

HEATS OF COMBUSTION OF HIGH TEMPERATURE POLYMERS

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ABSTRACT

The heats of combustion for forty-nine commercial and developmental polymers of known chemical structure were determined using an oxygen bomb calorimeter according to standard methods. The experimental results were compared to thermochemical calculations of the net heat of combustion from oxygen consumption and the gross heat of combustion from group additivity of the heats of formation of products and reactants. The polymers examined were thermally stable, char forming thermoplastics and thermoset resins containing a significant degree of aromaticity and heteroatoms including– nitrogen, sulfur, phosphorus, silicon, and oxygen in linear and heterocyclic structures. The gross and net heats of combustion calculated from polymer enthalpies of formation and oxygen consumption thermochemistry were within 5 percent of the experimental values from oxygen bomb calorimetry. The heat released by combustion per gram of diatomic oxygen consumed in the present study was $E = 13.10 \pm 0.78$ kJ/g-O₂ for polymers tested (n = 48). This value is indistinguishable from the universal value $E = 13.1$ kJ/g-O₂ used in oxygen consumption combustion calorimetry.

Key Words: Heat of combustion, polymers, thermochemistry, oxygen bomb calorimetry, heat release, fire

INTRODUCTION

Commercial passenger aircraft cabins contain several tons of combustible plastics, thermoset resins, and elastomers in sidewall panels, ceilings, seat parts, foamed cushions, carpets, etc. Using full- and bench-scale fire testing the Federal Aviation Administration determined that the fire hazard in an aircraft cabin is not only a function of the effective heat of combustion of the cabin materials but also the rate at which this heat is released by the burning material in a fire [1]. Consequently, FAA regulations were developed for both effective heat of combustion and heat release rate of large area cabin materials [2,3]. In the FAA test, convected heat released during flaming combustion is calculated from the temperature rise of an air stream flowing past a standard-sized sample of the burning material. Bench-scale fire calorimeters have since been developed which use the oxygen consumption principle [4] to determine the chemical heat release rate of burning materials [5-7]. The oxygen consumption principle is based on the observation that combustion of a wide range of organic compounds [4,8] and common polymers [5,8] produces 13.1 ± 0.7 kJ of heat per gram of diatomic oxygen consumed independent of the chemical composition of the organic material. The gases evolved during polymer decomposition are usually unknown and do not burn to completion in real fires. Oxygen consumption is a means of measuring heat release without detailed knowledge of the fuel species. The oxygen consumption principle has recently been adopted by the

FAA for measuring non-flaming heat release rate of milligram-sized research samples in a combustion flow calorimeter [9 - 11].

Oxygen consumption calorimetry measures the heat released by the burning of volatile polymer decomposition products [12], the net heat of complete combustion of which can be written

$$\Delta h_{c,v}^{\circ} = \frac{\Delta h_{c,p}^{\circ} \pm \mu \Delta h_{c,\mu}^{\circ}}{1 \pm \mu} \quad (1)$$

where $\Delta h_{c,v}^{\circ}$, $\Delta h_{c,p}^{\circ}$ and $\Delta h_{c,\mu}^{\circ}$ are the heats of complete combustion for the volatiles, polymer and char respectively and μ is the char fraction. The effective heat of combustion, Δh_c^{eff} , is obtained by multiplying equation 1 by the combustion efficiency in the flame, χ , $\Delta h_c^{\text{eff}} = \chi \Delta h_{c,v}^{\circ}$. The heat of combustion of the volatile fraction can differ significantly from that of the polymer and the char, so polymer heats of combustion should not be used to calculate flaming combustion efficiency of materials.

The FAA's Fire-Resistant Materials program is developing and evaluating new polymers with extremely low heat release rate in fires. Typically these materials tend to be char forming, thermally-stable polymers containing a high degree of chemical bond unsaturation, aromaticity, and the heteroatoms— nitrogen, sulfur, silicon, phosphorus, and oxygen. The original work for the oxygen consumption principle was based on hydrocarbon polymers[5, 7]. The objective of the present work was to measure and document the heats of combustion of some commercial, pre-commercial, and research polymers containing heteroatoms on the assumption that their decomposition products would also contain heteroatoms. The accuracy of the universal value of 13.1 kJ of heat per gram of O₂ for combustion thermally-stable, char-forming polymers and their decomposition products could then be determined. The heats of complete combustion of forty nine polymers were measured by the standard experimental procedure for determining gross and net calorific value using adiabatic oxygen bomb calorimetry and compared to the results of two different thermochemical calculations of the heat of combustion based on: 1) oxygen consumption, and, 2) group additivity of the heats of formation of products and reactants.

COMBUSTION THERMOCHEMISTRY

At constant pressure and when no non-mechanical work is done the heat (Q) and enthalpy (H) of a process are equal. The flaming combustion of polymers at atmospheric pressure satisfies these conditions. The high pressure adiabatic combustion of a polymer in a bomb calorimeter satisfies these conditions approximately, since the fractional pressure change is small. Consequently, the terms heat and enthalpy are used interchangeably in the following discussions.

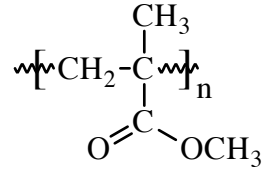
Oxygen Consumption: Heats of combustion calculated from oxygen consumption rely on the observation that a wide range of organic compounds, including polymers, have approximately the same heat of complete combustion per gram of diatomic oxygen consumed. This empirical quantity is derived from equation 2

$$E = \Delta h_c \left[\frac{n_p M_p}{n_{O_2} M_{O_2}} \right] = \frac{\Delta h_c}{r_o} = 13.1 \pm 0.7 \text{ kJ/g}\pm O_2 \quad (2)$$

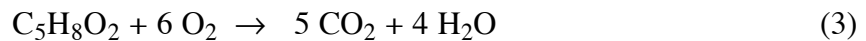
where E is the average value obtained, Δh_c is the net heat of complete combustion of the sample with all products in their gaseous state, n_p and M_p are the number of moles and molecular weight of the molecule or polymer repeat unit, respectively, n_{O_2} is the number of moles of O₂ consumed in the balanced thermochemical equation, and $M_{O_2} = 32 \text{ g/mol}$ is the molecular weight of diatomic

oxygen. In equation 2 the quantity, $r_o = [n_{O_2}M_{O_2}/n_pM_p]$, is the stoichiometric oxygen-to-fuel mass ratio.

