The Development of A New Technique for the Evaluation of Polymer Burning Behavior*

YOU-LO HSIEH[†] and KWAN-NAN YEH, Department of Textiles and Consumer Economics, University of Maryland, College Park, Maryland

Synopsis

A new research technique was developed for the evaluation of fundamental burning characteristics of polymers. Burning characteristics examined included heat release, mass change, oxygen consumption, and carbon monoxide and carbon dioxide generation. A laboratory apparatus was designed and constructed so environmental conditions could be controlled. The detection of selected parameters was realized by the use of various devices and instrumentation. Instrumental potentiometric outputs were processed with a data acquisition system to accommodate simultaneous data collection in the calibration and the material study. Each device used for parameter measurement was standardized and calibrated by itself as well as in connection with the system. Systematic errors were estimated to be less than 6%. The technique was tested with flame retardant systems containing antimony trioxide (Sb₂O₃) and decabromodiphenyl oxide (DBDPO) on polyethylene film. Significant different effects on the heat reduction and CO formation in the system containing DBDPO alone and that containing both DBDPO and Sb₂O₃ were observed. Different flame-retardation mechanisms for these two systems were postulated and confirmed by additional thermal and elemental analyses. Results demonstrated that this technique can be an effective mean in the evaluation of polymer-burning behavior and flame-retardant mechanisms.

INTRODUCTION

The burning of a polymeric material involves the initial thermal decomposition of the solid substrate with subsequent ignition and combustion of the volatile combustibles by a heat source. This involves a cyclic process¹ in which the solid-phase degradation supplies fuel for combustion whereas the vapor-phase combustion generates heat.

Thermoplastic materials melt and flow during the initial heating stage while most natural and thermoset polymers tend to maintain their structural integrity. As heating proceeds, it provides energy to break the cohesive bonds among, as well as within, the polymer chains to form volatile molecules. Combustion of these degradation products takes place when the combustibles are mixed with oxygen to a flammable limit resulting in a fast oxidative reaction. This is an exothermic reaction where heat is liberated. The heat can be returned in part to the substrate to further the decomposition of the polymer creating continuous supply of fuel for combustion.

The degradation and combustion processes of burning a polymer depend largely on the chemical and physical properties of the polymer and the envi-

[†] Present address: Division of Textiles and Clothing, University of California, Davis, California 95616.

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ronmental factors.² Because of the increasing use of additives and the possible combined effects from other environmental variables, burning of polymeric materials has become a very complex phenomenon.

Flame retardants are effective in resisting low-energy ignition and/or in lowering heat generation when energy in the environment is enough to support burning. In general, less heat is produced with flame-retardant polymers when forced to burn. However, the promotion of incomplete combustion by most retardants causes higher evolution of smoke and carbon monoxide and presents toxicological problems not previously realized.

Numerous approaches and techniques have been advanced in the evaluation of the burning behavior and the intrinsic flammability characteristics of polymeric materials. Since polymer burning behavior is highly material- and environmental-dependent, and design concepts for characteristic measurements vary widely among the different techniques, the translation of experimental data to material properties or fire hazards usually require full understanding of the test methods and their implications in particular end uses.

The generation of heat has been widely used in evaluating combustion of polymers, and sometimes flame-retardant efficiency and mechanisms. The heat generated from the combustion of polymer degradation products can contribute to the further decomposition of itself and/or the continuing burning of its degradation combustibles. The energetics as a polymer ignites and proceeds through its intricate combustion process, therefore, give good indication of the magnitude of the polymer flammability and efficiency of flame retardants when they are applied.

The principle of convective flow induced by heat emission has been utilized to monitor heat emission from burning phosphorus-containing cotton fabrics.^{3–6} Maximum heat emission rate was found to linearly relate to the quantities of flame retardants.⁷ However, convective heat release for nonluminous flame from burning materials has been found much higher than those for luminous flame.⁸ Convective heat measurement alone was found insufficient to predict the total heat release by luminous flame.

In another technique, scaling conditions for the burning intensity projection in full-scale fires were attempted.^{9,10} Burning intensity was related to the controlled external heat flux and mass fraction of oxygen in the burning environment. Combustion efficiency was found decreased strongly with increasing externally applied radiant heat.¹¹ More complete heat balance was also established by incorporating the heat of gaseous combustion products.¹²

The ratio of the combustion heat to oxygen consumption for a wide range of organic compounds was found uniform during burning of these compounds.¹³ This concept was also supported by the combustion of polymer,^{14,15} and has been recently adopted as a nonthermal means for determining heat release from burning polymers.¹⁶ This method, being tested against a thermal method, was found to give fairly accurate values and not to be confounded by heat transfer considerations in the thermal measurements.

