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Kinetics of Pyrolysis Mass Loss from Cured Phenolic Resin

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Knowledge of the kinetics of phenolic resin pyrolysis is critical to the accurate modeling of ablatives used in rocket nozzle and re-entry environments. Most employ thermogravimetry to study this phenomena. Nearly all of the previous studies on ablative materials have utilized fairly slow heating with respect to the use environment. This has forced analysts to extrapolate to the much higher rates occurring in the use environment. The high heating rate predictions of these models suggest that pyrolysis can be postponed to much higher temperatures. This has had dramatic effects on the predicted mechanical response of the material under flight conditions. To avoid these large extrapolations, laboratory data was required at or near the high heating rates seen in the use environment. A new facility was constructed that is capable of obtaining data at substantially higher heating rates than are currently available. Cured SC 1008 phenolic resin in powdered form was heated at eight heating rates ranging from 0.25 to 2500°C/min. The data indicates that the weight loss behavior of this material at very high heating rates exhibits a much reduced kinetic response over what was previously predicted, and that this may be due to a change in chemical reaction mechanism.

Nomenclature

A = pre-exponential or frequency factor
CP = Curie point
Ea = activation energy
n = order of reaction
TC = thermocouple
TG = thermogravimetry
Z = pre-exponential or frequency factor

Introduction

PHENOLIC-BASED composites are used extensively throughout the aerospace community in the design of ablative thermal insulators for rocket nozzles, exit cones, the leading edges of re-entry vehicles, missile magazines, and blast deflectors. Historically, these materials have behaved inconsistently.[1] The successful use of these materials depends, to a large part, on the knowledge of how the materials will respond to the various thermal and mechanical loads imposed by the severe environment in which they are employed.

Thermal analysis has been employed for the prediction of temperature as a function of time and location in ablative materials. These analyses are subsequently used to predict mechanical stress and strain levels at any location within a part at any time during heating or postshutdown. In addition, thermal analysis of ablative materials is used in the design stage of the manufacturing cycle. At present many of the more advanced analytical models access mechanical properties of the material as a function of the degree of char or conversion rather than temperature.[2–5] The reason for this is that the material is thought to be capable of assuming a number of different chemical states at any one temperature. This is due to the time dependency of chemical reactions (kinetics), which makes the chemical state of the material a function of heating rate as well as temperature. Kinetics has been used to explain the reaction rate dependence on the time that is required for two reacting molecules to collide in favorable positions with sufficient energy to overcome the activation energy of the reaction, i.e., transition state theory. The use of steric factors to explain the kinetic dependence of decomposition reactions of a solid is, however, more obscure. Nevertheless, there are numerous published papers in the literature on the kinetics of pyrolysis reactions in polymers, and more specifically, phenolics.[6–23] Most have employed thermogravimetry to study this phenomena. The weight loss of the material as a function of temperature is assumed synonymous with the rate of chemical conversion. Shifts in the weight loss curve to higher temperatures as the heating rate is increased has been taken to indicate the degree to which kinetics play a role in the pyrolysis reactions.

Many of the studies, however, have utilized fairly slow heating rates,[6,7,9,12–14,17–21,23] (less than 100°C/min) with respect to the ablation process. This has forced analysts to extrapolate the data to the higher rates occurring in the use environment. Extrapolation has usually entailed employing kinetic models based on the Arrhenius equation. Many of the high heating rate predictions of these models suggest that the pyrolytic conversion of phenolic network polymers can be postponed to much higher temperatures than those typically observed at lower heating rates. This has had dramatic effects on the predicted mechanical response of the material under flight conditions and led to some skepticism about the validity of the models being employed.

To avoid the large extrapolations empirical data at higher heating rates needed to be obtained. In order to accomplish this a new facility was designed and built that is capable of obtaining data at substantially higher heating rates than are currently available. SC 1008 cured resin in powdered form was heated at eight heating rates ranging from 0.25 to 2500°C/min and the weight monitored as a function of temperature. The data was compared to previous studies on phenolic resin and phenolic based composites.

Materials and Methods

Powdered material from cured SC 1008 resin (Borden Industries) was used in this study. The resin was prestaged at elevated temperature to increase its viscosity. The material was then press cured as a 25-mm- (1.0-in.-) diam by 76-mm- (3-in.-) long cylinder under 6.9 MPa (1000 psi) of applied pressure at 190°C (375°F) for a minimum of 2 h in a hand press curing facility.[24] The cured cylinder was subsequently sliced normal to the axis of the plug into 6.35-mm (0.25-in.) specimens. One of these specimens was then totally converted to powder using a rotary grinding tool. The powder-producing process was done in such a way to minimize the frictional

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heating of the specimen. Several measures were taken to avoid contamination of the generated powder with machine oils and other extramaterial substances. The powder was sieved through a precleaned precision metal screen that retained all particles above 75 μm. The material that passed through the sieve was subsequently used in this study. Previous studies have indicated that this size fraction gives the most reproducible data[25] and can be expected to have the most uniform and predictable thermal gradient.

