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MEASUREMENT OF THE SPECIFIC HEAT AND HEAT OF DECOMPOSITION OF A POLYMER COMPOSITE TO HIGH TEMPERATURES

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The specific heat and heat of decomposition of a glass-filled phenolformaldehyde (phenolic) resin have been determined from experimental data obtained using a simultaneous thermal analyzer capable of operation to 1500 °C. The measurements were conducted on powdered samples of the polymer to temperatures of approximately 1050 °C at a rate of 20 deg min^{-1} in an argon atmosphere. Both the mass loss and energetics were measured for the virgin component of the material, while only the energetics were measured for the char component. The combination of these data was used to calculate the specific heat of the virgin, char, and decomposing material, as well as the heat of decomposition. Also, in order to establish the accuracy of the instrument, the specific heat of pyroceram 9606 was measured and compared to previously published values.

Because of their insulating and erosion-resistant qualities, polymer composites are used in a wide variety of high-temperature thermal protection applications. In many of these applications, the materials are exposed to temperatures high enough to cause multiple-stage decomposition reactions and thermochemical expansion of the solid matrix. This, in turn, causes large changes in the thermal and transport properties, and significantly affects the thermal performance of the material. In order to properly design thermal protection systems for these applications, it is necessary to evaluate the changes in thermal performance and to predict the thermally-induced response of the material a priori. This requires the use of complex mathematical models which include the appropriate properties for the material of interest.

The specific heat of both the virgin and char material as well as the heat of decomposition for the pyrolysis reactions are of particular importance. For example, Henderson and Wiecek [1] have demonstrated that alteration of these properties induces large changes in the thermally-induced response of a certain glass-filled polymer composite. Therefore, the purpose of the work reported in this paper was to determine the temperature-dependent specific heat of the virgin, char, and decomposing material and the heat of

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decomposition for the pyrolysis reactions of a widely-used glass-filled polymer composite. Calculation of these properties required the measurement of both the mass loss and energetics. This was accomplished using a simultaneous thermal analyzer (STA) equipped with a new high-temperature furnace and measuring head. The properties of interest were computed from the experimental data using the well-known ratio method and numerical integration.

Background

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used for many years to study the calorimetric behavior of a wide variety of materials. Wendlandt [2], Blažek [3], and McNaughton and Mortimer [4], among others, have given excellent overviews of the basic principles of DTA/DSC as well as a host of application examples. In addition, Brennan, Miller, and Whitwell [5] developed an iterative technique to determine the specific heat of materials undergoing thermal decomposition. This technique was then used to study the thermal behavior of cotton and poly(methyl methacrylate). Later Henderson, Wiebelt, Tant, and Moore [6] used data obtained from DSC and thermogravimetric (TG) measurements to determine the specific heat and heat of decomposition of a variety of polymer composite materials.

Theory

The specific heat as a function of temperature and the heat of decomposition were determined from experimental mass-loss and energetics data obtained with an STA. Because this instrument allows simultaneous measurement of the mass loss (TG) and the energetics (DTA) it is well suited for this particular application. The basic principle of the DTA is straightforward. The instrument functions by measuring the temperature difference, ΔT, between a sample and a reference as it scans a predetermined temperature range at a constant heating rate. The temperature-dependent specific heat can be computed from these data using

$$C_{ps} = \frac{\Delta T_s E}{m_s \beta} \tag{1}$$

where C_p = specific heat, J g^{-1} deg^{-1}
ΔT = differential temperature, K
m = mass, g
β = heating rate, deg min^{-1}
E = instrument calibration J deg^{-1} min^{-1}

and the subscript s indicates sample. Equation (1) yields the specific heat of the virgin material before any decomposition occurs and the specific heat of the char when the sample mass is invariant at higher temperatures. However, when decomposition of the sample is occurring, equation (1) gives a combination of the specific heat and heat of decomposition, or the apparent specific heat. In order to calculate this apparent specific heat the instantaneous mass of the sample must be known. In the method proposed by Henderson et al [6], the instantaneous mass of the sample was obtained directly from mass-loss data taken at the same heating rate as that used in the DSC/DTA measurements. However, with the STA used in this work the TG and DTA data are obtained simultanously.