Hess' law of summation, which states that the transformation of heat is dependent of states but independent of routes, has been applied to derive the optimum possible heat generation from burning textiles.¹⁷ The heat of combustion of the substrate and of its char from an in-air burning was measured by static oxygen bomb calorimetry. The optimum heat of combustion in air for the substrate was then indirectly derived. This method provides measurement on the substrate-fuel generation process where the solid-phase flame retardants operate, and describes the efficiency of phosphorous-containing flame retardants on cotton fabrics.¹⁸

Later, the thermochemical theory of isoperibol calorimetry was extended and applied in the direct measurement of actual heat release from burning fabrics in air.¹⁹ The complete heat balance was established for fabrics by combining the oxygen bomb data and the isoperibol data. The modes of flame retardancy, i.e., vapor-phase as well as solid-phase mechanisms, and the efficiency of flame retardants were clearly elucidated on natural and synthetic fabrics.¹

The present research explored the development and applications of a basic research technique in monitoring polymer burning characteristics. A apparatus was designed to closely control the burning environment. Combustion data collected was manipulated to provide more thorough understanding on polymer combustion and its suppression mechanisms.

EXPERIMENTAL

A horizontal burning apparatus was designed and constructed so that the detection of the selected burning parameters could be monitored under a controlled atmosphere. Polymer sample weight was measured by a 2.5-lb load-cell transducer. Two paramagnetic oxygen analyzers were used to detect upstream and downstream oxygen contents in the flow. Carbon dioxide and carbon monoxide in the exhaust were each measured with a fixed-wavelength continuous infrared analyzer. Heat generation in the system was sensed by a four-junction chromel-constant thermopile.



Fig. 1. Burning apparatus: (A) blower; (B) valve and vent; (C) anemometer; (D) upstream oxygen; (E) thermocouples: cold junction; (F) propane inlet; (G) chamber cover; (H) viewing window; (I) load-cell; (J) thermocouples: 'hot junction; (K) downstream gas sampling.

Potentiometric outputs from all detection and instruments were simultaneously processed and recorded by a multichannel data acquisition system. This acquisition system consisted of a keyboard-programmable data station, an integrator, and a cassette recorder. The recorded data were manipulated and analyzed on a computer.

Apparatus

The constructed burning apparatus is situated on a levelled platform with dimension approximately 6 m wide, 1 m deep, and 0.5 m high (Fig. 1). The main structural components include a flow supply and control section, a diffusion elbow, a burning chamber, and an exhaust port.

Atmospheric flow in the apparatus is supplied by a blower (A), and the flow rate is controlled by an adjustable valve and vent (B). The flow is stabilized by passing it through a 35 in. long and 2 in. I.D. tubing, and its rate was monitored by a hot wire anemometer (C). The flow is then diffused through the glass bead and fiberglass-filled elbow section to the burning chamber.

The burning chamber is composed of two concentric cylinders with the inner diameter being 6 in. and the outer one being 9 in. Fiberglass is used to fill the space in between for insolation. At the center of the chamber, a horizontal platform is located on which the polymer specimen can be placed at a chosen angle. The material tested is ignited with a premixed propane–oxygen burner, which impinges onto the sample from the upstream direction. The burner is equipped with a Tesla coil that ignites the gas mixture simultaneously with the opening of a solenoid valve regulating the gas flow.

In both calibration and burning experiment, the flow carries heat and combustion products from the burning site to the exhaust port for measurement. Homogeneity of both the flow rates and flow compositions is essential in obtaining accurate and reproducible heat and off-gas measurements. Linear flow rates in the 4–15 cm/s range (volume flow rates of 44.8–164.2 L/min) at the main burning chamber were tested. Flow rates at two selected cross sections of the chamber, i.e., the center of the sample holder and the downstream sampling location, were checked with a hot wire anemometer. No significant flow rate differences at various points of these two cross sections were observed. An even distribution of flow rates in the entire system was thus assumed.

Homogeneity of flow composition upstream and downstream was examined by simulating oxygen depletion at a system volume flow rate of 125 L/min (11.4 cm/s linear rate). Nitrogen gas at rates of 0.1, 0.5, 1.0, and 1.5 kg/cc, was injected into the supply for 8 s to lower normal atmospheric oxygen concentration. At these injection rates, oxygen concentrations in the system flow were decreased to 20.4%, 17.9%, 15.9%, and 14.0%, respectively.

Figure 2 illustrates the changes of oxygen concentrations in the chamber during the simulated oxygen depletion runs. It is shown that the equilibrium were reached with 15–20-s time lags between upstream and downstream detection at these concentrations. These time delays are reasonably close to the actual time required, i.e., 16 s, for an 11.4 cm/s flow to travel between the upstream and downstream oxygen detection locations. This observation confirmed that the flow compositions sampled and measured at downstream were representative



Fig. 2. Oxygen depletion measurement: (---) upstream detection; (----) downstream detection.

of those in the system. The sampling locations for gases were proved to be appropriate.

Moisture and dirt in the downstream gaseous flow was filtered and the flow was fed separately into the oxygen, carbon monoxide, and carbon dioxide analyzers. Sampling rates were monitored by two precision flow meters. Outlets from these gas analyzers were led directly to the fume hood.

Calibration

Weight. Specimen weight is continuously measured by a load cell located directly under the sample holder (Fig. 1). The load cell is in connection with a transducer-amplifier for weight measurement. The load-cell transducer was standardized with known weights from 100 g to 900 g. Linear regression resulted in the standardization equation between outputs and weights as:

$$output (mV) = 0.044 \times wt (g) + 0.059$$
(1)

In order to measure the weights of specimens directly, the weight of the sample holder, which is 409.5 g, was suppressed with 18.5 mV calculated from eq. (1). With the suppression, weight calibration was carried with known weights up to 40 g.

