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The Impact of Bromine- and Phosphorous-Based Flame Retardants on Flame Stability and Heat Feedback from Laminar Wall Flames

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ABSTRACT

Flame retardants are widely used to improve the resistance and response of combustible materials to fire. Unfortunately, widespread bioaccumulation of brominated flame retardants has evoked growing concern with regards to the environmental hazards that flame retardants pose, thus industry is moving towards developing safer and equally effective alternatives. To develop new, efficient flame retardants, it is critical to understand the exact mechanisms by which they inhibit flaming combustion. Our research group has developed a systematic methodology to assess the flammability of polymeric materials through microscale combustion calorimetry (MCC) and experimental measurement of flame heat feedback and material burning behavior during upward flame spread. In this work, that experimental framework is used to quantify the mechanisms of action of bromine- and phosphorous-based flame retardants. Here, a series of experiments was conducted in which flame heat transfer and sample mass loss rate were measured as a flame spread over 7 cm tall, 5 cm wide glass-reinforced poly(butylene terephthalate) (PBT) samples manufactured with increasing amounts (12, 16, and 24 wt %) of the brominated flame retardant, poly(pentabromobenzyl acrylate). In an additional series of tests, similar measurements were obtained for PBT samples manufactured with increasing amounts (8, 12, 16, and 20 wt %) of the phosphorous-based flame retardant, aluminum diethyl-phosphinate (trade name: Exolit OP 1230). These tests allow for the study of the impact of flame retardants on key features of the system including: peak flame heat flux, flame stability, and condensed phase decomposition behaviors (i.e. charring). Current measurements identify an optimal loading concentration of Exolit OP 1230 for the PBT samples tested in this work, identify each flame retardant’s impacts on char yield and heat of combustion, and indicate that bromine- and phosphorous-based flame retardants (at least at the concentrations tested here) do not affect flame to surface heat transfer in the continuous region of wall flames and do not have a significant effect on flame stability at ignition. These measurements allow for greater understanding of tightly coupled condensed- and gas-phase processes that control flame spread and material burning behavior, thus providing a quantitative connection between material composition and the controlling mechanisms of fire growth.

KEYWORDS:

Fire retardants, wall flames, heat transfer, flame stability, flame spread

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INTRODUCTION

To improve their resistance and response to fire conditions or simply to meet fire safety regulations and standards, flame retardants are often added to combustible materials such as synthetic polymers. Typically, these flame retardants work in the condensed phase by interfering with pyrolysis (e.g. promoting char formation), reducing gas phase combustion efficiency, or both. Market demand for flame retardants is estimated at $2.3 billion with approximately 36% of this market share attributed to brominated flame retardants (BFRs), which are highly effective and relatively low in cost [1] via. [2]. With the rapid expansion in their use, BFRs have been found across the environment in the atmosphere, soil and sediment, bodies of water, and in the tissues of invertebrates, fish, birds, and mammals [3]. This bioaccumulation has evoked growing concern with regards to the environmental hazards that these flame retardants pose [4] and thus industry is moving towards developing safer and equally effective replacements.

To understand how flame retardants reduce material flammability and to develop new, efficient alternatives, it is critical to determine the mechanisms by which they inhibit flaming combustion. One approach is to propose a chemical reaction mechanism through which a flame retardant or a class of flame retardants works. This can allow for the identification of structural chemical features that may be responsible for observed flammability reduction performance; however, this approach does not allow for quantitative prediction of material flammability performance for varied material compositions (e.g. different flame retardant loading) or in response to a range of fire scenarios. Alternatively, one can perform bench scale flammability tests such as ASTM D2863 (Limiting Oxygen Index, LOI) [5] or UL-94 [6]. ASTM D2863 determines the lowest oxygen concentration that will “just support flaming combustion of a material”. Although LOI can be quantified in this test, it is not an intrinsic property of the material (it is configuration and scale dependent) thus the material may undergo flaming combustion at significantly lower oxygen concentrations in fully developed fires. UL 94 tests are a better qualitative assessment of ignition and flame spread over a material; however, test results are only expressed in terms of a relative ranking scale and it has been shown that no broad, quantitative relationship exists to predict material flammability performance (i.e. burning behavior in the cone calorimeter [7]) using UL-94 ratings [8]. Ultimately, although widely applied, many test standards show limited ability to predict material response outside of particular test conditions [9] and conflicting assessments often arise between different tests [10].