To illustrate this thermochemical calculation the net heat of combustion was determined for poly(methylmethacrylate) (PMMA) which has the chemical structure



The methylmethacrylate repeat unit shown has the atomic composition $C_5H_8O_2$ so the balanced chemical equation for complete combustion is



From equation 3 it is seen that 6 moles of O_2 are required to completely convert 1 mole of PMMA repeat unit to carbon dioxide and water. From equation 1 E was calculated for PMMA using the measured net heat of combustion in the present study, $\Delta h_c = -25.0$ kJ/g (see table 1)

$$E = (\pm 25.0 \text{ kJ/g}_{\pm\text{PMMA}}) \frac{(1 \text{ mol PMMA})(100 \text{ g}_{\pm\text{PMMA/mol}})}{(6 \text{ mol } O_2 \text{ consumed})(32 \text{ g/mol}_{\pm O_2})} = \pm 13.02 \frac{\text{kJ}}{\text{g}_{\pm O_2}}$$

This calculation was performed for each polymer to determine E from its known atomic composition and measured heat of combustion. Inverting equation 1

$$\Delta h_c = E \left[\frac{n_{O_2} M_{O_2}}{n_p M_p} \right] = E r_o \quad (4)$$

shows that the net heat of complete combustion of a polymer is simply calculated if the atomic composition of the polymer is known *a priori* so that the balanced thermochemical reaction equation can be written.

Molar Group Additivity of Heats of Formation: Calculation of the heat of the combustion reaction of polymers was carried out using the principle of molar additivity of the heats of formation of the combustion products and reactants [13, 14]. The concept derives from the fact that enthalpy (H) is a state function and therefore its change in any process is independent of the path from reactants to products. Thus, the overall enthalpy of a reaction is the simply the sum of the enthalpies of the component reactions. In practice, the heat of combustion of the reaction can be calculated by subtracting the heat of formation of the products from the heat of formation of the reactants

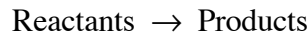
$$\Delta h_c = \sum_i n_p \Delta h_{f,p}^o \pm \sum_j n_r \Delta h_{f,r}^o \quad (5)$$

where p and r denote products and reactants, respectively, in the standard state at temperature, 298 K.

For polymeric reactants the molar heat of formation can be estimated from the tabulated molar contributions of the chemical groups which constitute the monomer or repeat unit. Using PMMA as an example again with the monomer/repeat unit chemical structure shown previously, the heats of formation of the methylmethacrylate constituent groups at $T = 298\text{K}$ are [13]:

$$\begin{array}{rcl}
1(\text{C=O}) & = & 1 \times (-132,000 + 40T) = -120.08 \text{ kJ/mol} \\
1(-\text{O}-) & = & 1 \times (-120,000 + 70T) = -99.14 \text{ kJ/mol} \\
2(\text{CH}_3) & = & 2 \times (-46,000 + 95T) = -35.38 \text{ kJ/mol} \\
1(\text{CH}_2) & = & 1 \times (22,000 + 102T) = 8.40 \text{ kJ/mol} \\
1(-\text{C}-) & = & 1 \times (20,000 + 140T) = 61.72 \text{ kJ/mol} \\
\hline
& & \textit{Total} = -184.48 \text{ kJ/mol}
\end{array}$$

Summing these group contributions gives the molar heat of formation of the methylmethacrylate monomer, $\Delta H_f = -184.48 \text{ kJ/mol}$ at standard conditions ($T = 298\text{K}$). From the stoichiometry of complete combustion shown in equation 3



and the tabulated standard heats of formation of the products

$$\Delta H_f (\text{H}_2\text{O}) = -241.8 \text{ kJ/mol}; \quad \Delta H_f (\text{CO}_2) = -393.5 \text{ kJ/mol}$$

and reactants

$$\Delta H_f (\text{O}_2) = 0 \text{ kJ/mol}; \quad \Delta H_f (\text{PMMA}) = -184.5 \text{ kJ/mol}$$

in their standard states, the molar heat of combustion of PMMA is:

$$\begin{aligned}
\Delta H_c (\text{PMMA}) &= \Delta H_{\text{prod}} - \Delta H_{\text{react}} \\
&= [5 (\text{CO}_2) + 4 (\text{H}_2\text{O})] - [(\text{C}_5\text{H}_8\text{O}_2) + 6 (\text{O}_2)] \\
&= [5 (-393.5 \text{ kJ/mol}) + 4 (-241.8 \text{ kJ/mol})] - [-184.5 \text{ kJ/mol} + 6 (0)] \\
&= -2748.7 \text{ kJ/mol}
\end{aligned}$$

The gross heat of combustion per unit mass is then

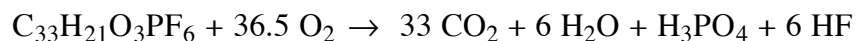
$$\begin{aligned}
Q_c (\text{PMMA}) &= \Delta H_c / M_p \\
&= [-2748.7 \text{ kJ/mol}] / [100 \text{ g-MMA/mol}] \\
&= -27.5 \text{ kJ/g}
\end{aligned}$$

which compares favorably to the oxygen bomb value $Q_c = -26.81 \text{ kJ/g}$ reported in table 1 and literature values $Q_c = -26.20 \text{ kJ/g}$ [15] and -26.64 kJ/g [8] for PMMA.