Oxygen. The two oxygen analyzers for upstream and downstream oxygen measurements were standardized individually. Two-point calibration with oxygen-free nitrogen as the zero gas and dry air as the reference gas was sufficient because of the good linear input-output relationship of the analyzers. Analyzers were then connected to the upstream and downstream gas sampling probes on the burning apparatus. Systematic oxygen measurement was further checked with a system volume flow of 125 L/min and a sampling flow of 150 cc/min to the oxygen analyzers.

 CO/CO_2 . The carbon monoxide and carbon dioxide analyzers are each equipped with a plug-in linearization circuit board to allow suppression of po-

Carbon Monoxide			Carbon Dioxide			
Concentration		Output	Concentration		Output	
(%)	(cc/m)	(mV)	(%)	(cc/m)	(mV)	
0.50	3.6	6.5	1.0	7.2	6.1	
2.02	14.6	22.8	6.0	43.5	31.5	
5.13	37.0	52.5	12.1	87.1	60.6	
8.10	58.5	81.0	17.6	127.1	88.0	

TABLE ILinearization of CO/CO2 Measurement

tentiometric outputs linearly proportional to the known concentrations. Four standard $CO/CO_2/N_2$ mixtures were used to verify the linearity of the responses from both analyzers outputs (Table I). The linear relationships were confirmed (Fig. 3), and the derivation of CO and CO_2 concentrations from potentiometric outputs were obtained by linear regression of the above data through origin as

 $CO \operatorname{concn}(\%) = 0.0987 \ (\pm 3.1\%) \times \operatorname{output}(\mathrm{mV}) \tag{2}$

$$CO_2 \operatorname{concn}(\%) = 0.199 (\pm 3.5\%) \times \operatorname{output}(mV)$$
 (3)

Volumetric calibration for CO and CO₂ measurements was conducted by metering a mixture of 0.508% of CO, 1.0% of CO₂, and 98.492% of N₂ into the two analyzers at a rate of 102 cc/min for various length of time in the range of 20–270 s. The integration data were verified with the theoretical calculation for the standard mixtures.

Heat. Heat measurement was detected by a four-junction chromel-constantan thermopile with the cold junctions placed in the center of the diffusion cone (E in Fig. 1) and the hot junctions installed in the exhaust port at four equally spaced locations. The source for both heat calibration and ignition was supplied by burning propane of 99% purity.

Figure 4 illustrates the set-up for the propane heat source. A commercial energy-efficient gas range burner was modified for heat calibration at the position of the sample holder. Heat calibration was conducted under 125 L/min volumetric flow rate in the system. A precision flow meter previously calibrated with



Fig. 3. CO (\odot) and CO₂ (\triangle) concentration calibration.



Fig. 4. Heat calibration setup.

propane gas was used to regulate the propane gas supply rate. Combustion efficiency of propane gas was optimized by premixing with oxygen to produce a bright blue flame. Assuming complete combustion of propane, gas flow rate of propane, and the calorific rate were related to the flow meter mark as

gas flow rate (cc/m) =
$$0.101 (\pm 0.0005\%) \times \text{mark} + 0.06$$
 (4)

calorific rate (cal/m) =
$$2.121 (\pm 0.01\%) \times \text{mark} + 1.2$$
 (5)

Figure 5 shows a typical temperature-time response curve detected by the thermocouples. A post-extinction trail was observed and could last 30 min or longer for the higher heat inputs. This observed phenomenon may be explained by the absorption and reemission of radiant heat by the luminuous flames and possible increase of heat capacity of the exhaust gases. The temperature response was found to become a single exponential function of time at a certain time after the extinction of the flame. It could be described as

$$T = Ce^{bt} \tag{6}$$

where T is temperature at time t and C and b are the constant and cooling constant, respectively.



Fig. 5. Typical temperature-time curve.

Calorific rates at 107, 157, and 209 cal/s were chosen for heat calibration. A period of 300 s (t_2) was found to be common for various burning time at all heat input rates. The area under the curve up to $t_2(A_1)$ could be obtained from the integration data on the recorder. After t_2 , the area under the curve (A_2) was calculated according to

$$A_2 = \int_{t_2}^{\infty} T \, dt = \int_{t_2}^{\infty} C e^{bt} = C/b \times e^{bt} \big|_{t_2}^{\infty} = -C/b \times e^{bt_2} \tag{7}$$

 $\ln T = \ln C + bt$ can be derived from $T = Ce^{bt}$ so that the values of b and C can be obtained from the slope and intercept in the $\ln T$ vs. t plot.

Theoretically, when the temperature follows a single exponential function of time, the total area calculated from any chosen time after t_2 should be the same. To verify the above assumption with a t_2 of 300 s, comparisons of total area calculated at $t_2 = 300$, 360, and 420 s were performed as various heat rates and burning time (Table II). No distinctive differences were observed for total area values calculated at the three t_2 's for each heat rate and burning time. A t_2 of 300 s was, therefore, concluded to be sufficient for the current measurements. Burning time ranged from 10 s to 120 s at these heat rates resulted in total heat in the range of 1–19 kcal.