Using a combination of TG/DTA data, equation (1) could be used to calculate the specific heat directly; however, any errors in E or the instrument scanning rate, β, would reduce the accuracy of the results. By using experimental data obtained from a known mass of sapphire in conjunction with the experimental data for the sample, the need for accurate calibration of the instrument is eliminated. Further, any errors in β are cancelled. Writing equation (1) for the sapphire standard and taking the ratio of equation (1) and the sapphire standard equation yields

$$C_{ps} = C_{pstd} \frac{m_{std}}{m_s} \frac{\Delta T_s}{\Delta T_{std}} \tag{2}$$

where the subscript std indicates sapphire standard. Equation (2) constitutes the ratio method any may be used to determine the apparent specific heat of the decomposing material and the specific heat of the virgin and char materials directly from the TG/DTA data. Only the ordinate deflections, ΔT, from the sample, standard, and baseline runs and the instantaneous sample mass are required. It should also be pointed out here that only the microvolt signal representing ΔT is required. Since the specific heat is calculated from the ratio of the signals, the need to convert to physical quantities is eliminated. The temperature-dependent specific heat of artificial sapphire is well defined and is given by Ginnings and Furukawa [7].

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

$$C_{pd} = FC_{pv} + (1-F)C_{pc} \tag{3}$$

where the subscripts d, v, and c represent the decomposing, virgin, and char materials, respectively. The instantaneous mass fraction of non-inert material remaining, F, is given by

$$F = \frac{m - m_f}{m_o - m_f} \tag{4}$$

where the subscripts o and f represent the initial and final states, respectively.

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 equation (4), the specific heat of the decomposing material is calculated by equation (3). The resulting specific heat of the decomposing material is then used to determine the heat of decomposition by numerically integrating the area between the specific heat of the decomposing material given by equation (3) and the apparent specific heat as given by equation (2). This technique has been described in greater detail by Henderson et al [6].

Experimental

Material

The material studied, H41N, was supplied by Ametek, Haveg Division. The material consists of 39.5 percent phenol-formaldehyde resin and 60.5 percent glass and talc filler. Powdered samples were machined from larger blocks of material and then filtered through a No. 20 sieve. Samples were stored overnight in a vacuum desiccator maintained at 35° to remove traces of moisture.

Instrumentation

A Netzsch model 409 STA equipped with a new platinum furnace and platinum/rhodium sample carrier was used for the measurements. The platinum furnace produces a consistent and uniform heat flux to the sample carrier. Hence, the baseline drift is quite small and the reproducibility is excellent. The measuring probe consists of a platinum-10% rhodium sample carrier head mounted on an alumina support stem. The sample carrier head functions both as a holder for the sample and reference crucibles and as the platinum/rhodium leg of the monitoring thermocouple. The sample crucible and lids are constructed of a platinum-20% rhodium alloy and are approximately 6.0 mm diameter by 3.0 mm deep. The large contact area between the crucible and sample carrier results in excellent sensitivity. Both the furnace and sample carrier are capable of operation to over 1500° at heating rates ranging from 0.1 to 100 deg min^{-1}. Also, experiments can be conducted under a vacuum or in a static or dynamic gas atmosphere. Finally, the temperature calibration of the instrument was checked using a set of standard reference materials. A drawing of the measuring probe is shown in Figure 1.