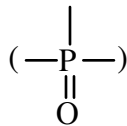
A variation in the complete combustion reaction is exemplified by the hydrogen-deficient polymer polytetrafluoroethylene (C_2F_4) (see table 1) which requires the addition of water as a reactant in the stoichiometric equation (and the heat of formation calculation) to obtain correct estimates of the heat of combustion, i.e., the balanced reaction equation for this polymer is



In practice a milliliter of water is added to the bomb calorimeter prior to the combustion test and is available for reaction with the fluorine atoms to yield the mineral acid HF. The hexafluoroethertriphenyl-phosphineoxide (6F-ETPP) polymer (see table 1) contains sufficient hydrogen for the water reaction products so the net balanced stoichiometric equation for this combustion reaction is



Unfortunately, the molar group contribution of the phosphine oxide group



to the heat of formation of the 6F-ETPP polymer, SiO to the heat of formation of PDMS and the naphthyl group to the heat of formation of PEN was not available and could not be calculated. Similarly, the molar group contribution of the cyanurate to the heat of formation of several cyanate ester polymers was also missing and was not calculated. The calculation method for the heat of combustion from group contributions is seen to be more complex than the oxygen consumption calculation and requires detailed knowledge of the chemical structure of the molecule and its atomic composition.

EXPERIMENTAL

Materials: The polymers examined were commodity plastics as well as thermally stable, char forming thermoplastics and thermoset resins containing a significant degree of aromaticity and heteroatoms including– nitrogen, sulfur, phosphorus, silicon, and oxygen in linear and heterocyclic structures. The materials chosen were pure homopolymers of known structure without modification by fillers or other additives. All materials tested in this analysis were used as received from the supplier without further modification with the exception of several of the thermosetting resins which had to be cured.

Calibration: Prior to sample testing with the oxygen bomb calorimeter, the thermal mass of the system had to be defined. The bomb calorimeter was calibrated using the method described below by combusting a known mass, m , of standard benzoic acid which has a known heat of combustion of 26.453 kJ/g. Ten benzoic acid samples of size ranging from 0.3717 to 1.9964 grams were tested. The calibration factor for the bomb calorimeter, C , was calculated from the benzoic acid calibrations as

$$C = (m \cdot 26.453 \text{ kJ/g}) / (T_{\max} - T_o) = 10.13 \pm 0.13 \text{ kJ/}^\circ\text{K} \text{ (n= 10)}.$$

Gross Heat of Combustion: The gross heat of combustion was measured in an oxygen bomb calorimeter (Model 1341, Plain Jacket Oxygen Bomb Calorimeter, Parr Instrument Co., Moline, Illinois) according to a standard procedure, ASTM D2382-88 [16]. A weighed sample of approximately 1 gram is placed inside a calibrated adiabatic bomb calorimeter with 1 milliliter of deionized water. A Chromel (chromium nickel alloy) wire is connected to the two electrodes in the pressure vessel (bomb) and placed in contact with the sample for ignition. The bomb is then assembled, sealed and purged twice by pressurizing to 0.5 MPa with pure (99.99%) oxygen then venting. The vessel is then pressurized with pure oxygen to 2.0 MPa for the test and placed inside a bath containing 2 liters of water in an insulated jacket. A motorized stirrer is placed inside the water bath to circulate the water around the bomb creating a uniform temperature. The temperature of the water is measured using a precision thermistor (Omega Model 5831A). The equilibrium temperature of the bath prior to the test is recorded as the initial temperature, T_o , in the experiment. The sample is then ignited by passing an electric current through the Chromel wire causing the sample to burn to completion in the high pressure oxygen. The temperature of the water bath rises a few degrees Celsius above the initial temperature, typically, and reaches a maximum value, T_{\max} , which is recorded. The bath temperature then slowly decreases due to convective heat losses to the environment. The gross heat of combustion of the hydrocarbon polymers was calculated from the sample mass, m , and the difference between the initial and maximum bath temperature, $\Delta T_{\max} = (T_{\max} - T_o)$, after correcting for the heat of combustion of the wire. Three replicates are performed for each sample.

For samples containing atoms besides C, H, and O, combustion products in addition to CO₂ and H₂O are formed and corrections must be made for the heat of formation and/or heat of solution of these compounds. An ignition correction (e₁) is made for the heat contribution from burning the nickel chromium alloy fuse wire. The wire is weighed before and after combustion and the weight loss is multiplied by the heat of combustion of the alloy, 5.8576 kJ/g, to calculate the ignition energy, e₁. A correction for the heat of product formation (e₂) and heat of solution of the products (e₃) is required for samples which contain elements other than carbon, hydrogen, and oxygen. A pH titration is performed to determine the heats of formation and solution (in water) of the additional products, typically mineral acids. In practice the bomb is rinsed with distilled water and the acidic washings are titrated with 0.1 M NaOH to the appropriate pH break point using a benchtop pH meter (Orion Model 611). Some of the acids formed are HF, HNO₃, H₃PO₄, or H₂SO₄ depending on the element(s) in the sample. The moles of mineral acid formed during combustion are calculated from the stoichiometric endpoint multiplied by the energy of formation of the relevant compound to calculate the heat of formation, e₂, and heat of solution, e₃, corrections for the acids formed [17]. The gross heat of combustion, Q_c, is then calculated as

$$Q_c = (C \Delta T_{\max} - e_1 - e_2 - e_3) / m \quad (6)$$

The average standard error for this technique is 0.51 kJ/mol.