Material Studies

Polymer samples studied were pure polyethylene films and polyethylene films with three groups of additives. The selection was based on the simple chemical

Comparison of Total Area Calculated with Three Selected t_2						
Heat rate (cal/s)	Burning time t _b (s)	t_2	Total area ^a (mV \cdot s) t_{2}'	t 2"		
107	20.8	323.1	321.6	320.2		
	40.3	575.7	574.9	583.0		
	59.3	486.6	485.1	483.3		
	80.2	696.6	695.6	694.5		
	100.0	1051.1	1050.6	1050.1		
157	20.6	329.5	332.1	343.3		
	27.8	397.1	396.6	395.7		
	40.2	726.5	724.9	723.5		
	50.3	716.1	716.1	714.8		
	60.8	974.4	973.9	973.5		
	71.2	1236.0	1235.7	1235.1		
	80.1	1333.2	1333.3	1333.3		
	90.6	1579.8	1579.2	1579.0		
209	20.2	456.1	455.7	454.5		
	29.8	715.4	690.2	689.6		
	38.9	935.5	933.5	937.4		
	50.3	1227.6	1258.1	1256.7		
	61.0	1372.5	1372.4	1372.2		
	69.6	1416.5	1424.2	1425.1		
	85.2	2144.2	2144.6	2144.4		

TABLE II

^a $t_2 = t_b + 300, t_2' = t_b + 360, t_2'' = t_b + 420.$

structure of polyethylene and the relative low-soot in-air-burning of this polymer.

Decabromodiphenyl oxide (DBDPO) and antimony trioxide (Sb₂O₃) were added both individually and in combination in the polymer. Antimony trioxide was added at three levels of 2.5%, 4.6%, and 6.5%. Four levels of DBDPO at 5.1%, 9.2%, 12.9%, and 14.8% were incorporated in polyethylene. In the combined system, the DBDPO and Sb₂O₃ weight ratio was held at 2:1 (3:1 Br/Sb atomic ratio) at three additive levels. This ratio was reported in the literature to exert the optimum flame retardancy.^{20,21} A sample of 2.5 cm × 10 cm dimension with 1 mm thickness was prepared by the high pressure melt molding technique. Specimens were laid on a wire support at a 20° angle to the horizontal platform, and triplicate burning was performed.

The complete heat of combustion per gram of the original samples as well as the burned residues of these samples was determined using a Parr adiabatic oxygen bomb calorimeter. Bromine and antimony elemental analyses were performed on residues from the additive incorporated samples.

RESULTS AND DISCUSSION

Calibration

Weight. With the sample holder weight being suppressed, signal outputs for known weights up to 40 g were recorded. A good linear relationship was observed (Fig. 6), and linear regression was performed to derive weight conversion from potentiometric output as

wt (g) =
$$1.15 (\pm 0.5\%) \times \text{output (mV)} - 0.57$$
 (8)

Oxygen. Two-point calibration for oxygen concentration was performed with nitrogen and dry air. The conversion of oxygen concentration from output for both analyzers is described as

oxygen concn (%) =
$$0.54 \times \text{output (mV)}$$
 (9)

Detection of dry air with a 125-L/min volume flow rate in the apparatus was confirmed with the above conversion.



Fig. 6. Weight calibration.

CO/CO₂. The conversions of CO and CO₂ concentrations from instrumental outputs were expressed in eqs. (2) and (3) carbon monoxide and carbon dioxide volume derivations from integration data was tested with the theoretical calculations. Theoretically the total volume of CO and CO₂ in a sampling flow of known concentration is described as

sampled vol (cc) = sampling rate (cc/s)
$$\times$$
 concn (%)/100 \times time (10)

By substituting the concentration equations (2) and (3), i.e., concn = $b \times$ output, and the integration equation, i.e., output/100 × time, into eq. (8), the sampled volume can be related to the integration value as

sampled vol (cc) = sampling rate (cc/s)
$$\times$$
 b \times integration (11)

where b is the slope in the concentration equation. With a 102 cc/min (or 1.7 cc/s) sampling rate, the CO- and CO₂-sampled volume can be expressed as follows:

sampled CO vol (cc) = $0.168 \times integration$ (12)

sampled
$$CO_2$$
 vol (cc) = $0.338 \times integration$ (13)

The above equations were verified by comparing volume derived from eq. (8) using a mixture of 0.508% CO, 1.0% CO₂, and 98.492% N₂. Both the theoretical values [from eq. (10)] and measured values [from eqs. (12) and (13)] for CO and CO₂ were obtained (Table III). Cross-examination of these two sets of data showed that the difference between the two was well within the experimental error. Therefore, volume derived from the integration value, i.e., eqs. (12) and (13) were confirmed to be the appropriate measures.

With 1.7 cc/s sampling rate and a volumetric flow rate of 125 L/min through the apparatus, a factor of 1225.5 was used to convert the volume CO and CO_2 in

Concn (%) Sampling flow (cc/s)	Carbon monoxide 0.508 1.7		Carbon dioxide 1.00 1.7		
Time (s)	V _{th} a (cc)	$V_m{}^b$ (cc)	V _{th} a (cc)	V_m^c (cc)	
20.1	0.17	0.15	0.34	0.27	
40.0	0.35	0.34	0.68	0.60	
59.9	0.52	0.53	1.02	0.94	
69.9	0.60	0.60	1.19	1.10	
90.9	0.78	0.81	1.53	1.46	
104.9	0.91	0.95	1.78	1.72	
120.2	1.04	1.19	2.04	1.98	
150.0	1.30	1.38	2.55	2.54	
180.0	1.56	1.64	3.06	2.98	
209.9	1.81	1.88	3.57	3.54	
240.1	2.07	2.28	4.08	4.10	
270.1	2.33	2.54	4.59	4.64	

TABLE III CO/CO₂ Volumetric Comparison in Sampling Flow

^a Theoretical volume from eq. (10).

