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A novel thermogravimetric technique for determining flammability characteristics of polymeric materials [1]

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Abstract

This paper reports a new thermogravimetric (TG) technique. Gases evolved during TG runs are analyzed for flammability characteristics including chemical heat release rate. Computations for two composites (glass–polyphenylene sulfide and graphite–phenolic) are presented and compared to literature data.

INTRODUCTION

The reported work is part of an effort to demonstrate that thermoanalytical techniques can predict flammability properties of polymeric materials. Earlier experiments examined the relationships between TG char and limiting oxygen index at elevated temperatures [1]. This paper applies a method developed by Tewarson, Factory Mutual Research Corporation (FMRC), Norwood, MA for the FMRC heat release apparatus, to the burning behavior of materials in a TG furnace [2,3]. It utilizes the principle that heat generated by a burning specimen leads to the generation of CO and CO_2, which may be used to calculate its chemical heat release rate.

Other techniques for measurement of chemical heat release rate include the "Ohio State" heat release rate apparatus [4], and the "National Institute of Standards and Technology" cone calorimeter [5]. Under the conditions of these techniques, a specimen is exposed to a constant heat flux and such data as the evolved gases produced by the burning specimen

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and mass loss are analyzed. The underlying principle common to these chemical heat release measurement techniques involves exposing a specimen in a furnace to a calibrated heat flux. This principle can be applied to the TG analyzer.

In addition to being able to operate under constant heat flux or isothermal conditions, as the above chemical heat release rate instruments, the TG furnace has the capacity to operate under a temperature gradient and with a variety of purge gas conditions. TG instruments are commonly found in laboratories, so the cost associated with the set-up of chemical heat release rate experiments can be minimized. Another advantage of TG instrumentation is that it uses small samples. Large samples are not always available for analysis.

Quantitative data are provided to support the hypothesis that TG techniques utilizing small samples may provide an alternative approach to determining chemical heat release rates. The primary purpose of this paper, however, is to provide the methodology required to perform the flammability calculations.

EXPERIMENTAL

Instrumentation

Figure 1 is a schematic of the experimental set-up necessary for the Du Pont 951 TG analyzer to function as a chemical heat release rate apparatus. The air flow entering the TG furnace was controlled by a Matheson Model 8102-1433 mass flow controller. The speciments were heated at a rate of 20°C min^{-1} in the air atmosphere flowing at 500 ml min^{-1}. The air purge gas along with gases that evolve from the heated specimen were transported between components of the experimental set-up via flexible

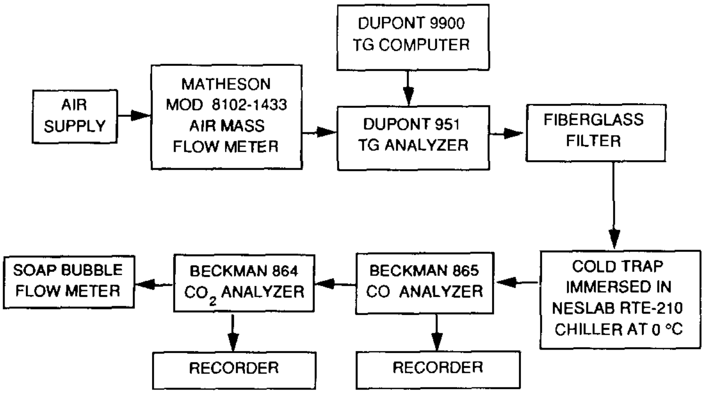

Fig. 1. Flow diagram of TG evolved gas instrumentation.

plastic and copper tubing. A glass wool filter and cold bath at 0°C were positioned upstream from the Beckman 865 CO and 864 CO_2 IR analyzers. This prevented soot and water from entering the gas analyzers. A soap bubble rotameter was used to monitor the exit flow to ensure that it was the same as the incoming flow.

