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A METHOD FOR THE DETERMINATION OF THE SPECIFIC HEAT AND HEAT OF DECOMPOSITION OF COMPOSITE MATERIALS

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ABSTRACT

A method has been developed to determine the specific heat of a material during thermal decomposition using a combination of DSC and TGA data obtained at the same heating rate. The heat of decomposition is calculated simultaneously using the same data. This technique was used to determine the specific heat and heat of decomposition of a widely used fiberglass-filled phenol–formaldehyde resin and a fiberglass-filled acrylonitrile–butadiene (AB) copolymer. Experimental data are presented for the specific heat of both the virgin and char components for temperatures between 60 and 730°C. The calculated specific heat of the mixture during decomposition for both materials is also presented.

INTRODUCTION

Many materials such as wood, plastics and composite ablatives undergo thermal decomposition when heated to sufficiently high temperatures. Modeling of the thermal response of these materials requires accurate knowledge of their thermal and kinetic properties. These properties must not only be known for the virgin and char (residual) states, but for the partially decomposed material as well. Additionally, the energy transformation of the decomposition must also be known.

The purpose of this work was to determine the values of the temperature dependent specific heat and heat of decomposition of composite ablative materials for use in a thermal model. This resulted in a new technique for calculating the specific heat of the partially pyrolized material and the associated heat of decomposition. Application of this method required

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measurement of the specific heat of the virgin and char components, which was carried out using standard differential scanning calorimetry (DSC). Also, it was necessary to know the weight loss of the material as a function of temperature at the same heating rate as the DSC scan. This was carried out by standard thermogravimetric analysis (TGA). Using both the DSC and TGA data, the remaining properties were calculated using the new method.

BACKGROUND

Differential scanning calorimetry has been used for several years to study the calorimetric behavior of a variety of materials. This includes the measurement of such properties as heats of fusion, glass transition temperatures, energetics of polymerization, etc. McNaughton and Mortimer [1] have given an excellent overview of some of these applications as well as the basic principles of DSC. O'Neill [2] described a procedure to calculate specific heats of materials in the absence of any weight loss using a sapphire standard. In more recent applications of DSC, Brennan [3] studied the qualitative behavior of the heat-sealing characteristics and cross-linking of polyethylene by peroxides. Also, Brennan [4] has characterized phase transitions in a variety of polymeric materials. Brennan et al. [5] developed an iterative technique to determine the specific heat of a material undergoing thermal decomposition, and used it to study the thermal behavior of cotton and poly(methyl methacrylate).

The materials of interest in this work behave similarly to those studied by Brennan et al. [5] inasmuch as they decompose at elevated temperatures. As a result, it was necessary to employ a technique which accounts for the changes in sample weight during pyrolysis.

THEORY

The basic theory of DSC is straightforward. The instrument simply maintains a sample and reference pan at very nearly the same temperature as it scans a predetermined temperature range at a constant heating rate. The differential energy required to maintain the reference pan and the sample at the same temperature is measured. From these data the temperature dependent specific heat before and after any decomposition reactions occur can be calculated using the following equation

$$C_p(T) = \frac{\mathrm{d}q/\mathrm{d}t}{m\,\mathrm{d}T/\mathrm{d}t} \qquad (1)$$

where $\mathrm{d}q/\mathrm{d}t$ = measured differential heat input (cal s^{-1}), $\mathrm{d}T/\mathrm{d}t$ = temperature scanning rate (°C s^{-1}), and m = mass of sample (g).

Both the specific heat and heat of decomposition for a volatile sample can be obtained using the technique proposed by Brennan et al. [5]. This is accomplished by a DSC scan of both the virgin material, through pyrolysis, and the residual char. These scans are depicted qualitatively by Fig. 1. Lines 2 and 3 represent the virgin and char material scans, respectively. Line 1 represents the empty sample and reference pan baseline scan. The extrapolated line, AE, represents the assumed linear energy input for the reactant as if no thermal decomposition was occurring. During the decomposition process, it was assumed that the energy input consisted of sensible and latent components which could be separately determined. The sensible portion of this energy was assumed to be represented by linear interpolation between the points A and B for the first estimation. At the completion of the analysis, the actual sensible component was not linearly related to the temperature. The area contained by AMB represents the estimated heat of decomposition. The sensible energy added to the combination of the active and char components is given by