^b Measured volume from eq. (12).

^c Measured volume from eq. (13).



Fig. 7. Primary heat calibration. Heat rates (cal/s): (Δ) 107; (O) 157; (\Box) 209.

the sampling flow into the total volume in the system. The total volumes were therefore expressed as:

total CO vol (cc) =
$$205.98 \times integration$$
 (14)

total
$$CO_2$$
 vol (cc) = 415.52 × integration (15)

Heat. Heat calibration was conducted in the apparatus with three selected heat rates of 107, 157, and 209 cal/s to produce total heat in the range of 1–18 kcal. The total areas under the temperature-time detection curves were the summation of A_1 and A_2 , which were previously described. Plots of total heat values versus total areas show a linear relationship between the two (Fig. 7). Linear regression of these data resulted in the conversion of heat from area as

heat (cal) = 8.91 (
$$\pm 1.4\%$$
) × area (mV · s) + 56.8 (16)

Test results with pure polyethylene indicated a lower heat release rates than those calibrated, but within the total heat calibration limit. A second calibration was therefore proceeded with lower heat rates at 33, 45, and 58 cal/s in the same total heat range. A linear relationship was also obtained from the plots between heat and area values (Fig. 8), and is described as

heat (cal) =
$$4.64 \ (\pm 2.9\%) \times \text{area} \ (\text{mV} \cdot \text{s}) + 1649.1$$
 (17)

There is a significant difference between the two conversion equations for heat measurement. It appears that the thermal response of the apparatus may be dependent upon the heat release rate of the heat source, although the response



Fig. 8. Second heat calibration. Heat rates (cal/s): (\Box) 58; (O) 45; (Δ) 33.

seems to be consistant within each range of heat rate. Equation (17) was concluded to be more appropriate for estimating heat values in the material study.

Ignition. From the results of burning pure polyethylene films, propane flow rate of 5.11 cc/s (107 cal/s) for 5 s was found to provide the most consistant ignition. Ignition time varied with material contents and was expected to be longer for the flame-retardant added polymers. Ignition heat correction for heat release from burning different materials thus became necessary.

Some degree of incomplete combustion from the ignition burner was also observed from the increased amount of orange flame. It seemed that a separate calibration for ignition was required. Total ignition heat was calibrated at 107 cal/s for 5–18 s. Total ignition heat was derived from the area under the temperature-time curve the same way as in the heat calibration. Heat conversion equation in the primary heat calibration at 107 cal/s, i.e., heat (cal) = 8.6 ($\pm 2.5\%$) × area (mV \cdot s) + 19.3, was used. Figure 9 illustrates a linear relation between the heat values and time, and the relationship is described as follows:

ignition heat (cal) =
$$93.01 (\pm 3\%) \times \text{time} (s) - 54.4$$
 (18)

In addition to heat, ignition could also contribute an extra amount of carbon dioxide and carbon monoxide if the observed incomplete combustion led to CO formation. Carbon dioxide and carbon monoxide were, therefore, monitored at four ignition times of 6.1, 10.8, 15.1, and 20.0 s. Carbon dioxide was detected and measured, whereas carbon monoxide was not detected.



Fig. 9. Ignition heat calibration.

Assuming complete combustion, the total volume of CO_2 can be obtained by the oxidation reaction of propane, i.e., $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O_3$. Since the molecular weights of propane and carbon dioxide are the same, and if density difference between them (density of propane = 2.0096 g/L and density of carbon dioxide = 1.976 g/L) is neglected, volume of CO₂ yielded is three times that of propane consumed. At propane flow rate of 5.11 cc/s, the theoretical carbon dioxide formation from ignition can be expressed as

$$CO_2$$
 from ignition = 3×5.11 (cc/s) × time (19)

At the chosen ignition time, both the theoretical calculation from eq. (19) and the measured volume derived from eq. (15) were compared in Table IV. Up to 11-s ignition time, the measured volumes were within 6% of the theoretical values. The theoretical values were thus selected for calculating carbon dioxide formation from ignition.

TARLE IV

CO_2 Formation in Ignition				
Ignition time (s)	Vol _{measured} (cc)	Vol _{theoret} (cc)		
6.1	99.7	93.5		
10.8	170.3	165.6		
15.1	299.1	231.5		
20.0	361.3	306.0		

Applications of Technique

From the standardization and calibration of the detected parameters, conversions were established between the detected outputs and the actual quantities of the known inputs. In the burning experiments, signal outputs could then be translated to meaningful quantities of the products yield.

Equation (17) was used to derive total heat release value from total area under the temperature-time curve. Heat of ignition [eq. (18)] was then deducted from the total heat measurement to obtain the gross heat value. Normalization of heat value was then performed so that heat value per gram polymer consumed was obtained. The total CO and CO₂ measured are converted with eqs. (14) and (15), respectively. A correction of CO₂ generated from ignition [eq. (19)] was made to derive the gross amount generated from the burning.