Specimens

A glass–polyphenylene sulfide (PPS) composite AG 40–70 (supplied by Phillips Petroleum Company) was one of two specimens used in this experiment. The second specimen was a graphite–phenolic composite (fabricated at David Taylor Research Center). The sample was made from a woven fabric prepreg which was autoclaved at 177°C for two hours. After the autoclave treatment, the graphite–phenolic composite was postcured at a series of elevated temperatures in a convection oven. The thickness of the cured panel was 4.4 mm and had a 55–60% fiber volume fraction. Specimens were cut from the bulk composites into sizes approximately $2 \times 3 \times 5$ mm, weighing approximately 50 mg.

Procedure

The controller was set to flow at 500 ml min^{-1} and the CO and CO_2 analyzers were calibrated with span gases. Before each run, a control run was made with an empty sample holder. The control run was checked for evolution of CO and CO_2. After the furnace had cooled, a specimen was placed in the TG platinum specimen holder and heated at a rate of 20°C min^{-1}. Measurements of weight loss, CO, and CO_2 began immediately. Heating and data collection were terminated at 1100°C.

RESULTS

In order to prove the effectiveness of the TG technique for measurement of combustion efficiency, the portion of each of the TG curves shown in Figs. 2(top) and 2(bottom) associated with weight loss of resin was analyzed separately from the fiber component. This allowed for the TG data for the resin component to be compared to literature data. It was assumed that the glass fibers of the glass–PPS run shown in Fig. 2(top) did not lose weight. For the graphite–phenolic run shown in Fig. 2(bottom), mass loss and generation of CO_2 originating from phenolic resin was assumed to occur between 100 and 60%.

Combustion efficiency has been calculated from values for maximum possible yield of CO_2, average generation of material vapors, and average generation of CO_2. As a qualitative comparison, the combustion efficiency calculations are compared to the value of polystyrene calculated using the

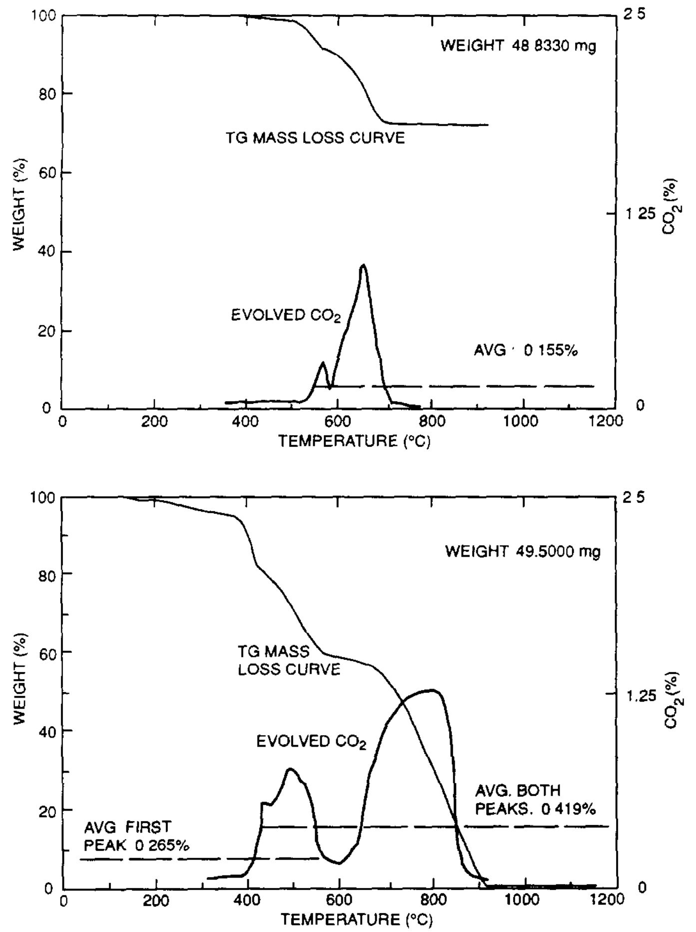

Fig. 2. TG runs: (top) glass–PPS composite; (bottom) graphite–phenolic composite.