$$\left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)_{s'} = (1-f)m_v C_{pv}(T)\frac{\mathrm{d}T}{\mathrm{d}t} + f m_c C_{pc}(T)\frac{\mathrm{d}T}{\mathrm{d}t} \qquad (2)$$

where $(\mathrm{d}q/\mathrm{d}t)_{s'}$ = the fraction of total $\mathrm{d}q/\mathrm{d}t$ attributed to the sensible component, f = fraction reacted $A_1/(A_1+A_2)$, $C_{pv}(T)$ = specific heat of the virgin material (cal g^{-1} °C^{-1}), $C_{pc}(T)$ = specific heat of the char material (cal g^{-1} °C^{-1}), m_v = mass of virgin material (mg), m_c = mass of char material (mg), A_1 = area contained by AMO, and A_2 = area contained by BMO.

The procedure outlined by Brennan is

(1) assume line AB represents the sensible energy component;

(2) calculate f at various points between A and B;

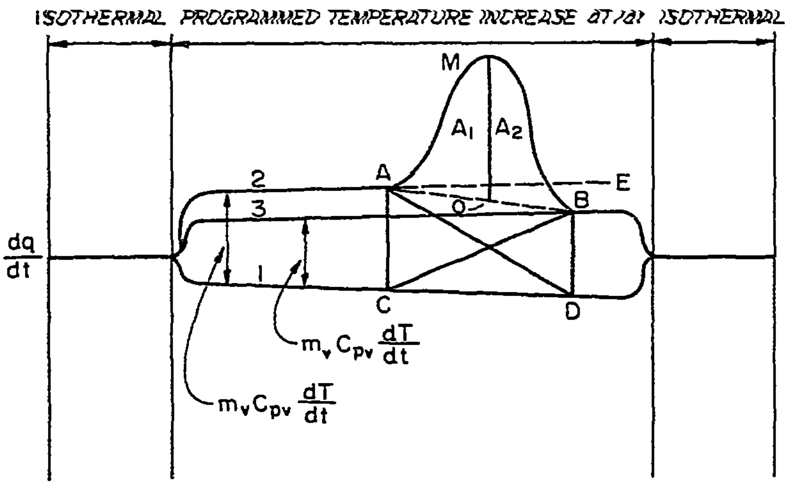

Fig. 1. Qualitative diagram of a programmed temperature scan for empty pan, virgin and char material [5].

(3) calculate $(\mathrm{d}q/\mathrm{d}t)_s$, at each point from eqn. (2);

(4) using the newly established line, AB, repeat steps 2 and 3;

(5) continue iterations until convergence is achieved and a new line AB is established.

Once the sensible energy portion is established, the area contained by AMB represents the heat of decomposition of the material.

Brennan et al. [5] demonstrated feasibility of this technique by determining the heat of decomposition and specific heat of cotton and poly(methyl methacrylate). No details of the measurements or resulting values from the calculations were given.

The method of Brennan is unique in that no values for the mass of the virgin material components are required during decomposition. The method does, however, require the assumption that the fraction of mass reacted at a given temperature is equal to the fraction of energy liberated or consumed at the same temperature. Additionally, the assumption that $m_v C_{p_v}\, \mathrm{d}T/\mathrm{d}t$ may be extrapolated along line AE is required.

In contrast, the technique proposed here involves using eqn. (1), where the temperature dependent mass of the sample is known. These data can be obtained by decomposing samples in a TGA system at the same heating rate used in the DSC measurements. Equation (1) may be rewritten with the temperature dependent mass as

$$C_{p_s}(T) = \frac{\mathrm{d}q/\mathrm{d}t}{m(T)\, \mathrm{d}T/\mathrm{d}t} \tag{3}$$

Equation (3) yields the specific heat of the virgin material before any decomposition occurs. During decomposition, eqn. (3) results in a combination of the specific heat and heat of decomposition, or the apparent specific heat. The specific heat of the char may also be calculated directly by eqn. (3) when the sample weight is invariant at the higher temperatures.