Flame spread is known to be controlled by a positive feedback between coupled processes of solid phase material degradation and gas phase combustion [11]. As gaseous degradation products react with the ambient oxidizer in a diffusion flame, a fraction of the heat produced in this reaction is transferred back to the solid, causing further degradation and production of flammable gases. Quantifying how flame retardants affect these processes is critical to understanding existing and developing new flame retardants and to predicting material flammability performance. Our research group has developed a systematic methodology to assess the flammability of polymeric materials through microscale combustion calorimetry (MCC) [12] and experimental measurement of flame heat feedback and material burning behavior during the early stages of upward flame spread [13, 14]. This experimental framework is used in this work to quantify the mechanisms of action of bromine- and phosphorous-based flame retardants, which are known to act through different mechanisms: primarily in the gas and solid phase, respectively [15]. Here, a series of experiments was conducted on glass-reinforced poly(butylene terephthalate) (PBT) samples manufactured with increasing amounts (8 to 24 wt. %) of either a bromine- or phosphorous-based flame retardant. These tests allow for the quantification of the impact of flame retardants on key features of the system including: peak flame heat flux, flame stability, and mass loss rate during vertical burning, as well as heat of combustion, and char yield.

EXPERIMENTAL SETUP

The PBT used in this study was obtained from BASF in the form of 6 mm thick, 5 cm wide, and 7 cm tall slabs. All samples were reinforced with chopped glass fibers (25 wt. %). Samples were manufactured with either the brominated flame retardant poly(pentabromobenzyl acrylate) (trade name FR 1025) or the phosphorous-based flame retardant, aluminum diethyl-phosphinate (trade name Exolit OP1230). Additional tests examined samples manufactured with two flame retardants (potential synergists): FR 1025 with antimony trioxide or Exolit OP 1230 with Melapur M200. Table 1 identifies the formulation of samples tested in this work.

MCC experiments were conducted in accordance with ASTM D7309 [12] using 3 to 5 mg material samples that were pyrolyzed in nitrogen at a heating rate of 1 K s⁻¹. The heat of complete combustion of gaseous pyrolyzates (ΔHc) and char yield (μcharr) were determined. The chopped glass fibers were assumed not to react in MCC tests and their influence on calculated ΔH and μcharr was subtracted accordingly. Each material was sampled and tested in the MCC three times to ensure reproducibility.
Table 1. Sample compositions and preheating and ignition times in flame spread experiments.

| Flame Retardant Concentration (wt. %) | Sample Preheat Duration (s) | Burner Application Duration, $t_{ign}$ (s) |
|--------------------------------------|----------------------------|------------------------------------------|
| No Flame Retardant *                 | 0                          | 120                                      |
| 8% Exolit OP 1230                    | 420                        | 20                                       |
| 12% Exolit OP 1230                   | 420                        | 40                                       |
| 16% Exolit OP 1230                   | 600                        | 55                                       |
| 20% Exolit OP 1230                   | 600                        | 70                                       |
| 8% Exolit OP 1230 & 4% Melapur M200  | 600                        | No Sustained Ignition                     |
| 12% FR 1025                          | 300 or 600                 | 30                                       |
| 16% FR 1025                          | 600                        | 20                                       |
| 24% FR 1025                          | 720                        | 10                                       |
| 9% FR 1025 & 3% Antimony Trioxide    | 720                        | No Sustained Ignition                     |

* Tests on PBT without a flame retardant were conducted in a previous work [13]. Ignition was achieved without external heating, using a non-premixed propane burner that heated the lower 2.5 cm of samples.

* Ignition could be achieved with 300 s preheating; however, tests were repeated with a 600 s preheat to allow for direct comparison of mass loss rate after ignition of samples with different FR 1025 loading.

* Ignition achieved by a handheld, premixed propane torch applied to the lower 3 cm of samples.

Flame spread experiments were conducted in the apparatus shown in Fig. 1. Samples were insulated at their back surface and all four sides using 6.0 mm thick sheets of Kaowool PM Insulation and secured within a steel holder that exposed only the front surface of the sample slab. Sample preparation is presented in detail elsewhere [13]. Tests began by positioning an electric radiant heater to provide an external heat flux ($q_{ext}$) of 10 kW m$^2$ across the sample’s front surface. This heat flux, $q_{ext}$, remained constant throughout the duration of tests and varied by less than 10 % across the sample’s front surface. Samples were then ignited using a premixed methane/oxygen burner, which was kept in place at the bottom edge of the sample ($y = 0$) just long enough for sustained, uniform ignition across the sample’s width. Immediately after sample ignition, the burner was removed and the radiant heater was repositioned to provide $q_{ext} = 20$ kW m$^2$. Samples were allowed to burn until self-extinction occurred. Sample preheating ($q_{pre} = 10$ kW m$^2$) and burner application durations, were selected to best maintain similar ignition conditions between samples; however, as shown in Table 1, higher flame retardant loading concentrations necessitated longer preheating to achieve ignition.