FMRC rate of heat release apparatus. Polystyrene is less thermally stable than PPS and phenolic resins, so one would expect polystyrene to be better at supporting combustion.

Values for chemical heat release rate have been calculated from the average generation of CO_2, which has been estimated from data for density of air, purge gas flow rate, and average concentration of CO_2. Calculations for average concentration of CO_2 generated utilized the mean for all combustible components.

Maximum possible yield of CO_2

Assuming combustion will proceed to completion, oxidation of glass–PPS composite in air may be written as

$$C_6H_4S + 38.10(0.21O_2 + 0.79N_2) \rightarrow 6CO_2 + 2H_2O + SO_2 + 60.20N_2$$

Because the glass fibers did not undergo oxidation, the maximum possible yield of CO_2 (k_{CO_2}) may be determined from the above stoichiometric equation, which assumes conservation of mass [3,6], as

$$k_{CO_2} = \frac{\text{Weight of } CO_2 \text{ generated}}{\text{Weight of PPS repeat unit}} = 2.44$$

In the case of the graphite–phenolic composite, both phenolic resin and graphite fibers may react with oxygen to produce CO_2: $k_{CO_2} = 2.90$ for polyphenolic resin $(-C_7H_6O-)_n$; $k_{CO_2} = 3.66$ for graphite (C).

Generation of material vapors

The rate at which material vapors are generated $\dot{m}$ is derived from the slope of the TG mass loss curve and the associated heating rate; for the glass–PPS composite run provided in Fig. 2(top)

$$\dot{m} = \frac{(0.0482 - 0.0358)\ \text{g}}{(701 - 504)°\text{C}}(0.333°\text{C s}^{-1}) = 2.10 \times 10^{-5}\ \text{g s}^{-1}$$

Upon heating at 20°C min^{-1} in the range 504–701°C, the glass–PPS composite decomposes at a average rate of 2.10×10^{-5} g s^{-1}, producing vapors, heat, and fire products.

For both components in the graphite–phenolic composite TG run shown in Fig. 2(bottom), the average generation of material vapors is

$$\dot{m} = \frac{(0.0472 - 0.000330)\ \text{g}}{(925 - 374)°\text{C}}(0.333°\text{C s}^{-1}) = 2.83 \times 10^{-5}\ \text{g s}^{-1}$$

The generation of material vapors associated with the first weight loss transition representing phenolic resin is

$$\dot{m} = \frac{(0.0472 - 0.0294)\ \text{g}}{(579 - 374)°\text{C}}(0.333°\text{C s}^{-1}) = 2.88 \times 10^{-5}\ \text{g s}^{-1}$$

Generation of CO_2

The gases evolved during the TG runs were measured downstream from the TG furnace after flowing through a cold trap at 0°C. At 0°C, the density of CO_2 is 0.00197 g ml^{-1}. Therefore, the calculation for the average generation rate of CO_2 ($\dot{G}_{CO_2}$) for glass–PPS composite at an air flow rate of 8.33 ml s^{-1} is

$$\dot{G}_{CO_2} = (0.00197\ \text{g ml}^{-1})(8.33\ \text{ml s}^{-1})(\%CO_2/100)$$

$$\dot{G}_{CO_2} = (0.000164\ \text{g s}^{-1})\ \%CO_2$$

The average concentration of CO_2 calculated from the glass–PPS composite data shown in Fig. 2(top) is 0.155% CO_2. Therefore, the average mass of CO_2 generated is

$$\dot{G}_{CO_2} = 2.54 \times 10^{-5} \text{ g s}^{-1}$$

For both components of the graphite–phenolic composite

$$\dot{G}_{CO_2} = 8.05 \times 10^{-5} \text{ g s}^{-1}$$

The average generation of CO_2 for the resin portion of the graphite–phenolic composite is