Some flame retardants are effective in reducing heat generation by promoting incomplete combustion of the polymer. Incomplete combustion normally results in the formation of small fragments of the polymer chains, interaction products of these molecules, carbon monoxide, and smoke. The detection of carbon monoxide could elucidate some quantitative information on the mode of additives in promoting incomplete combustion.

The increase of CO formation in proportion to the reduction of heat generation could be estimated from heat calculation. The net heat reduction, $\delta(\Delta H_1)$, can be calculated as:

$$\delta(\Delta H_1) = (\Delta H_1)_{\text{additive polymer}} - (\Delta H_1)_{\text{pure polymer}}$$
(20)

The increase in CO generation can also be calculated as

$$\delta(\text{vol}_{\text{CO}}) = (V_{\text{CO}})_{\text{additive polymer}} - (V_{\text{CO}})_{\text{pure polymer}}$$
(21)

Carbon monoxide, with a heat of combustion of 67.636 kcal/mol and a density of 1.25 g/L, is calculated to have a heat of combustion of 3.02 cal/cc. The reduction of heat release contributed by the increase of CO generation was calculated to be

$$\delta(\Delta H_{\rm CO}) = 3.02 \,(\rm cal/cc) \times \delta(\rm vol_{\rm CO}) \tag{22}$$

The proportion of CO in the incomplete combustion products could then be described in fraction as $\delta(\Delta H_{\rm CO})/\delta(\Delta H_1)$.

The flame-retardation mechanisms can also be revealed by manipulating the heat data. The complete heat of combustion for both the original polymer specimens, $(\Delta H_c^0)_{\text{polymer}}$, and the burned residues from these samples, $(\Delta H_c^0)_{\text{residue}}$, are measured by an adiabatic bomb calorimeter. The optimum amount of fuel available per gram of sample consumed can then be calculated from these complete combustion heat data as

$$\Delta H_2 = \frac{(\Delta H_c^0)_{\text{additive}} \times W_t - (\Delta H_c^0)_{\text{residue}} \times W_r}{\text{wt consumed}}$$
(23)

where W_t and W_r are the weights of the original sample and that of the residue.

Combustion efficiency, which is defined as the ratio of $\Delta H_1/\Delta H_2$ describes the fraction of total available fuel actually consumed in the in-air burning. According to Yeh's model,¹ constant combustion efficiency describes a solid-

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Specimen additive content (%)	Heat releases (cal/g)	Carbon monoxide (cc)	Carbon dioxide (cc)	
Polyethylene	8834 (4.4%)	52.3 (4.4%)	2084 (7.2%)	
Sb_2O_3				
2.5%	8582 (2.6%)	51.0 (11.2%)	2014 (17.7%)	
4.6%	8653 (1.7%)	43.9 (22.0%)	1759 (3.3%)	
6.5%	8504 (3.1%)	47.7 (17.1%)	2041 (7.7%)	
DBDPO				
5.1%	7562 (4.0%)	104.2 (7.8%)	1967 (14.4%)	
9.3%	7255 (2.3%)	137.4 (9.2%)	1790 (4.1%)	
12.9%	6524 (4.4%)	173.5 (14.7%)	1686 (16.7%)	
14.8%	6116 (3.9%)	173.0 (15.2%)	1422 (12.9%)	
Sb ₂ O ₃ /DBDPO				
0.6%/1.3%	7115 (11.2%)	261.2 (12.8%)	1804 (3.9%)	
0.98%/1.97%	6433 (11.7%)	539.3 (10.8%)	1794 (3.7%)	
1.5%/3.0%	3238 (19.9%)	1811.2 (29.8%)	1481 (17.7%)	

 TABLE V

 Burning Characteristics of Additive Polyethylene

phase retardation mechanism. The solid-phase flame retardants alter the fuel generation process but does not affect the vapor-phase combustion of the fuel resulting a constant combustion efficiency. On the other hand, vapor-phase flame retardants only influence the combustion of the degradation products leaving the fuel generation process unaffected. A variable combustion efficiency, therefore, describes vapor-phase retardant mechanism.

Material Study

As shown in Table V, heat release from samples treated with antimony trioxide at all three levels were slightly lower than that of the pure polyethylene, yet within the standard deviation of the pure material. Antimony trioxide was considered not to have any flame retardant effect on polyethylene. Decabromodiphenyl oxide, on the other hand, introduced a linear reduction on the heat release of polyethylene as the additive contents increased (Fig. 10). In the DBDPO and Sb₂O₃/DBDPO combined systems, a tremendous reduction of heat release was observed at significantly lower contents of either component. A more than additive effect of these two components become apparent, and the synergistic effect seems to be obvious from the heat reduction values. Similar observation on the increased oxygen index of polyethylene was previously made on the additive of DBDPO and Sb₂O₃ at 2:1 weight ratio.²⁰

In terms of CO formation, antimony trioxide was not found to exert any effect, whereas DBDPO increased CO formation linearly as its contents increased. A very drastic increase in the amount of CO was also observed with the combined system (Fig. 10). Carbon dioxide formation by the addition of antimony trioxide was expected to be the same as that of pure polyethylene, since no effects was observed on the heat release data of the same specimens. The lower carbon dioxide generation at 4.6% Sb₂O₃ was suspected to be an experimental error. For DBDPO, a gradual decrease in the CO generation was observed as the additive contents increased (Fig. 10). The decreasing pattern of carbon dioxide generation with increasing DBDPO contents were found parallel to those observed



Fig. 10. Additive effects on polyethylene: Heat, CO, and CO_2 generation. (\Box) Sb₂O₃; (Δ) DBDPO; (O) Sb₂O₃/DBDPO.

in the heat release data. A more profound decrease in the carbon dioxide generation as additive content increased was shown in the combined system.