**Figure 1.** Experimental setup for vertical burning and upward flame spread experiments.

Sample mass loss rate and flame to surface heat flux were measured during flame spread tests. These measurements were obtained in separate experiments to avoid potential interference between the corresponding diagnostic tools. To measure sample mass loss rate, the sample holder was placed on top of a Mettler Toledo XS4002S balance, which recorded sample mass at a frequency of 1 Hz. Mass loss rate, $\frac{dm}{dt}$, was calculated as the numerical derivative of measured sample mass, using a 1 s time step. For flame heat flux measurements, a 0.95 cm diameter, water-cooled ($T_{HFg} = 291$ K) Schmidt-Boelter heat flux gauge was positioned at the top of the sample ($y = 7$ cm) such that its face was flush with that of the slab and the surrounding insulation (above). Calibration, mounting, and maintenance of the heat flux gauge is described in detail elsewhere [13,14]. Total heat flux (from the flame and external heater) measured by this water-cooled heat flux gauge, $q_{HFg}$, was recorded at 2 Hz using an NI USB-9211A data acquisition module (DAQ) connected to a computer. For each sample and measurement type, tests were successfully repeated 2-3 times (up to six samples were tested for each material, some did not ignite). Measurements from repeated tests were averaged together and this combined dataset was smoothed using a 5 s running average. All tests were videotaped.
RESULTS AND DISCUSSION

Figure 2 shows burning behavior during upward flame spread over PBT with and without flame retardants. Without a flame retardant, PBT flames spread and remain continuous and laminar across the full length of the sample. Soot deposition is observed across the sample’s surface, downstream of the pyrolysis front. Extinction occurs only after complete sample burnout, leaving behind a residual structure (char and chopped glass fibers). Samples containing the phosphorous-based flame retardant Exolit OP 1230 developed a thin, flaky char layer at their surface that thickened while burning. This char acts as an insulator and physically separates the flame from the sample. This produces non-uniform burning across the sample’s width and local extinction of the flame, with flamelets primarily found attached to cracks in this layer. Removal or destruction of this char layer allows for the formation of a larger flame that burns uniformly across the width of the newly exposed sample. With the bromine-based FR 1025 (not shown in Fig. 2) flames remain continuous and laminar across the sample; however, flame extinction occurs much sooner in experiments beginning with flickering at the base of the flame, followed shortly thereafter by partial liftoff of the base of the flame (oscillations that increase in magnitude), and complete flame extinction. The destabilizing effect of this flame retardant on the base of the diffusion flame (and resulting liftoff) is consistent with previous observations [16,17].

![Figure 2. Vertical burning behavior of glass-reinforced PBT samples without (left) and with (right) 8 wt. % of a phosphorous-based flame retardant. Note: timestamps indicate time, t, after sample ignition.](image)

Figure 3 plots $\Delta H_f$ and $\mu_{\text{char}}$ of PBT samples studied in this work; error bars for $\Delta H_f$ are calculated based on the 5% uncertainty of oxygen consumption calorimetry measurements and for $\mu_{\text{char}}$ as two standard deviations of the mean. As shown here, increasing the loading of Exolit OP 1230 from 0 to 20 wt. % yields an increase in $\mu_{\text{char}}$ from 3.1 to 12.2 % but produces a negligible impact on $\Delta H_f$. Increasing the loading of FR 1025 from 0 to 24 wt. % decreases $\Delta H_f$ by 38.2% while slightly increasing $\mu_{\text{char}}$ from 3.1 to 7.2%. The potential synergists Melapur M200 and antimony trioxide appear to have a negligible impact on measured $\Delta H_f$ and $\mu_{\text{char}}$; however, peak heat release rate measured throughout the duration of MCC experiments decreases by approximately 20 % for samples with 9 wt. % FR 1025 and 3 wt. % antimony trioxide (versus PBT with only 12 wt. % FR 1025).