$$\dot{G}_{CO_2} = 4.35 \times 10^{-5} \text{ g s}^{-1}$$

Combustion efficiency

The actual yield of CO_2 (Y_{CO_2}) produced during the TG run may be calculated from the relationship [3,6]

$$Y_{CO_2} = \frac{\dot{G}_{CO_2}}{\dot{m}}$$

Combustion efficiency (f_{CO_2}) then may be calculated [3,6] by

$$f_{CO_2} = \frac{Y_{CO_2}}{k_{CO_2}}$$

The yield of CO_2 and combustion efficiency for the glass–PPS composite are

$$Y_{CO_2} = \frac{2.54 \times 10^{-5} \text{ g s}^{-1}}{2.10 \times 10^{-5} \text{ g s}^{-1}} = 1.21$$

$$f_{CO_2} = \frac{1.21}{2.44} = 0.50$$

The yield of CO_2 and combustion efficiency for the phenolic composite based upon resin and graphite contributions are

$$Y_{CO_2} = 2.84 \qquad f_{CO_2} = 0.43$$

The above yield is approximately equal to the maximum for phenolic resin (2.90). The high value indicates that both components of the composite, have undergone oxidation. Analysis of just the first weight loss transition representing phenolic resin shows that

$$Y_{CO_2} = 1.51 \qquad f_{CO_2} = 0.52$$

Chemical heat release rate

The generation of CO and CO_2 may be used to calculate the chemical heat release rate ($\dot{Q}_{\mathrm{Ch}}$) by the relationship [3,6]

$$\dot{Q}_{\mathrm{Ch}} = \frac{\Delta H_{\mathrm{T}}}{k_{\mathrm{CO_2}}}\dot{G}_{\mathrm{CO_2}} + \frac{\Delta H_{\mathrm{T}} - \Delta H_{\mathrm{CO}}}{k_{\mathrm{CO}}}\dot{G}_{\mathrm{CO}}$$

where ΔH_{T} is the net heat of complete combustion, ΔH_{CO} is the heat of combustion of CO and k_{CO} is the maximum possible theoretical yield of CO.

The generation of carbon monoxide in the TG experiments was small (0.010% and 0.047% for glass–PPS and graphite–phenolic, respectively), so the second half of the equation is close to zero; owing to its insignificant value, it was omitted for estimating purposes. The mean empirical value [7] of $\Delta H_{\mathrm{T}}/k_{\mathrm{CO_2}}$ is roughly equal to 12.3 kJ g^{-1}. Under these conditions, $\dot{Q}_{\mathrm{Ch}}$ for the glass–PPS composites is

$$\dot{Q}_{\mathrm{Ch}} = (12.3\ \mathrm{kJ\ g^{-1}})(2.54 \times 10^{-5}\ \mathrm{g\ s^{-1}}) = 3.12 \times 10^{-4}\ \mathrm{kJ\ s^{-1}}.$$

The surface area of the top side of the TG specimens is roughly 1.54×10^{-5} m^2. Therefore, the chemical heat release rate per unit area for the glass–PPS composite under conditions of the TG furnace is approximately

$$\dot{Q}''_{\mathrm{Ch}} = \frac{3.12 \times 10^{-4}\ \mathrm{kJ\ s^{-1}}}{1.54 \times 10^{-5}\ \mathrm{m^2}} = 20.3\ \mathrm{kW\ m^{-2}}$$

Calculations for the graphite–phenolic composite show $\dot{Q}''_{\mathrm{Ch}} = 64.3$ kW m^{-2}.

DISCUSSION

Combustion efficiency

The calculated combustion efficiency for the PPS and phenolic composites (0.50 and 0.52, respectively) are lower than the value associated with polystyrene (0.69) [6]. This is appropriate because the aromatic group is part of the backbone structure of PPS and phenolic resins, producing a thermally stable structure. However, polystyrene has its aromatic structure in the pendant position, which produces a more flammable material [8].