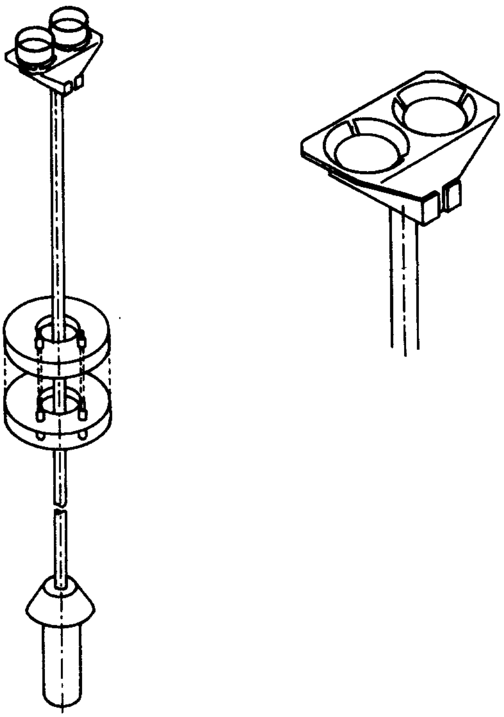

Fig. 1 Measuring probe for STA system

Temperature control of the STA is provided by a Netzsch model 413 programmer and model 413 controller. The analog signals representing sample temperature, mass, rate of mass loss, and differential temperature are conditioned by a Netzsch temperature linearization module, carrier frequency amplifier, derivative amplifier, and differential temperature amplifier, respectively. Data acquisition and instrument control are provided by a 16/32 bit computer system with peripheral units and the appropriate software.

Procedure

The accuracy of the STA was checked by measuring the specific heat of pyroceram 9606 and comparing the results with published values. Three scans were required to obtain the necessary experimental data. Empty sample required one scan each.

Two additonal scans were required in order to obtain the experimental data to calculate the specific heat of the polymer. The virgin and char samples each required one scan. The mass-loss data for the polymer were obtained during the virgin sample scan. The char material sample was obtained by precharring a sample of the virgin material in the STA unit to 1050° under the same conditions as the other tests. All experiments were conducted at heating rates of 20 deg $\min^{-1}$. Small sample weights ranging from 10 to 15 mg were used in order to reduce the temperature gradients in the material. During testing the samples were maintained in an argon atmosphere at a purge rate of 100 ml/min. This prevented thermo-oxidative degradation of the polymeric samples.

Results and discussion

After applying the baseline correction, equation (2) was used to calculate the specific heat of pyroceram 9606. A comparison of the published [8] and measured values of the specific heat in the temperature range of 50 to 1080° is shown in Figure 2. Clearly the results are quite good. The maximum deviation between the measured and published values is approximately 1.5% and the average deviation over the entire temperature range is about 0.6%.

Figure 3 depicts the fraction of mass remaining, m/m_o, and the normalized rate of mass loss as a function of temperature for H41N for both the low-temperature pyrolysis reactions and the high-temperature carbon-silica reactions. As can be seen, the pyrolysis reactions occur in the temperature

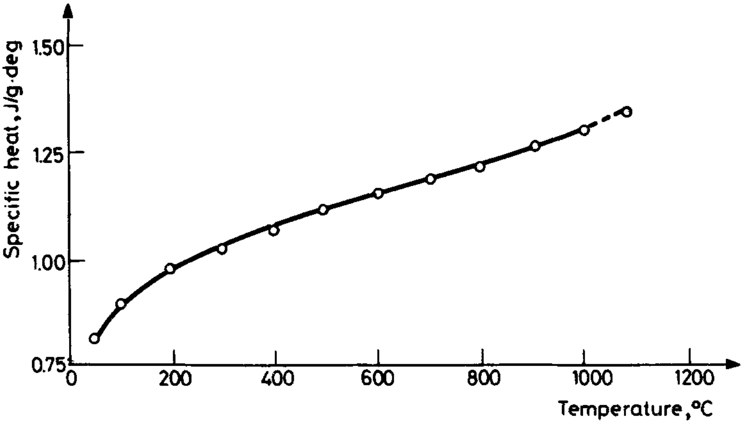

Fig. 2 Comparison of measured and published values of the specific heat of pyroceram 9606. – literature, ○ measured

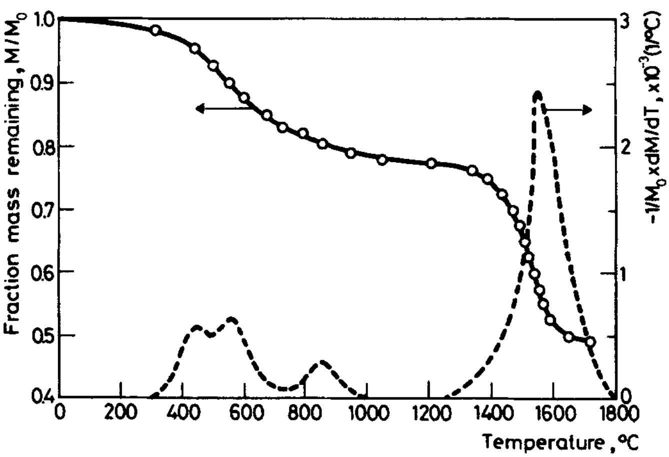

Fig. 3 Fraction of mass remaining and normalized rate of mass loss of H41N. Heating rate 20 deg/min.