Using the combination of DSC and TGA data, eqn. (3) could be used to calculate the specific heat directly; however, any errors in $\mathrm{d}q/\mathrm{d}t$ or $\mathrm{d}T/\mathrm{d}t$ would reduce the accuracy of the results. By using data obtained from a known mass of sapphire in conjunction with sample data, the need for accurate calibration of $\mathrm{d}q/\mathrm{d}t$ is eliminated. Further, any errors in $\mathrm{d}T/\mathrm{d}t$ will be cancelled out. Writing eqn. (3) for the sapphire standard results in

$$C_{p_{std}}(T) = \frac{(\mathrm{d}q/\mathrm{d}t)_{std}}{m_{std}(\mathrm{d}T/\mathrm{d}t)} \tag{4}$$

where the subscript std indicates sapphire standard.

Taking the ratio of eqns. (3) and (4) yields

$$\frac{C_{p_s}(T)}{C_{p_{std}}(T)} = \left[\frac{(\mathrm{d}q/\mathrm{d}t)_s}{m(T)_s\, \mathrm{d}T/\mathrm{d}t}\right] \Big/ \left[\frac{(\mathrm{d}q/\mathrm{d}t)_{std}}{m_{std}(\mathrm{d}T/\mathrm{d}t)}\right] \tag{5}$$

where the sample is indicated by the subscript s. Rearranging and eliminating dT/dt results in eqn. (6)

$$C_{ps}(T) = \frac{(dq/dt)_s}{(dq/dt)_{std}} \frac{m_{std}}{m(T)_s} C_{pstd}(T) \tag{6}$$

Equation (6) may be used to determine the temperature dependent apparent specific heat of the virgin material and the specific heat of the char materials directly from the DSC and TGA data. Only the two ordinate deflections, dq/dt from the DSC scan, and $m(T)$ from the TGA scan are required. The temperature dependent specific heat of artificial sapphire is well defined and is given by Ginnings and Furukawa [6].

Once the specific heats of the virgin and char materials are obtained, the specific heat of the mixture can be calculated directly using the following equation

$$C_{pm}(T) = FC_{pv}(T) + C_{pc}(T)(1-F) \tag{7}$$

where C_{pm} = specific heat of the decomposing material (cal g^{-1} °C^{-1}) and F is given by

$$F = \frac{m(T)-m_f}{m_0-m_f} \tag{8}$$

where m_0 = initial mass of the sample (mg); and m_f = final mass of the sample (mg).

The specific heat of the virgin material after decomposition begins is assumed to be given by a linear extrapolation based on a curve fit of the experimental data prior to the onset of decomposition. By using the measured specific heat of the char and F as given by eqn. (8), the specific heat of the mixture is calculated by eqn. (7). The resulting specific heat of the mixture is then used to determine the heat of decomposition by numerically integrating the areas between the specific heat of the mixture given by eqn. (7) and the apparent specific heat as given by eqn. (6).

EXPERIMENTAL

Materials

The composite ablative materials used in this study were supplied by Fiberite Corporation. The contents of each of these materials are shown in Table 1. The materials were converted to powder form by machining. They were filtered through a number 20 sieve and stored for approximately 24 h in a vacuum desiccator to remove traces of moisture.

Apparatus and procedure

A Perkin-Elmer TGS-2 thermogravimetric system was used for the TGA measurements. Temperature control was provided by a Perkin-Elmer System

TABLE 1

Composition of materials tested

Contents	Material composition (%)	
	Fiberite MXB-360	Fiberite MXBE-350
Fiberglass	59.0	41.0
Glass powder	14.5	15.5
Total filler content	73.5	56.5
Phenol–formaldehyde resin	26.5	
Acrylonitrile–butadiene copolymer		43.5

4 microprocessor controller. The sample temperatures were monitored with a chromel–alumel thermocouple which was calibrated using a set of five Curie standards [7].

A Perkin-Elmer DSC-2C differential scanning calorimeter was used for the DSC measurements. The DSC output was recorded on a Linear Instruments Model 595 strip-chart recorder. The samples were weighed on a Perkin-Elmer AD-2Z microbalance. Temperature calibration of the DSC-2C was accomplished using a set of standards recommended by Perkin-Elmer [8].

In order to reduce temperature gradients in the material, small sample weights were used in both the TGA and DSC measurements. Samples weighing between 7.5 and 9.0 mg were heated from approximately 50°C to 950°C in the TGA, and from approximately 50°C to 730°C in the DSC at a heating rate of 20°C min^{-1}. The samples were maintained in nitrogen atmospheres in both instruments, with a purge rate of 100 ml min^{-1}. When the programmed temperature scan in the TGA measurements reached 950°C, the purge gas was automatically switched to oxygen to thermo-oxidatively degrade the remaining resin. The amount of inert filler was verified by holding the temperature at 950°C until the resin component had completely degraded.

