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MEASUREMENT OF THE SPECIFIC HEAT OF A GLASS-FILLED POLYMER COMPOSITE TO HIGH TEMPERATURES

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ABSTRACT

The specific heat and heat of decomposition of a glass-filled phenol–formaldehyde (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 ° C 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

INTRODUCTION

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 large 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

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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 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 all given excellent overviews of the basic principles of DTA/DSC as well as a host of application examples In addition, Brennan et al [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 et al [6] used a combination of DSC and thermogravimetric analysis (TGA) data 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

$$C_{\mathrm{ps}} = \frac{\Delta T_{\mathrm{s}} E}{m_{\mathrm{s}} \beta} \tag{1}$$

where C_{p} is the specific heat (J g^{-1} K^{-1}), ΔT is the differential temperature (K), m is the mass (g), β the heating rate (K min^{-1}) and E is the instrument calibration (J K^{-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, eqn (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 simultaneously

Using a combination of TG/DTA data, eqn (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 eqn (1) for the sapphire standard and taking the ratio of eqn (1) and the sapphire standard equation yields

$$C_{\mathrm{ps}} = C_{\mathrm{pstd}} \frac{m_{\mathrm{std}}}{m_{\mathrm{s}}} \frac{\Delta T_{\mathrm{s}}}{\Delta T_{\mathrm{std}}} \tag{2}$$

where the subscript std indicates sapphire standard Equation (2) constitutes the ratio method and 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

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

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

$$F = \frac{m - m_{\mathrm{f}}}{m_0 - m_{\mathrm{f}}} \tag{4}$$

where the subscripts 0 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 eqn. (4), the specific heat of the decomposing material is calculated by eqn (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 eqn. (3) and the apparent specific heat as given by eqn (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% phenol–formaldehyde resin and 60 5% 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 °C 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 constant 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 °C at heating rates from 0 1 to 100 °C min^{-1} Also, experiments can be conducted under a high 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 Fig 1

Temperature control of the STA is provided by a Netzsch model 413 programmer and model 413 controller The analog signals representing

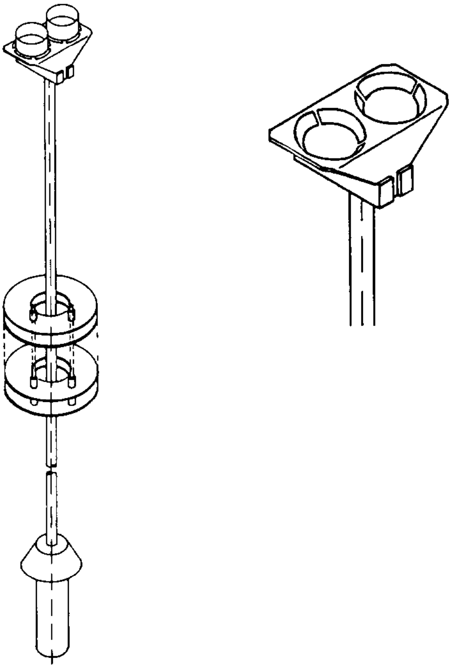

Fig 1 Measuring probe for STA system

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 sophisticated 16/32 bit computer system with peripheral units and the appropriate software

Procedure

Four scans were required in order to obtained the necessary experimental data to calculate the specific heat The virgin and char samples required one scan each. An empty sample pan was run to establish a baseline and a sapphire standard was run in order to utilize eqn (2) The mass-loss data 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 °C under the same conditions as the other tests All experiments were conducted at heating rates of 20 °C min^{-1} from approximately 30 to 1050 °C Small sample masses 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^{-1} to prevent thermo-oxidative degradation

RESULTS AND DISCUSSION

Figure 2 depicts the fraction of mass remaining, m/m_0, 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 range of approximately 300–1100 ° C and result in a mass loss of about 22% The carbon–silica reactions occur at temperatures above 1200 ° C and result in a much larger mass loss The thermally-induced behavior of this particular material has been described in detail by Henderson et al [8] and will not be repeated here It should be pointed out that Fig. 2 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 eqn (2)

The analog STA data were digitized at 1 5 s intervals These data were interpolated to even temperature increments of 2 ° C After applying the baseline correction, eqn (2) was used to compute the specific heat of the virgin and char samples 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 extrapolated values of C_{pv}, C_{pc}, and the mass-loss data were then used in eqns (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

The results of the specific heat calculations are shown in Fig 3 and are summarized in Table 1 Comparison of Figs 2 and 3 reveals that the peaks

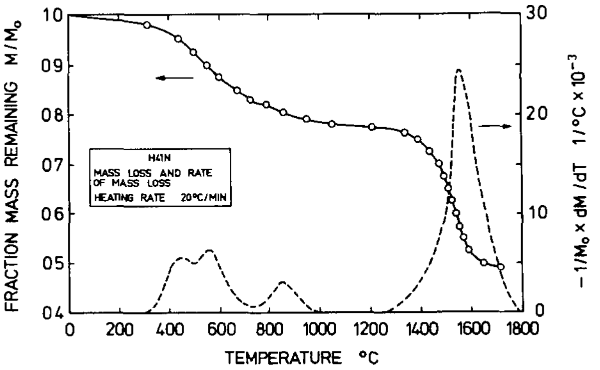

Fig 2 Fraction of mass remaining and normalized rate of mass loss

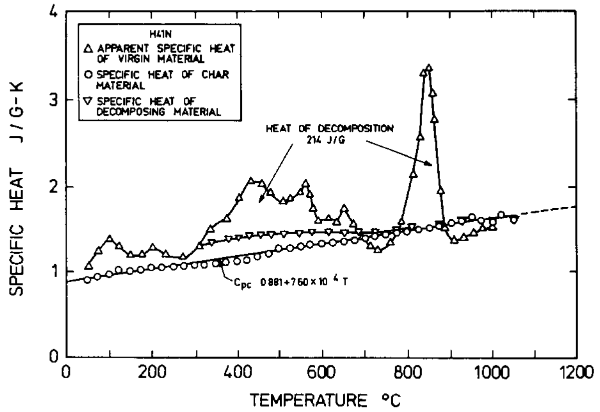

Fig 3 Specific heat and heat of decomposition

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 Fig. 3 is the fact that at 1050 °C 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 °C It is constructive here to point out 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 eqn (2) would yield an apparent specific heat approximately 22% below the correct value This, in turn, would result in an incorrect value for the heat of decomposition This error, of course, would become larger for a polymer with a greater mass loss

CONCLUDING COMMENTS

Calculation of the apparent specific heat of the virgin material and the specific heat of the char material is straightforward using STA data. The

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} ($J\ g^{-1}\ K^{-1}$)		Virgin material, C_{pv} ($J\ g^{-1}\ K^{-1}$)		
Intercept (0 °C)	Slope	Intercept (0 °C)	Slope	
0 881	$7\ 60 \times 10^{-4}$	1 051	$9\ 76 \times 10^{-4}$	214

technique discussed in this paper also allows separation of the specific-heat effects and the heat-of-reaction effects in the decomposition region In addition, utilization of eqns (3) and (4) in conjunction with least-squares curve fits for C_{pv} and C_{pc} and the mass-loss data gives the necessary temperature-dependent properties in functional form

A very large advantage of this technique is that the instantaneous sample mass during decomposition is known and is used in the calculations. As a result, the apparent specific heat and the heat of decomposition can be calculated directly and accurately The primary disadvantage of this technique is the same as with the method proposed by Brennan et al [5], that 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, of course, is the case with the material used in this work

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