![Figure 3. MCC-measured heats of complete combustion of gaseous pyrolyzates ($\Delta H_f$) and char yield ($\mu_{\text{char}}$).](image)

Figure 4 shows mass loss rate, $\frac{dm}{dt}$, and total flame heat flux, $q_{HF}$, of PBT samples during upward flame spread tests. Note: for mass loss rate and flame heat flux tests, samples with 12 % FR 1025 were preheated for 600 and 300 s, respectively. With higher loading of FR 1025, peak mass loss rate increases and is observed sooner after ignition; however, with more FR 1025, extinction occurs earlier and total mass loss decreases. Data from PBT with 9 wt. % FR1025 and 3 wt. % antimony trioxide is not shown in Fig. 4 because sustained flaming ignition of this material could not be achieved; however, given similar preheating, these samples
ignited briefly and supported approximately the same peak mass loss rate, but 35% lower total mass loss, as PBT with 12% FR 1025. Increased FR 1025 loading does not significantly alter measured $q_{HFg}$. This indicates that flame to surface heat transfer in the continuous region of these laminar wall flames is not impacted by this flame retardant at these concentrations, even if it has been shown to act in the gas phase.

Figures 4c and 4d show measured mass loss rate and $q_{HFg}$ from tests on PBT with Exolit OP 1230. Note: increased scatter in Figs. 4c, 4d arises due to greater variation in material burning behavior (e.g. local flame extinction and/or attachment across the sample’s surface) in repeated tests on PBT with Exolit OP 1230. Compared to results from tests on samples with FR 1025 – mass loss rate in these tests gradually decreased prior to extinction, as a char layer developed. With higher loading of Exolit OP 1230 (from 0 to 16 wt. %) peak mass loss rate and total mass loss both decrease; however, with even greater loading (from 16 to 20 wt. %), both peak mass loss rate and total mass loss increase. This indicates that, for this series of PBT tests, 16 to 20 wt. % Exolit OP 1230 may be optimal for reducing material flammability. Depending on the structure and proximity of flamelets to the heat flux gauge (Fig. 2) significant variations in $q_{HFg}$ are observed. However, when a steady, continuous flame is established over the surface of the heat flux gauge (in Fig. 4d, these measurements are highlighted by a thick, black, dashed outline) $q_{HFg}$ is similar to that measured for brominated samples and does not demonstrate a distinct dependence on flame retardant loading.

Flame stability can be assessed by calculating the minimum energy release rate needed for sustained flaming of PBT samples as: $Q_{\text{req}} = \left(\frac{1}{w} \frac{dm}{dt} \right) \times \Delta H_c$, where $w$ represents flame width (at ignition, $t = 0$, this is equal to sample width, 5 cm). $Q_{\text{req}}$ equals 5.0, 5.9, and 7.5 kW m$^{-2}$ for PBT with 12, 16, and 24 wt. % FR 1025, respectively. This apparent increase in $Q_{\text{req}}$ with loading of FR 1025 does not appear to be significant (i.e. variations are within two standard deviations of the mean). For PBT samples with 8, 12, 16, and 20 wt. % Exolit OP 1230, $Q_{\text{req}}$ equals 5.6, 6.4, 5.7, and 2.4 kW m$^{-2}$, respectively. Note: for 20 wt. % Exolit OP 1230, $Q_{\text{req}}$ is determined based on a single experiment. These measurements show that flame stability at ignition does not demonstrate a strong dependence on the loading of either the bromine-based FR 1025 or the phosphorous based Exolit OP 1230. PBT samples with mixtures of two flame retardants (see Table 1) did not ignite; this may indicate that certain flame retardant combinations affect flame stability at ignition.

**Figure 4.** Measured mass loss rate, $\frac{dm}{dt}$, and total heat flux, $q_{HFg}$, of PBT samples with bromine- or phosphorous-based flame retardants: FR 1025 (plots a & b) and Exolit OP 1230 (plots c & d), respectively.

**CONCLUSIONS**

In this work, the mechanisms of action of bromine- and phosphorous-based flame retardants were assessed by measuring key parameters controlling composite material burning behavior including: flame heat flux, sample mass loss rate, heat of combustion, and char yield. Key findings include: flame to surface heat flux in the
continuous region of a laminar wall flame is not affected by the flame retardants tested here (even those known to act in the gas phase), quantification of the critical energy release rate, $Q_{cr}$, required for sustained flaming (this measure of flame stability does not demonstrate a clear dependence on flame retardant loading, at least at the concentrations tested here), and the identification of an optimal loading concentration (wt. %) for the phosphorous-based flame retardant, Exolit OP 1230, to reduce peak mass loss rate and total mass loss of PBT samples burning in the vertical configuration.

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