range of approximately 300 to 1100° and result in a mass loss of about 22%. The carbon-silica reactions occur at temperatures above 1200° and result in a much larger mass loss. The thermally-induced behaviour of this particular material has been described in detail by Henderson, Tant, Doherty and O'Brien [9]. It should be pointed out that Figure 3 was presented in order to depict the character of the polymer over the entire range of decomposition. These data were obtained with a Netzsch model 409 STA equipped with a high-temperature furnace and are not the data used to compute the instantaneous mass of the sample used in equation (2).

As with pyroceram 9606, equation (2) was used to compute the specific heat of the virgin and char samples of H41N. A linear least-squares fit of the virgin material specific heat prior to the onset of decomposition was made and extrapolated through the decomposition region. The mass-loss data, C_{pc}, and the extrapolated values of C_{pv} were then used in equations (3) and (4) to calculate the specific heat during decomposition. The heat of decomposition was calculated using a numerical integration scheme. Also, a linear least-squares fit of the char material specific heat was made.

Table 1 Summary of specific heat and heat of decomposition analysis

Linear temperature-dependent specific heat				Heat of decomposition $J\,g^{-1}$
char material C_{pc}, $J\,g^{-1}\,deg^{-1}$		virgin material C_{pv}, $J\,g^{-1}\,deg^{-1}$		
intercept (0 °C)	slope	intercept (0 °C)	slope	
0.881	$7.60 \cdot 10^{-4}$	1.051	$9.76 \cdot 10^{-4}$	214

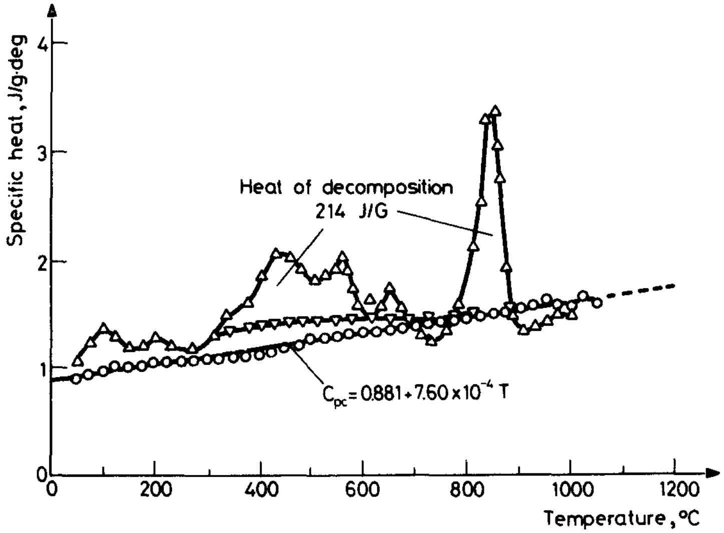

Fig. 4 Specific heat and heat of decomposition of H41N.
△ apparent specific heat of virgin material
○ specific heat of char material
▽ specific heat of decomposing material

The results of the specific heat calculations for H41N are shown in Figure 4 and are summarized in Table 1. Comparison of Figures 3 and 4 reveals that peaks in the apparent specific heat curve generally correspond to those in the rate of mass loss curve over the temperature range of the pyrolysis reactions. This is the expected behavior since an increase in the rate of mass loss is generally accompanied by higher endothermic activity. Also of interest in Figure 4 is the fact that at 1050° the magnitude of the apparent specific heat is in close agreement with the char specific heat. Again this is the expected behavior because the material used in the char test was conditioned to 1050°.

It is constructive to point out here that calculation of the apparent specific heat using the instantaneous sample mass is essential. As previously discussed, this particular polymer loses about 22% of its mass during the pyrolysis reactions. Hence, using the original sample mass in equation (2) yields an apparent specific heat approximately 22% below the correct value at 1050°. This, in turn, results in an incorrect value for the heat of decomposition. This error, of course, becomes larger for a polymer with a greater mass loss. Figure 5 clearly shows the effect of using the instantaneous sample mass to compute the apparent specific heat.