Net Heat of Combustion: There are no direct methods for measuring the net heat of combustion— which is the gross heat of combustion minus the latent heat of vaporization of the water produced during the reaction. The net or lower heat of combustion is relevant to flaming combustion where water is in the gaseous state at flame temperatures of ≈ 1000 K. As a result, the latent heat of water at 298 K is subtracted from the gross heat of combustion because this amount of heat is required to maintain the combustion product water in the gaseous state. The gross heat of combustion measured by the procedure stated above is corrected for the heat of vaporization of the water formed during the combustion to give the net heat of combustion, Δh_c, using the relation in equation 7 as described by Babrauskas [8].

$$\Delta h_c = Q_c - 21.96w_H \quad (7)$$

where w_H is the weight fraction of hydrogen in the sample and Δh_c, Q_c are in kJ/g.

RESULTS

Although the heat/enthalpy of combustion is a negative (exothermic) quantity, positive (absolute) values are listed in the following tables and figures for convenience. Table 1 is a compilation of all of the polymeric materials tested listed by chemical and/or common name, abbreviated name, and Chemical Abstracts Service (CAS) registry numbers where available. Trade names and manufacturer or sample source are listed in table 1 along with atomic composition of the polymer repeat unit. The gross heat of combustion (Q_c), net heat of combustion (Δh_c), and the net heat of combustion divided by the oxygen-to-fuel mass ratio (Δh_c/r_o) are listed for each polymer. Values for Q_c are averages of triplicate determinations ± 1 standard deviation. When no standard deviation is shown, Q_c is the result of a single test.

Table 1: Combustion data for polymeric materials

	Material (abbreviated name), [CAS Registry Number]	Trade Name, Manufacturer/Supplier	Repeat Unit Composition	Q _c (kJ/g)	Δh _c (kJ/g)	Δh _c /r _o (kJ/g-O ₂)
1	Poly(oxymethylene) (POM) [9002-81-7]	Aldrich Chemical Company, Inc.	CH ₂ O	17.39 ± 0.13	15.93	14.93
2	Polytetrafluoroethylene (PTFE) [9002-84-0]	Aldrich Chemical Company, Inc.	C ₂ F ₄	6.68	6.68	10.44
3	Polyvinylalcohol (≥99%) (PVOH) [9002-89-5]	Aldrich Chemical Company, Inc.	C ₂ H ₄ O	23.31 ± 0.54	21.31	11.72
4	Polyethylene (PE) [9002-88-4]	LDPE Polysciences, Inc.	C ₂ H ₄	47.74	44.60	13.01
5	Poly(dimethylsiloxane) (PDMS) [9016-00-6]	Dow Corning 346	C ₂ H ₆ OSi	19.53 ± .74	17.75	13.68
6	Polypropylene (PP) [25085-53-4]	Polysciences, Inc.	C ₃ H ₆	45.80 ± 0.48	42.66	12.44
7	Poly(methylmethacralate) (PMMA) [9011-14-7]	Aldrich Chemical Company, Inc.	C ₅ H ₈ O ₂	26.75 ± 0.14	24.99	13.02
8	Poly(methylmethacrylate) (PMMA) [9011-14-7]	Polycast acrylic (black)	C ₅ H ₈ O ₂	26.86 ± .61	25.10	13.07
9	Poly(1,4-phenylenesulfide) (PPS) [9016-75-5]	Aldrich Chemical Company, Inc.	C ₆ H ₄ S	29.62 ± 0.71	28.81	13.89
10	Poly(phenylenesulfide) (PPS) [9016-75-5]	KETRON PPS™ DSM Engineering	C ₆ H ₄ S	28.39 ± .37	27.58	13.30
11	Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [25134-01-4]	Noryl 0.4 IV™ virgin General Electric	C ₈ H ₈ O	34.21 ± 0.36	32.75	12.93
12	Polystyrene (PS) [9003-53-6]	Polysciences, Inc.	C ₈ H ₈	43.65	41.96	13.64
13	Polyethyleneterephthalate (PET) [25038-59-9]	Polysciences, Inc.	C ₁₀ H ₈ O ₄	24.13 ± 0.39	23.22	13.93
14	Epoxy Novolac, catalytic cure (phenoxy-N) [028064-14-4]	DEN-438™ Dow Chemical	C ₁₀ H ₁₁ O	31.37 ± .14	29.73	11.15
15	Poly(1,4-phenyleneethersulfone) (PES) [25667-42-9]	BASF Ultrason™ E1010/ Natural	C ₁₂ H ₈ O ₃ S	25.42 ± 0.55	24.66	14.30
16	Poly(1,4-butanediolterephthalate) (PBT) [26062-94-2]	Polysciences, Inc.	C ₁₂ H ₁₂ O ₄	27.91	26.71	14.13
17	Poly(hexamethyleneadiapamide) (nylon 66) [32131-17-2]	Polysciences, Inc.	C ₁₂ H ₂₂ O ₂ N ₂	30.90 ± 0.15	28.76	12.31
18	Poly(etherketone) (PEK) [27380-27-4]	P22 (virgin) Victrex USA	C ₁₃ H ₈ O ₂	31.07 ± 0.70	30.17	13.20
19	Poly(benzoyl-1,4-phenylene)	POLYX-1000™ MAXDEM, Inc.	C ₁₃ H ₈ O	38.35	37.37	14.50
20	Poly(p-phenylenebenzobisoxazole) (PBO) [852-36-8]	PBO DOW Chemical Co.	C ₁₄ H ₆ O ₂ N ₂	29.18 ± 0.21	28.62	14.43
21	Poly(m-phenylene isophthalamide)	Nomex™ Dupont	C ₁₄ H ₁₀ O ₂ N ₂	26.45 ± 0.09	25.53	12.25
22	Aramid-arylester copolymer	Aramid Z-200™ Dupont	C ₁₄ H ₁₀ O ₂ N ₂	25.27 ± 0.81	24.35	11.68
23	Poly(p-phenylene terephthalamide)	KEVLAR™ Dupont	C ₁₄ H ₁₀ O ₂ N ₂	26.92 ± 0.54	26.00	12.48
24	Polyamideimide (PAI)	TORLON 4203L™ Amoco	C ₁₅ H ₈ O ₃ N ₂	24.97 ± 0.13	24.31	12.94
25	Poly(acrylonitrilebutadiene-styrene) (ABS) [9003-56-9]	Polysciences, Inc.	C ₁₅ H ₁₇ N	39.84	38.07	13.04
26	Bisphenol-E Cyanate Ester [47073-92-7]	AroCy L-10™ Ciba Specialty Chemicals	C ₁₆ H ₁₂ O ₂ N ₂	29.38 ± 0.06	28.38	13.01