RESULTS

The original TGA thermograms were digitized at 0.01 intervals of the fraction of weight remaining. The temperatures were corrected using the Curie standard calibrations. The results of the fraction of weight remaining as a function of the corrected temperatures for both materials are shown in Fig. 2.

The original DSC data were digitized at 20°C intervals. These tempera-

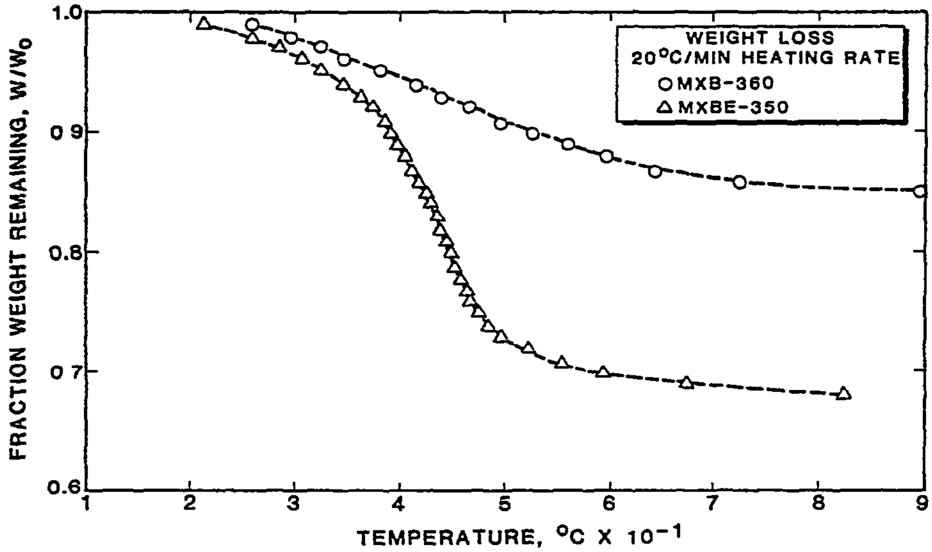

Fig. 2. Fraction of weight remaining for MXB-360 and MXBE-350

tures were then corrected using the recommended standards. The fraction of weight remaining at the temperatures corresponding to corrected DSC temperatures were obtained by a linear interpolation of the TGA data. The specific heats of the virgin and char materials were then calculated using eqn. (6). A linear least squares fit of the virgin material specific heat data was made and extrapolated through the decompostion region. From these data the specific heat of the mixture and the heat of decomposition were calculated using the procedure previously outlined. Also, a least squares fit of the

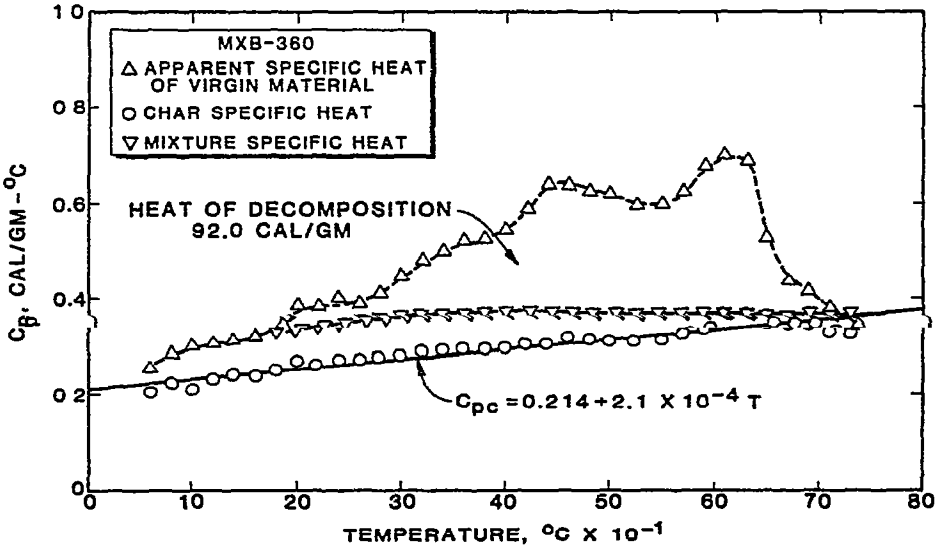

Fig. 3. Specific heat and heat of decomposition of MXB-360.