The increase in the incomplete combustion of polyethylene in DBDPO and the combined systems was demonstrated both by the deduction of heat release and the increases of CO generation with increasing additive contents. The increased CO formation, reduced heat generation, and the ratio of CO formation to the total incomplete combustion in the DBDPO and the combined systems were calculated according to eqs. (18), (19), and (20) (Table VI).

In the DBDPO system, CO formation increased with increasing DBDPO contents. However, as shown in Table VI, the ratio of $\delta(\Delta H_{\rm CO})/\delta(\Delta H_1)$, did not show the corresponding increase. This tends to indicate that large portion of heat release reduction was probably due to the formation of combustibles other than carbon monoxide.

However, in the antimony trioxide and DBDPO combination system, a definite relationship between the heat release reduction and the corresponding increased CO generation was observed. These data indicated that the promotion of incomplete combustion by the combined system resulted in CO as major incomplete combustibles, whereas DBDPO alone encouraged the formation of combustibles other than CO. This would tend to suggest that these two systems may impose flame retardation through different mechanisms.

Theoretical values for heat of combustion of the same materials were estimated to confirm the postulated mechanisms. The theoretical heat value for antimony trioxide treated specimen was calculated as

$$(\Delta H_c^0)_{\rm Sb_2O_3+PE} = (1 - X)(\Delta H_c^0)_{\rm PE}$$
(24)

Heat Release Reduction and CO Generation					
Specimen	ΔH_1 (cal/g)	$\delta(\Delta H_1)^{\mathrm{a}}$ (cal/g)	$\delta({ m Vol}_{ m CO})^{ m b} \ ({ m cc/g})$	$\delta(\Delta H_{ m CO})^{ m c}$ (cal/g)	$\delta(\Delta H_{\rm CO})/\delta(\Delta H_1)$ (%)
Polyethylene DBDPO	8833.8		52.5		
5.1%	7913.3	920.5	57.5	173.7	18.9
9.3%	7890.7	943.1	98.9	298.8	31.7
12.9%	7341.6	1492.2	146.9	443.5	29.7
14.7%	7002.8	1831.0	150.7	455.2	24.9
Sb ₂ O ₃ /DBDPO					
0.6%/1.3%	7238.9	1594.9	159.6	640.5	40.2
0.98%/1.97%	6590.7	2243.0	500.7	1512.2	67.4
1.5%/3.0%	3358.4	5475.4	1784.4	5547.2	100.0

TABLE VI ...

^a Calculated from eq. (20).

^b Calculated from eq. (21).

^c Calculated from eq. (22).

where X is the fraction of antimony trioxide in the samples. Both the measured and theoretical values listed in Table VII indicated that antimony trioxide has no calorific effect on the heat of combustion of its treated polyethylene.

Heat of combustion of DBDPO was estimated under the assumption that total • heat of combustion of a mixture was the summation of heat from each of the components. Thus, the theoretical heat of combustion for DBDPO and the combined system can be calculated as

$$(\Delta H_c^0)_{\text{DBDPO+PE}} = (1 - Y)(\Delta H_c^0)_{\text{PE}} + Y(\Delta H_c^0)_{\text{DBDPO}}$$
(25)

$$(\Delta H_c^0)_{\text{combined}+\text{PE}} = (1 - Z)(\Delta H_c^0)_{\text{PE}} + Z/3(\Delta H_c^0)_{\text{DBDPO}}$$
(26)

where Y and Z are the fractions of additives in the specimens. Theoretical values for DBDPO treated as well as the 2:1 DBDPO and antimony-trioxide-treated specimens were calculated according to their compositions (Table VII). Excellent agreement between the experimental values and the theoretical values was found.

Specimen	Origina	Residue.		
(% content)	Exptl	Theoret	exptl	
Polyethylene	11,106	<u> </u>	10,978	
Sb_2O_3				
2.5%	10,860	10,828	9907	
4.6%	10,579	10,595	8686	
6.5%	10,543	10,384	7631	
DBDPO				
5.1%	10,650	10,592	10,716	
9.4%	10,283	10,173	10,623	
12.9%	9741	9801	10,457	
14.8%	9809	9611	10,376	
17.4%	9390	9308	10,484	
Sb ₂ O ₃ /DBDPO				
0.6%/1.3%	10,938	10,906	10,905	
0.98%/1.97%	10,836	10,797	10,935	
1.5%/3.0%	10,700	10,634	10,868	