27	Polycarbonate of bisphenol-A (PC) [24936-68-3]	Polysciences Inc. 32-36K mol.wt.	$C_{16}H_{14}O_3$	31.53 ± 0.88	30.32	13.37
28	Polycarbonate of bisphenol-A (PC) [24936-68-3]	LEXAN 141 TM General Electric	$C_{16}H_{14}O_3$	31.06 ± 0.08	29.85	13.16
29	Hexafluorobisphenol-A Cyanate Ester [32728-27-1]	AroCy F-10 TM Ciba Specialty Chemicals	$C_{17}H_8O_2N_2F_6$	18.71 ± 0.03	18.25	12.23
30	Bisphenol-A Cyanate Ester [1156-51-0]	AroCy B-10 TM Ciba Specialty Chemicals	$C_{17}H_{14}O_2N_2$	29.92 ± 0.27	28.81	12.84
31	Bisphenol-A Epoxy, catalytic cure (Phenoxy-A) [001675-54-3]	DER-332 TM Dow Chemical	$C_{21}H_{24}O$	32.50 ± 0.15	30.94	11.40
32	Poly(etheretherketone) (PEEK) [29658-26-2]	450F TM Victrex USA	$C_{19}H_{12}O_3$	31.07 ± 0.53	30.16	13.24
33	Poly(etheretherketone) (PEEK) [29658-26-2]	KETRON PEEK 1000 TM DSM	$C_{19}H_{12}O_3$	31.48 ± 0.44	30.57	13.42
34	Tetramethylbisphenol F Cyanate Ester [101657-77-6]	AroCy M-10 TM Ciba Specialty Chemical	$C_{19}H_{18}O_2N_2$	31.23 ± 0.05	29.94	12.72
35	Poly(etherketoneketone) (PEKK)	G040 TM (virgin flake) Dupont	$C_{20}H_{12}O_3$	31.15 ± 0.17	30.27	13.20
36	Polybenzimidazole (PBI) [25928-81-8]	CELAZOLE TM PBI Hoechst Celanese	$C_{20}H_{12}N_4$	31.65 ± 0.35	30.79	12.90
37	Polyimide (PI) [26023-21-2]	Aldrich Chemical Company, Inc.	$C_{22}H_{10}O_5N_2$	26.03 ± 0.77	25.45	13.81
38	Novolac Cyanate Ester [P88-1591]	AroCy XU-371 TM Ciba Specialty Chemical	$C_{23}H_{15}O_3N_3$	28.61 ± 0.53	27.77	12.99
39	Novolac Cyanate Ester [P88-1591]	Primaset PT-30 TM Allied Signal, Inc.	$C_{23}H_{15}O_3N_3$	30.65 ± 0.05	29.81	13.95
40	Bisphenol-M Cyanate Ester [127667-44-1]	AroCy XU-366 TM Ciba Specialty Chemical	$C_{26}H_{24}O_2N_2$	34.39 ± 0.15	33.06	13.20
41	Polysulfone of bisphenol-A (PSF) [25135-57-7]	Aldrich Chemical Company, Inc.	$C_{27}H_{22}O_4S$	30.28 ± 0.47	29.19	13.22
42	Polysulfone of bisphenol-A (PSF) [25135-57-7]	UDEL TM Amoco	$C_{27}H_{22}O_4S$	30.63 ± 0.35	29.54	13.38
43	Polybenzoxazine of bisphenol-A/aniline (b-a benzoxazine)	Case Western Reserve University	$C_{31}H_{30}O_2N_2$	34.89 ± 0.19	33.46	12.88
44	Arylether of hexafluorobisphenol - A and triphenylphosphine oxide	6F-ETPP TM DAYCHEM	$C_{33}H_{21}O_3F_6P$	26.50 ± 0.25	25.74	13.35
45	Polyetherimide (PEI) [61128-46-9]	Polysciences, Inc.	$C_{37}H_{24}O_6N_2$	29.59 ± 0.28	28.70	13.27
46	Polyetherimide (PEI) [61128-46-9]	ULTEM 1000, General Electric	$C_{37}H_{24}O_6N_2$	$29.06 \pm .06$	28.17	13.03
47	Polyester of hydroxybenzoic and hydroxynaphthoic acids [70679-92-4]	VECTRA C LCP TM (virgin/unfilled) Hoechst Celanese	$C_{39}H_{22}O_{10}$	26.54 ± 0.39	25.80	13.27
48	Polyethylenephthylate (PEN)	Eastman Chemical Company	$C_{14}H_{10}O_4$	25.92 ± 0.09	25.01	13.06
49	Dicyclopentadienyl bisphenol	XU-71787 TM Dow Chemical	$C_{17}H_{17}NO$	33.64 ± 0.24	32.14	11.88

The quantity, $E = \Delta h_c/r_o$ is the heat released by combustion per unit mass of oxygen consumed in a fire where all combustion products are in their gaseous state. An accurate and representative value of E is thus important for calculating the heat released during flaming combustion of polymers from oxygen consumption measurements. Values for E from the present work are listed in the last column of table 1 for comparison to the universal value used in oxygen consumption fire calorimetry, $E = 13.1$ kJ of heat released per gram of diatomic oxygen (O_2) consumed.

