimental). The

MFFS data are shown in Fig. 8. These results demonstrate that 42 flame retarded polymer formulations can be prepared and characterized in about 1 week. Furthermore, in terms of interactions between the two flame retardant systems (intumescent and nanocomposite) the data show that low loadings of APP/PER (10 %, 15 %, and 20 %) combined with a 2 % loading of organo-clay produces an increase in the MFFS in excess of what would be obtained simply by adding additional APP/PER (see red boxes in Fig. 8). Moreover, in the formulations with higher loadings of both flame retardants, the combinations produce a reduction in the MFFS. It is not clear what the origins are of these seemingly contradictory results.



Mass Fraction % Total Additive Content

FIG. 8—*MFFS* data for the PS flame retarded formulations. The uncertainty is shown as error bars ( $\pm$  one  $\sigma$ ) in the plot.

Since flame spread is dependent on the burning configuration, HRR (or flame heat flux), and the ignition properties [8] of the material, it is difficult to determine the origin of the MFFS results. Therefore, we measured the ignition properties of the flame retarded PS formulations, at

three heat fluxes, using the flux gradient approach as shown in Fig. 4. The results for the members of the matrix with lower loadings are shown in Fig. 9. These data show that addition of APP/PER to PS lowers the ignition time ( $t_{ign}$ ) at most of the fluxes where  $t_{ign}$  was measured (see 10 %, 15 %, 20 %, and 30 % APP/PER data in Fig. 9). Therefore, for the formulations where the MFFS is better than that of pure PS (MFFS = 0 kW/m<sup>2</sup>), the APP/PER must significantly reduce the HRR of the formulation. In contrast, the addition of organo-clay to PS has very little effect on  $t_{ign}$  (see PS with 2 %, 4 %, and 6 % 15A in Fig. 9). Finally, these  $t_{ign}$  versus flux data reveal that for each of the formulations where the APP/PER and 15A were combined *and* an improvement in MFFS was observed, the  $t_{ign}$  was actually shortened (see PS with 10/2 APP-PER/15A, PS with 15/2 APP-PER/15A, and PS with 20/2 APP-PER/15A in Figs. 8 and 9). This indicates that the HRR must be substantially reduced in these formulations to counteract the shorter  $t_{ign}$  and still result in a net improvement in MFFS. The analysis of these two data sets (MFFS and  $t_{ign}$  vs. flux), where flammability is evaluated over a range of fluxes, demonstrates both the efficiency and quality of this approach for the study of flame retardant polymers.



FIG. 9—Ignition data for some of the flame retarded PS formulations (Table 1) measured in the radiant panel apparatus. The uncertainty in the ignition time, averaged over all fluxes where  $t_{ign}$  was measured, is  $\pm 10 \% (\sigma)$ .

To further improve this method, a smaller gradient flux region and, therefore, a shorter sample was evaluated using the Cone heater in the NIST Cone Calorimeter prototype (see Fig. 6). The main advantage offered by using an electric heater is the greater safety and ease of use versus the gas fired panel used in the radiant panel. The flux gradient which results from using the Cone heater tilted at 22° above the horizontal plane of the sample is shown in Fig. 7 (lower curve). The gradient occurs over a smaller distance, therefore allowing a shorter sample to be used. This is valuable since it allows use of the mini-twin screw (DACA) where 4 g strands are prepared. Using the mini twin screw instead of the B&P bench-scale twin screw lowers the quantity of materials needed to prepare a set of samples by a factor of ten. A comparison of the MFFS data taken on two polyethylene formulations (one with 60 % magnesium hydroxide and a control with 60 % calcium carbonate) is shown in Fig. 10. The samples are shown after burning in the Cone gradient flux field in Fig. 11.

The results (Fig. 10) are identical, within the uncertainty in the data; although the uncertainty in the MFFS using the Cone heater is larger than that in the radiant panel. This should improve if rectangular electric panels are used instead of the cone-shaped heater. An additional advantage of using the Cone calorimeter is that it provides the opportunity to measure standard parameters normally measured, such as HRR and smoke. Shown in Fig. 12 are the HRR data for the PP formulations, which were taken during the MFFS experiment. Although these data are not normalized to the burning area, it is hoped that through the use of image analysis of video data taken during the burning, a plot of HRR versus flux could be obtained from a single test. Accomplishing this later goal is the topic of ongoing work.



FIG. 10—Comparison of MFFS data taken in the radiant panel and using the Cone heater.



FIG. 11—250 mm samples used in the Cone gradient flux field. MFFS determined at position where sample self-extinguishes. Top sample was burned from left to right; bottom samples were burned from right to left.



FIG. 12—HRR data taken in the Cone calorimeter during a MFFS test.

## Conclusion

It has been demonstrated that the characterization of flammability over a range of fluxes provides efficient (high throughput) methods to quantitatively characterize the fire behavior of materials. These results combined with those published previously [7] indicate that significant progress has been made toward the goal of developing high throughput flammability analysis techniques that can be used to predict material behavior in other fire tests.

## References

- [1] Hanak, J. J., "The 'Multiple-Sample Concept' in Materials Research: Synthesis, Compositional Analysis and Testing of Entire Multicomponent Systems," *Journal of Materials Science*, Vol. 5, 1970, p. 964.
- [2] Gilman, J. W., Bourbigot, S., Shields, J. R., Nyden, M., Kashiwagi, T., Davis, R. D., et al., "High Throughput Methods for Polymer Nanocomposites Research: Extrusion, NMR Characterization and Flammability Property Screening," *Journal of Materials Science*, Vol. 38, No. 22, 2003, pp. 4451–4460.
- [3] Lyon, R. E., "Ignition Resistance of Plastics," *SAMPE 2003*, SAMPE, Covina, CA, 2003, pp. 1452–1458.
- [4] Panagiotou, J. and Quintiere, J. G., "Generalizing Flammability of Materials," *Interflam2004 10th International Fire Science & Engineering Conference*, Interscience Communications Ltd, S. Grayson, Ed., Greenwich, London, England, 2004, pp. 895–905.
- [5] Bundy, M. and Ohlemiller, T., "Bench-Scale Flammability Measures for Electronic Equipment," *NISTIR 7031*, July 16, 2003, p. 20.
- [6] Babrauskas, V. and Peacock, R., Fire Safety Journal, Vol. 18, 1992, p. 255.
- [7] Gilman, J. W., Davis, R. D., Shields, J. R., Wentz, D., Brassell, L. D., Morgan, A. B., et al., "Development of High Throughput Methods for Flammability Property Characterization," *SAMPE Proceedings*, SAMPE, 2004.
- [8] Quintiere, J. G., "Surface Flame Spread," *SFPE Handbook of Fire Protection Engineering*, 2<sup>nd</sup> ed., NFPA, 1995, Ch. 14.aa.