TABLE VII

Element Contents (%)							
Specimen	Original (calcd)		Residue (measured)				
(% content)	Sb	Br	Sb	Br			
$6.5\%~{ m Sb_2O_3}$	5.43	0	33.51	0			
14.8% DBDPO	0	12.35	0	4.72			
$1.5\% { m ~Sb_2O_3/3.0\% ~DBDPO}$	1.25	2.5	0.74	0.33			

TABLE VIII Element Contents (%)

In terms of the heat of combustion of the residues, combustion heat values in the antimony trioxide system were considerably lowered as the amounts of additive increased. This suggests that almost all antimony trioxide remained in the residues after the polymer was consumed. For the DBDPO system, the combustion heat values for residues being slightly lower than that of the untreated polyethylene supported the theory that the majority of DBDPO was removed from the polymer during burning. The residues from the combined system had essentially the same combustion heat values as the pure polyethylene. Elemental analyses of the burned residues also indicated similar trend (Table VIII). All these seem to support the argument that halogen compounds provides means of transport for antimony trioxide to escape from solid substrate during burning. $^{21-24}$

CONCLUSION

This new technique has been developed in the direct and simultaneous measurements of selected burning characteristics of polymeric materials in a controlled environment. The error terms in the calibration for the detection of total heat evolution, carbon monoxide and carbon dioxide generation, oxygen consumption, and sample weight change are all within three per cent. The systematic error is estimated to be less than 6%.

Burning behavior and the suppression of combustion of polymeric materials by flame retardants can be clearly elucidated by this technique. The suppression of combustion is usually accomplished by promoting incomplete combustion which resulted in reduced heat generation. Products of incomplete combustion include fragments of polymer chains, the interaction products of these fragments, CO, and smoke. The detection of CO, which is one of the most common incomplete combustion products, provides quantitative measure of the modes in which the additives control incomplete combustion. A low proportion of CO formation accompanying a large reduction of heat generation gives indication that the additive suppresses heat generation by promoting the formation of combustibles other than CO.

Results from the material study further confirm the flame-retardant effects of decabromodiphenyl oxide and its synergism with antimony trioxide on polymers reported in the literature. In addition, manipulation of data obtained by this technique suggests that the flame retardation mechanisms of these two systems were significantly different. This newly developed technique has demonstrated to be an effective research mean in the evaluation of polymerburning behavior and flame-retardant mechanisms of additives.

References

1. K. Yeh, M. J. Drews, and R. H. Barker, J. Fire Retardant Chem., 7, 99 (1980).

2. H. F. Mark, S. M. Atlas, S. W. Shalaby, and E. M. Pearce, *Flame Retardant Polymeric Materials*, Plenum, New York, 1975, Chap. 1.

3. L. Miles, G. R. Bhat, and R. L. Sun, J. Consumer Product Flammability, 3, 166 (1976).

4. B. Miller, Proceeding, Tenth Annual Meeting of the Information Council on Fabric Flammability, December, 1976, p. 198.

5. B. Miller, J. R. Martin, and C. H. Meiser, Jr., Thermochemica Acta, 20, 253 (1977).

6. "TRI Explores New Method for Measuring Heat Emission," Am. Dyestuff Rep., 65(6), 46 (1976).

7. B. Miller and C. H. Meiser, Text. Res. J., 48, 238 (1978).

8. A. Tewarson, paper presented at National Symposium on Fire Safety Aspects of Polymeric Materials, Division of Industrial and Engineering Chemistry, American Chemical Society, Washington, D.C., June 1977.

9. A. Tewarson, Fire Technol., 11, 274 (1975).

10. A. Tewarson and R. F. Pion, Combustion Flame, 26, 85 (1976).

11. A. Tewarson, Fire Materials, 1(3), 90 (1976).

12. A. Tewarson, J. Fire Flammability, 8, 115 (1977).

13. W. M. Thornton, Phil. Mag., 33, 196 (1917).

14. C. Hugget, Fire Mater., 4, (1979).

15. D. L. Sensenig and W. J. Parker, paper presented at the Eastern Section Meeting, The Combustion Institute, Miami Beach, Fla., November 1978.

16. R. F. Krause and R. G. Gann, J. Fire Flammability, 12, 117 (1980).

17. K. Yeh and R. H. Barker, Text. Res. J., 41, 932 (1971).

18. K. Yeh, M. M. Birky, and C. Hugget, J. Appl. Polym. Sci., 17, 255 (1973).

19. E. A. Boettner, G. L. Ball, and B. Weiss, report, Office of Research and Monitoring, U.S. Environmental Protection Agency, February 1973.

19. K. Yeh, M. J. Drews, and R. H. Barker, J. Fire Retardant Chem., 7, 99 (1980).

20. T. E. Tabor and S. Bergman, Fire Retardants: Proceedings of 1974 International Symposium on Flammability & Fire Retardants, sponsored by Alena Enterprise of Canada, May 1974.

21. S. K. Brauman and A. S. Brolly, J. Flame Retardant Chem., 3, 66 (1976).

22. S. K. Brauman, J. Flame Retardant Chem., 3, 117 (1976).

23. S. K. Brauman, J. Flame Retardant Chem., 3, 138 (1976).

24. S. K. Brauman, N. Fishman, A. S. Brolly, and D. L. Chamberlain, J. Flame Retardant Chem., 3, 225 (1976).

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