Table 2: Measured and calculated heats of combustion for polymers

	Polymer	Bomb Calorimeter Gross (kJ/g)	Group Contribution Gross (kJ/g)	Bomb Calorimeter Net (kJ/g)	Oxygen Consumption Net (kJ/g)
1	Polyoxymethylene	17.39	18.20	15.93	13.97
2	Polytetrafluoroethylene	6.68	7.57	6.68	8.38
3	Polyvinylalcohol	23.31	26.20	21.31	23.82
4	Polyethylene	47.74	46.00	44.60	44.91
5	Polydimethylsiloxane	19.53	N/A	17.75	16.99
6	Polypropylene	45.80	46.00	42.66	44.91
7/8	Polymethylmethacrylate	26.81	27.50	25.05	25.15
9/10	Poly(1,4-phenylenesulfide)	29.01	30.80	28.20	27.17
11	Poly(2,6-dimethyl-1,4 phenyleneoxide)	34.21	34.70	32.75	33.19
12	Polystyrene	43.65	41.30	41.96	40.31
13	Polyethyleneterephthalate	24.13	24.10	23.22	21.83
14	Epoxy novolac	31.37	32.06	29.73	34.93
15	Poly(1,4-phenyleneethersulfone)	25.42	25.70	24.66	22.59
16	Poly(1,4-butanediol terephthalate)	27.91	26.90	26.71	24.77
17	Poly(hexamethylenedipamide)	30.90	32.80	28.76	30.61
18	Poly(etherketone)	31.07	31.45	30.17	29.94
19	Poly(benzoyl-1,4-phenylene)	38.35	35.90	37.37	33.77
20	Poly(p-phenylene benzobisoxazole)	29.18	29.00	28.62	25.98
21	Poly(m-phenyleneisophthalamide)	26.45	29.30	25.53	27.30
22	Aramid-arylester copolymer	25.27	29.30	24.35	27.30
23	Poly(p-phenyleneterephthalamide)	26.92	29.30	26.00	27.30
24	Poly(amideimide)	24.97	26.75	24.31	24.61
25	Poly(acrylonitrile-butadiene-styrene)	39.84	39.43	38.07	38.24
26	Bisphenol E Cyanate Ester	29.38	N/A	28.38	28.58
27/28	Polycarbonate of bisphenol-A	31.30	31.20	30.09	29.71
29	Hexafluorobisphenol A Cyanate Ester	18.71	N/A	18.25	19.55
30	Bisphenol-A Cyanate Ester	29.92	N/A	28.81	29.40
31	Bisphenol-A Epoxy	32.50	33.50	30.94	30.79
32/33	Poly(etheretherketone)	31.28	31.50	30.37	29.84
34	Tetramethylbisphenol F Cyanate Ester	31.23	N/A	29.94	30.82
35	Poly(etherketoneketone)	31.15	31.50	30.27	30.04
36	Polybenzimidazole	31.65	33.40	30.79	31.30
37	Polyimide	26.03	26.30	25.45	24.14
38/39	Phenol Novolac Cyanate Ester	29.63	N/A	28.79	28.00
40	Bisphenol M Cyanate Ester	34.39	N/A	33.06	32.82
41/42	Polysulfone	30.46	31.20	29.37	28.93
43	Poly(bisphenol-A/aniline) benzoxazine	34.89	35.80	33.46	34.03
44	Polyhexafluorobisphenol-A-TPPO	26.50	N/A	25.74	25.26
45/46	Polyetherimide	29.33	30.00	28.44	28.32
47	Polyester of HBA-HNA	26.54	26.81	25.80	25.47
48	Polyethylenenaphthylate	25.92	N/A	25.01	25.09
49	XU-71787	33.64	N/A	32.14	35.44

Table 2 lists experimental values for the gross and net heats of combustion measured in the present study by oxygen bomb calorimetry. The fourth column in table 2 lists the gross heats of combustion calculated from molar group additivity of the heats of formation according to the method described. Column 5 lists the net heats of combustion calculated from the gross heat of combustion using equations 4 and 7. Column 6 lists the net heats of combustion calculated from oxygen consumption with the universal value, $E = 13.1 \text{ kJ/g-O}_2$. Data for identical polymers from different sources have been combined in tables 2 and 3.

Table 3: Comparison of experimental gross heats of combustion to literature values for several polymers [8]

Polymers	Q_c (kJ/g) (Present Study)	Q_c (kJ/g) [Ref. 8]
Polycarbonate of bisphenol-A	31.3	31.0
Polyethylene	47.7	46.2
Polyethyleneterephthalate	24.1	22.2
Polyhexamethyleneadipamide	30.9	29.6
Polymethylmethacrylate	26.8	26.6
Polyphenyleneoxide	34.2	34.6
Polypropylene	45.8	46.4
Polystyrene	43.7	42.5
Polyvinylalcohol	23.3	25.0

Figure 1 is a plot of the net heats of combustion calculated from oxygen consumption *versus* experimental net heats of combustion obtained from oxygen bomb calorimetry in table 2. The average relative deviation for the oxygen consumption technique for estimating the net heat of combustion was found to be $\pm 4.4\%$ (shown by the error bars in figure 1).