TABLE 2

Digitized data

Corrected temp. (°C)		Apparent virgin material[a] specific heat ($cal^{-1}g^{-1}°C^{-1}$)		Virgin material[b] specific heat ($cal^{-1}g^{-1}°C^{-1}$)	
MXB-360	MXBE-350	MXB-360	MXBE-350	MXB-360	MXBE-350
60.0	59.5	0.257	0.288		
80.0	79.4	0.291	0.334		
100.0	99.2	0.303	0.317		
120.0	119.1	0.307	0.310		
140.0	138.9	0.313	0.309		
160.0	158.8	0.324	0.320	0.322	
180.0	179.2	0.354	0.320	0.330	
200.0	199.5	0.391	0.329	0.337	
220.0	219.8	0.381	0.322	0.345	
240.2	240.2	0.402	0.317	0.353	
260.7	260.6	0.398	0.319	0.360	
281.1	280.9	0.419	0.327	0.368	
301.6	301.3	0.460	0.339	0.376	
322.0	321.7	0.482	0.339	0.383	0.333
342.5	342.1	0.505	0.263	0.391	0.335
363.0	362.5	0.525	0.136	0.399	0.338
383.4	382.9	0.526	0.133	0.407	0.340
403.9	403.3	0.551	0.409	0.414	0.342
424.4	423.7	0.594	0.636	0.422	0.344
444.8	444.1	0.645	0.755	0.430	0.346
465.3	464.4	0.636	0.797	0.438	0.348
485.7	484.8	0.631	0.852	0.445	0.350
506.2	505.2	0.625	0.823	0.453	0.352
526.7	525.5	0.600	0.835	0.461	0.354
547.1	545.9	0.604	0.847	0.468	0.356
567.6	566.3	0.636	0.893	0.476	0.358
588.0	586.7	0.683	0.948	0.484	0.360
608.5	607.0	0.700	0.911	0.492	0.362
629.0	627.4	0.691	0.708	0.499	0.364
649.4	647.8	0.536	0.491	0.507	0.366
669.9	668.2	0.450	0.361	0.515	0.368
689.9	688.2	0.421	0.305	0.522	0.370
709.9	708.2	0.381	0.305	0.530	0.372
729.9	728.2	0.351	0.323	0.537	0.374

[a] Experimental DSC data.

[b] Calculated.

[c] Experimental TGA data.

char material specific heat data was made. The heat of decomposition was calculated using a trapezoidal integration scheme. The results of these calculations for MXB-360 and MXBE-350 are shown in Figs. 3 and 4,

Char material[b] specific heat C_{pc} (cal g^{-1} °C^{-1})		Fraction weight[c] remaining		Mixture[b] specific heat C_{pm} (cal g^{-1} °C^{-1})	
MXB-360	MXBE-350	MXB-360	MXBE-350	MXB-360	MXBE-350
0.206	0.195	1.00	1.00		
0.219	0.214	1.00	1.00		
0.217	0.201	1.00	1.00		
0.235	0.201	1.00	0.998		
0.241	0.197	1.00	0.996		
0.239	0.198	1.00	0.994	0 322	
0.255	0.198	0.997	0.992	0.329	
0.272	0.192	0.995	0.991	0.336	
0 263	0.198	0.993	0.988	0.342	
0.270	0.204	0.991	0.983	0.348	
0.273	0.204	0.989	0.978	0.354	
0.280	0.204	0.984	0.971	0.358	
0.283	0.205	0.978	0.961	0.361	
0.288	0.191	0.971	0.952	0.363	0.315
0.291	0.185	0.962	0.941	0.363	0.313
0.295	0.184	0 955	0.929	0.364	0.311
0.294	0.185	0.949	0.911	0 366	0 307
0.297	0.204	0.943	0 883	0.368	0 299
0.311	0.196	0.936	0.852	0.368	0 291
0.313	0.196	0.928	0.810	0.367	0.278
0.322	0.209	0.920	0.767	0 366	0 266
0.315	0.215	0.913	0.740	0.365	0.260
0.313	0.215	0.906	0.727	0.363	0.259
0.316	0.220	0.899	0.719	0.362	0 259
0.315	0 227	0 893	0.712	0 361	0.260
0.331	0.247	0.887	0.707	0.361	0.262
0.343	0 274	0.882	0.702	0.360	0.263
0.378	0.281	0.877	0.698	0 360	0 266
0.369	0.291	0.873	0.696	0.360	0.268
0.353	0.297	0.869	0.693	0.360	0.271
0.358	0.302	0.866	0.690	0.361	0.273
0.351	0.294	0.864	0.689	0 363	0 276
0.336	0.313	0.861	0.687	0.364	0 279
0.330	0.324	0.859	0.686	0.366	0.282