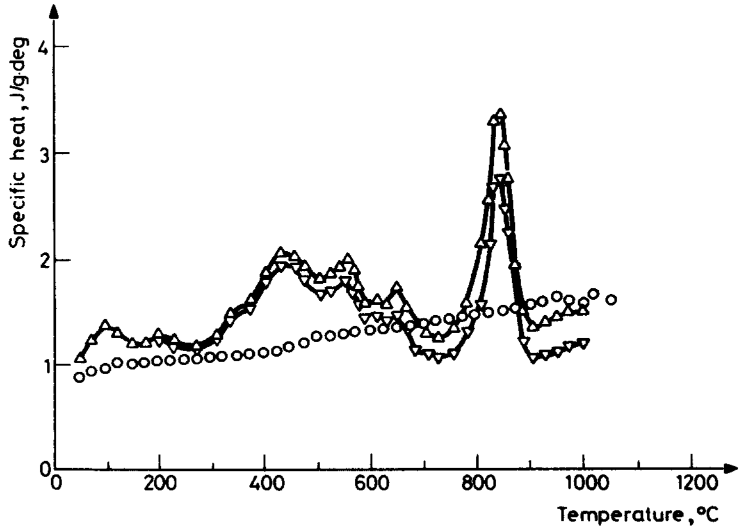

Fig. 5 Apparent specific heat of H41N with and without mass loss correction
△ apparent specific heat corrected for mass loss
▽ apparent specific heat not corrected for mass loss
○ specific heat of char material

Concluding comments

The results presented for pyroceram 9606 show that the STA 409 equipped with the new sample carrier system and platinum furnace can be used for accurate quantitative measurement of the specific heat over a wide range of temperatures. This is due primarily to the sensitivity of the sample carrier and the uniform and consistent heat flux produced by the furnace.

With regard to the polymer, determination of the apparent specific heat of the virgin material during decomposition is straightforward using TG/DTA data. As a result, simultaneous thermal analysis is well suited for this type of application. Also, when used in conjunction with the STA data, the computational technique described in this paper allows separation of the specific-heat effects and the heat-of-decomposition effects in the decomposition region. This permits accurate calculation of the specific heat of the mixture, as well as the heat of decomposition.

The primary disadvantage of the computational method is the danger of extrapolating the temperature-dependent specific heat of the virgin material through the decomposition region. In many instances it is necessary to extrapolate these data over several hundred degrees. This is the case with the material used in this work.

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Zusammenfassung – Die spezifische Wärme und die Zersetzungswärme eines glasgefüllten Phenol-Formaldehyd-Harzes wurden aus experimentellen Daten bestimmt, die mittels eines simultanen Thermoanalyse-Gerätes für Arbeiten bis 1500 °C gewonnen wurden. Die Messungen wurden an gepulverten Polymerproben bis zu Temperaturen von 1050 °C mit einer Aufheizgeschwindigkeit von 20 K min^{-1} in Argonatmosphäre durchgeführt. Massenverlust und Energieänderungen wurden für das jungfräuliche Material gemessen, die Energieänderung auch für das verkohlte Material. Zur Prüfung der Messgenauigkeit des Geräts wurde die spezifische Wärmekapazität von Pyroceram 9606 gemessen und mit früher publizierten Daten verglichen.

РЕЗЮМЕ — С помощью термического анализатора, позволяющего проводить измерения до температуры 1500°, были определены удельная теплоемкость и теплота разложения стеклонаполненной фенолформальдегидной (фенольной) смолы. Измерения были проведены с порошками полимера в атмосфере аргона при температурах до 1050° и скорости нагревания 20°/мин. Для первоначально выделяемой компоненты материала были измерены потеря веса и энергетические параметры, тогда как для обугленного остатка — только энергетические характеристики. Комбинация этих данных была использована для вычисления удельной теплоемкости первоначально выделяемой компоненты, обугленной компоненты и разлагающегося остатка, также как и теплота его разложения. С целью определения точности аппаратуры была измерена теплоемкость пироцерама 9606, сопоставленная с ранее опубликованными результатами.