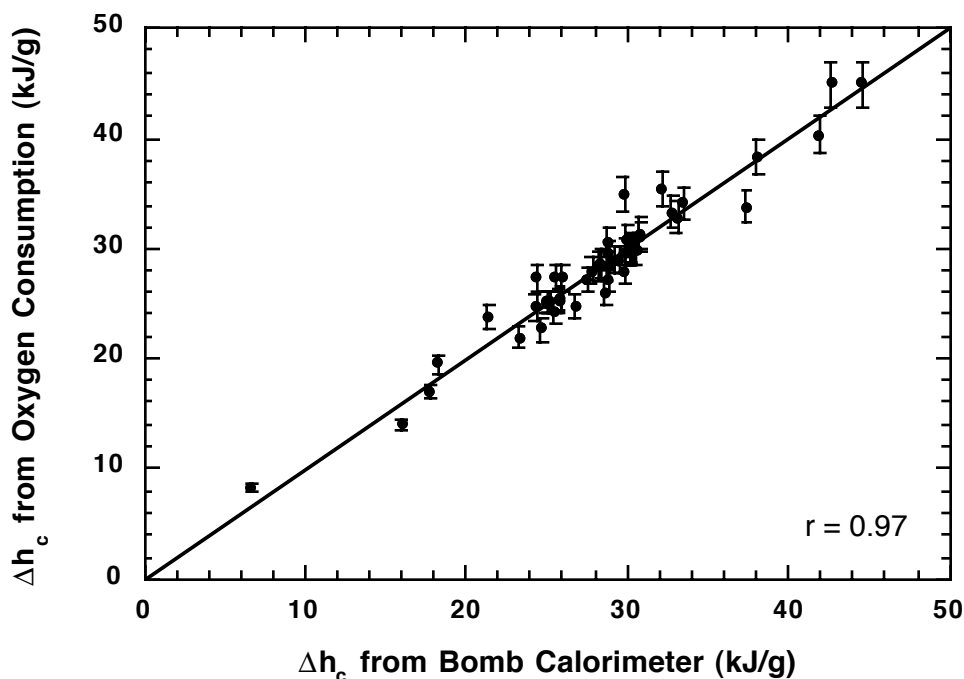


Figure 1: Correlation plot of the calculated heats of combustion using oxygen consumption versus experimental net heats of combustion for 49 polymers (line is $y = x$). Error bars shown are the 4.4% average relative deviation for the calculation.

Figure 2 is a plot of the gross heats of combustion calculated from group additivity of the heats of formation *versus* experimental gross heats of combustion obtained from oxygen bomb calorimetry in table 2. The average relative deviation for the group contribution technique for estimating the gross heat of combustion was found to be $\pm 4.2\%$ (shown by the error bars in figure 2).

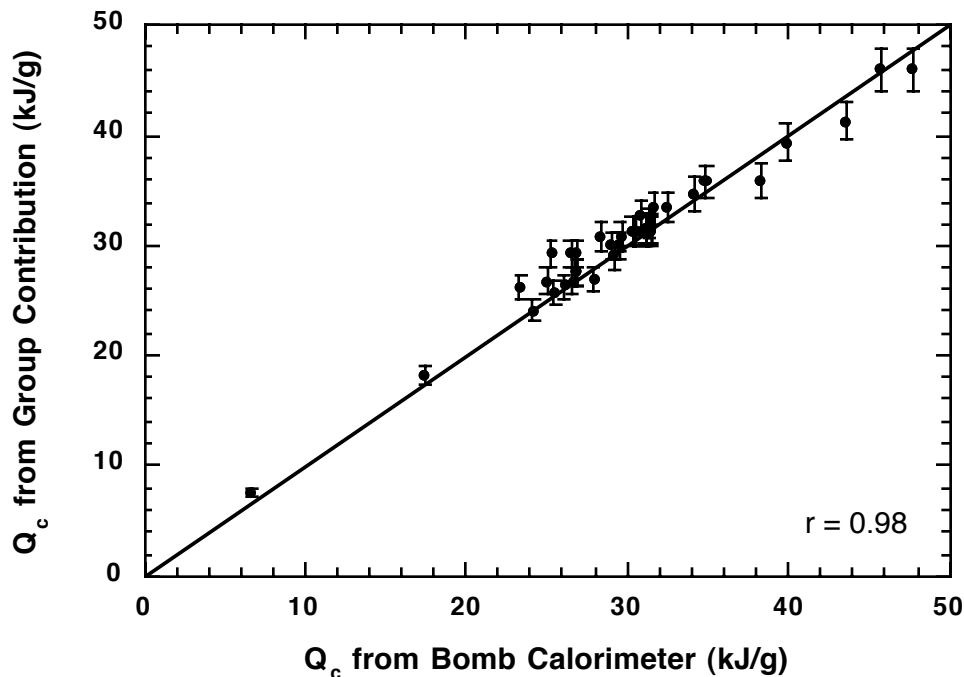


Figure 2: Correlation plot of the calculated heats of combustion using group contributions versus experimental gross heats of combustion for 38 polymers (line is $y = x$). Error bars shown are the 4.2% average relative deviation for the calculation.

Nine polymers with known gross heats of combustion [8] were included in the present study to benchmark the experimental method. Table 3 compares literature values for the heat of combustion for these polymers to those obtained experimentally in this study. The average relative deviation between the measured and reported gross heat of combustion of the nine polymers is 3.3%.

DISCUSSION

Reevaluation of the constant used for calculating the heat release rates of burning polymers based on oxygen consumption has been updated to include high performance plastics. A value of $E = 13.10 \pm 0.78$ kJ/g- O_2 was found for the net heat of combustion per gram of diatomic oxygen consumed from the data for all of the polymers in table 1 ($n = 48$). Included are the halogenated, phosphorus-, sulfur-, and, nitrogen-containing materials. The mean E value from this study is identical to the universal value used in oxygen consumption calorimetry, although the coefficient of variation of 6.0 percent is somewhat higher than the 5 percent usually reported for oxygen consumption calorimetry. Regardless, the uncertainty in E is significantly lower than the reported 15 percent uncertainty in peak heat release and mass loss rates in oxygen consumption fire calorimetry measurements [18] and will not be a factor in the accuracy of a heat release rate test.