respectively. The digitized data for both materials are shown in Table 2. Also, a summary of the least squares curve fits for both the virgin and char components are given in Table 3.

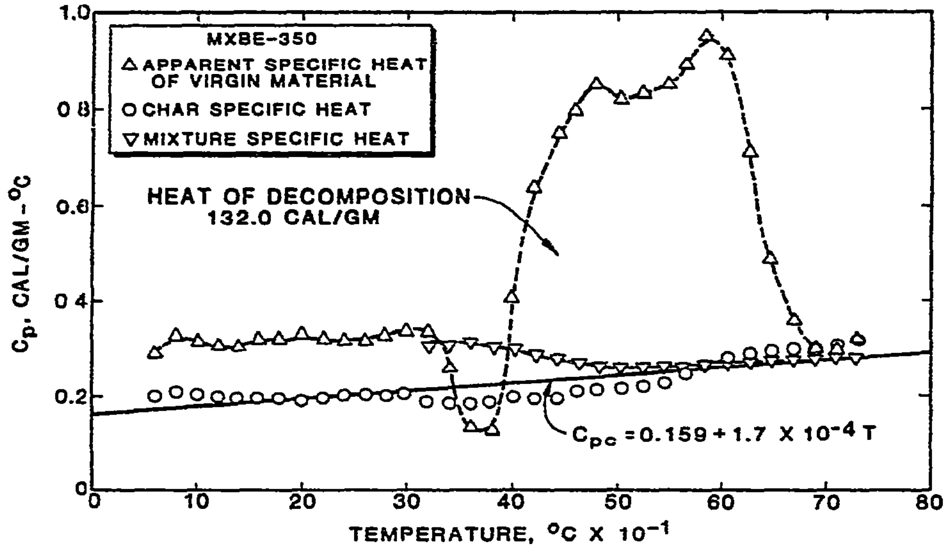

Fig. 4. Specific heat and heat of decomposition of MXBE-350

TABLE 3

Summary of least squares curve fits and heat of decomposition

Material	Linear temperature dependent specific heat of char material, C_{pc} (cal g^{-1} °C^{-1})		Linear temperature dependent specific heat of virgin material, C_{pv} (cal g^{-1} °C^{-1})		Heat of decomposition (cal g^{-1})
	Intercept at 0°C	Slope	Intercept at 0°C	Slope	
MXB-360	0.214	$2\ 1 \times 10^{-4}$	0.262	3.78×10^{-4}	92.0
MXBE-350	0.159	1.7×10^{-4}	0.301	1.10×10^{-4}	132.0

DISCUSSION

Calculation of the apparent specific heat of the virgin component and the specific heat of the char component is straightforward using a combination of DSC and TGA data. Equally important, the specific heat during thermal decomposition and the heat of decomposition are easily calculated using the proposed method. Utilization of eqn. (7) in conjunction with least squares curve fits of the virgin and char material specific heats gives the necessary temperature dependent properties in functional form. These results can then be easily integrated into a thermal model.

The advantages of this method are that (1) it is relatively straightforward, and (2) the weight of the sample as a function of temperature is known from previous thermogravimetric analysis. Therefore, the specific heat can be calculated directly without iteration, and no assumption regarding the fraction of mass reacted at a given temperature is required.

The primary disadvantage is the same as with the method proposed by Brennan et al. [5], i.e., the danger of extrapolating the temperature dependent specific heat of the virgin material through the decomposition region. In some cases, this extrapolation may cover several hundred degrees. This, of course, is the case with the materials of interest in this work.

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