Chemical heat release rate

In the TG run shown in Fig. 2(top), glass–PPS composite generated vapors between 504–701°C. These temperatures correspond to an external heat flux of 20–51 kW m^{-2} by the Stefan–Boltzmann fourth power law. Literature values for this glass–PPS composite indicate that it does not ignite when exposed to cone calorimeter radiant heat flux conditions of 25 kW m^{-2}. However, the composite generated an average chemical heat release rate of 25 kW m^{-2} when exposed to a 50 kW m^{-2} radiant heat flux [9]. Calculations for average chemical heat release rate using the TG evolved gas data yielded a value of 20.6 kW m^{-2}, which compares well with literature data. Although our TG experiments were conducted under a temperature gradient of 20°C min^{-1}, the evolved gas analysis for chemical heat release rate are of the same order of magnitude as the isothermal conditions of cone calorimetry experiments.

Figure 2(bottom) shows that the graphite–phenolic composite loses mass in the range 373–925°C. The associated external heat flux is 9–117 kW m^{-2}. Cone calorimeter runs of the same material [10] indicate that it does not ignite when exposed to an external heat flux of 25 kW m^{-2}. When the heat flux is increased to 75 kW m^{-2}, the average cone calorimeter chemical heat release rate is 80 kW m^{-2}. The average chemical heat release rate of 64.3 kW m^{-2} calculated from TG evolved gas data is also in agreement with literature values.

CONCLUSIONS

This new TG technique demonstrates correlation with current calorimetric methods for preliminary quantitative analysis of chemical heat release rates and other flammability characteristics of organic materials.

Advantages of the use of TG instrumentation for analysis of material flammability characteristics include: TG sample sizes are small, therefore associated sample preparation costs are low; TG instrumentation is widely available so costs are minimized; TG is versatile because experiments may be conducted under a broad range of furnace and purge gas conditions.

REFERENCES

1 T.D. Gracik and G.L. Long, Prediction of flammability of thermoplastics by TGA, in Proc. 18th North American Thermal Analysis Society Conference, San Diego, Cal. 24–27 September 1989, pp. 82–91.

2 A. Tewarson and R.F. Pion, Flammability of Plastics—I. Burning Intensity, Combustion and Flame, Vol. 26, 1976, pp. 85–103.

3 A. Tewarson, Flammability characteristics of fiber reinforced composite materials, Technical Report MTL TR 90-41, US Army Materials Technology Laboratory, Watertown, MA, August 1990.

4 ASTM E906-83, Standard test method for heat and visible smoke release rates for materials and products.

5 ASTM E1354-90, Standard test method for heat and visible smoke release rates for materials and products using an oxygen comsumption calorimeter.

6 A. Tewarson, Generation of heat and chemical compounds in fires, SFPE Handbook of Fire Protection Engineering, National Fire Protection Association, National Fire Protection Association, Quincy, MA, 1988, pp. 1–179.

7 G. Tewarson, Experimental evaluation of flammability parameters of polymeric materials, Flame Retardant Polymeric Materials, Vol. 3, Plenum, New York, 1982, pp. 97–153.

8 E.M. Pearce, Y.P. Khanna and D. Raucher, Thermal analysis in polymer flammability, in E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Acadamic Press, Orlando, FL, 1981.

9 U. Sorathia, T. Dapp and J. Kerr, Flammability characteristics of composites for shipboard and submarine internal applications, 36th Int. SAMPE Symp. San Diego, CA, 15–18 April 1991, pp. 1868–1878.

10 U. Sorathia, C.M. Rollhauser and W. Allen Hughes, Improved fire safety of composites for naval applications, 16th Int. Conf. on Fire Safety, San Francisco, CA 14–18 January 1991, pp. 300–312.