Using thermochemical calculations to estimate the net heat of combustion from the stoichiometric amount of oxygen consumed in a complete combustion reaction are simple to perform if the atomic composition of the polymer is known *a priori*. The average relative deviation of the experimental

and calculated heats of combustion from oxygen consumption thermochemistry using $E = 13.1$ kJ/g-O₂ is 4.4 percent for all of the polymers in table 2 ($n = 48$).

Thermochemical calculations for estimating the gross heat of combustion from heats of formation of products and reactants for the polymers listed in table 2 have an average relative deviation of 4.2 percent from the experimental (bomb) values ($n = 38$). Excluded from the comparison were the 6F-ETPP polymer, polydimethylsiloxane, polyethylenenaphthylate, XU-71787 and other cyanate esters for which the group contributions for the phosphine oxide, siloxane, naphthyl, norbornene, and cyanurate, respectively, were unknown or unavailable. Thus, thermochemical calculations of the gross heat of combustion from molar group additivity of the heats of formation of products and reactants achieves better accuracy than calculations based on oxygen consumption for the polymers examined in this study. This is not surprising since the group contributions to the heats of formation used in this study were originally determined from the gross heats of combustion of materials with known composition.

CONCLUSIONS

The heats of combustion of 49 polymers of known chemical composition were measured and calculated. The agreement between experimental values for the gross and net heats of combustion and thermochemical calculations of this quantity from heats of formation and oxygen consumption was 4.2 and 4.4 percent, respectively, for these two methods. Either method could be used to predict a reasonably accurate value for the heat of combustion from known polymer structure regardless of the constituent atoms. The thermochemical quantity used to calculate heat release rates based on the measured heats of combustion now encompasses a wider polymer range. The new average value, $E = 13.10 \pm 0.78$ kJ/g-O₂ ($n = 48$) for the net heat released by combustion per unit weight of diatomic oxygen consumed was obtained in the present study of high temperature, heteroatomic polymers. This value of E for the thermally-stable polymers is statistically indistinguishable from the universal value $E = 13.1$ kJ/g-O₂ used for calculating heat release rates of burning materials from oxygen consumption calorimetry. As new high performance materials are made modifications to the heat release constant will not be necessary for calculating the heat release rate of these heteroatomic polymers.

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REFERENCES

1. R.G. Hill, T.I. Eklund, and C.P. Sarkos, "Aircraft Interior Panel Test Criteria Derived from Full-Scale Fire Tests," DOT/FAA/CT-85/23
2. FAR 25.853, "Heat Release Rate Test for Cabin Materials," Aircraft Materials Fire Test Handbook, DOT/FAA/AR-00/12, April (2000).
3. "E906-99: Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products," in ASTM Fire Test Standards, American Society for Testing and Materials, West Conshohocken (2000).
4. W. Thornton, "The Role of Oxygen to the Heat of Combustion of Organic Compounds," Philosophical Magazine and J. of Science, 33(196) (1917).
5. C. Huggett, "Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements," Fire and Materials, pp. 61-65, 4 (2) (1980).

6. M.L. Janssens and W.J. Parker, "Oxygen Consumption Calorimetry," in Heat Release in Fires, V. Babrauskas, S.J. Grayson, eds., Chapter 3, pp. 31-59, Elsevier Applied Science, London (1992).
7. V. Babrauskas, "The Cone Calorimeter," in The SFPE Fire Protection Engineering (2nd Ed.), Section 3/Chapter 3, pp. 37-52, Society of Fire Protection Engineers, Boston, MA (1995).
8. V. Babrauskas, "Heat of Combustion and Potential Heat," in Heat Release in Fires, V. Babrauskas, S.J. Grayson, eds., Chapter 8, pp. 207-223, Elsevier Applied Science, London (1992).
9. R.N. Walters and R.E. Lyon, "A Microscale Combustion Calorimeter for Determining Flammability Parameters of Materials," Proc. 42nd Int'l SAMPE Symposium and Exhibition, 42(2), 1335-1344 (1997).
10. R.N. Walters and R.E. Lyon, "A Microscale Combustion Calorimeter for Determining Flammability Parameters of Materials," NISTIR 5904, K. Beall, ed., pp. 89-90 (1996).
11. U.S. Patent 5981290, Microscale Combustion Calorimeter, R.E. Lyon and R.N. Walters, 11/09 (1999).
12. R.E. Lyon, "Solid-State Thermochemistry of Flaming Combustion," in Fire Retardancy of Polymeric Materials, A.F. Grand and C.A. Wilkie, eds., pp. 391-447, Marcel Dekker, New York (2000).
13. D.W. Van Krevlen, "Thermochemical Properties: Calculation of the Free Enthalpy of Reaction from Group Contributions," in Properties of Polymers, 3rd Ed., Chapter 20, pp. 629-639, Elsevier, Amsterdam (1990).
14. S.W. Benson, Thermochemical Kinetics, Methods for the Estimation of Thermochemical Data and Rate Parameters, John Wiley, New York (1968).
15. W. Wunderlich, "Physical Constants of Poly(methyl methacrylate)," in Polymer Handbook, 3rd Ed., J. Brandrup and E.H. Immergut, eds., Section 5, pp. 77-88, John Wiley & Sons, New York (1989).
16. "D2382-88: Standard Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High Precision Method)," ASTM Fire Test Standards, 3rd Edition, pp. 230-238, American Society for Testing of Materials, Philadelphia (1990).
17. Experimental Thermochemistry, F.D. Rossini, ed., Interscience, NY (1956).
18. J.W. Gilman and T. Kashiwagi, "Nanocomposites: Radiative Gasification and Vinyl Polymer Flammability," Proc. 6th European Meeting of Fire Retardancy of Polymeric Materials, Lille, France, September 24-26 (1997).