The newly constructed thermogravimetric facility uses a null-type microbalance (Cahn D101-02) with a sensitivity of 1 μg, weight capacity to 100 g, and duel weight ranges (1 and 10 g). Samples ranging from 7–11 mg were placed in a platinum pan suspended from the balance and the heater and reaction vessel raised and secured around the pan. A type-K thermocouple was positioned directly under the pan. The ambient gas in the reaction vessel was then evacuated and replaced three times with high purity Argon (5.0). A continuous Argon purge was then supplied to the reaction vessel at approximately 20 cc/min. The sample was heated radiantly with an electrical resistance heater that was located within the reaction vessel. Figure 1 shows a schematic drawing of the geometric relationship between the heater, thermocouple, and sample pan. Each run consisted of a 20°C/min ramp to 100°C, followed by a 10 min hold at 100°C, and finally a fixed ramp rate from 100 to 1000°C. Eight thermocouple controlled heating rates were employed in this study for the final ramp, i.e., 0.25, 3, 20, 100, 300, 500, 750, and 1000°C/min. Raw weights were corrected for buoyancy and aerodynamic forces[26,27] by running multiple runs at each heating rate with the pan empty. All weight losses were calculated based on an initial weight obtained immediately following the 10 min hold at 100°C. The data from each run of weight-corrected weight-remaining as a function of thermocouple temperature was fitted with a cubic spline and the first derivative of this curve generated. Each curve fit was overlaid on the raw data and examined to insure a good fit. The number of replicate runs at each heating rate was progressively increased from three to nine with increasing heating rate. Each set of replicate data by heating rate was weight-averaged to obtain the corresponding mean weight corrected *TG* curve. Mean derivative *TG* curves were produced in a similar manner.

Significant temperature differences were anticipated between the thermocouple and the sample. Furthermore, at the highest heating rates the thermal gradient within the sample was expected to be significant. In order to correct for these temperature differences, Curie point calibrations were conducted with five different metals as a function of heating rate. Over 230 such calibrations were performed for the seven highest heating rates. The temperature difference between the thermocouple and each Curie point metal (*TC* temperature − *CP* temperature) was plotted as a function of the thermocouple temperature. For heating rates above 300°C/min, extremes in the temperature differences accounted for by sample thermal gradients and test variability were each fitted with a curve. The mean weight corrected data was then temperature corrected once for the lowest difference between thermocouple and sample (1) and a second time for the largest difference (2) by subtracting the temperature difference between *TC* and sample (*CP*) at each thermocouple temperature.

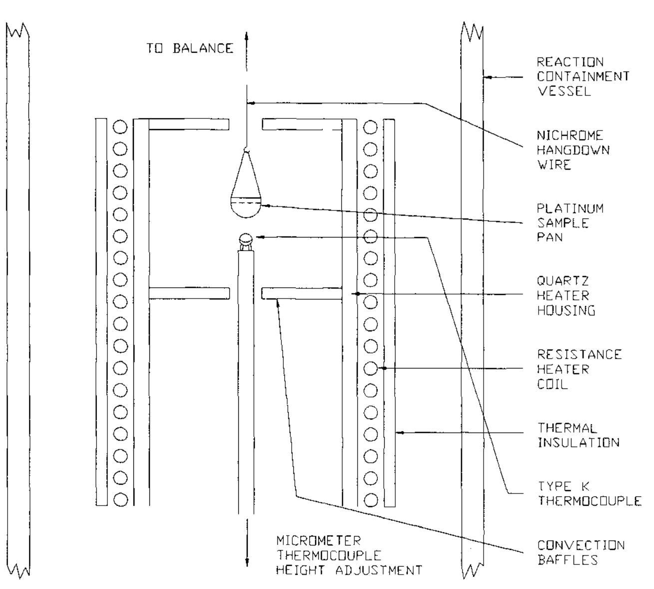

Fig. 1 Schematic of heated zone in high heating rate thermogravimetric facility.

Results

Because of the extensive data generated in this program to determine the actual sample temperature at the seven highest heating rates over a 900°C temperature range, this presentation will focus on the 1000°C/min (*TC*) data. Figure 2 shows a plot of the difference between thermocouple and Curie point temperatures as a function of the thermocouple temperature at a heating rate of 1000°C/min (*TC*). Arrows indicate the points that were used to fit the correction curves. A "1" represents the coldest recorded sample temperature (center of the sample), and a "2" represents the hottest recorded sample temperature (sample/pan interface). Note that these are not average differences between these locations and the *TC*, but extreme values used to bound the problem. The average material temperature can be expected to be somewhere between 1 and 2. Figure 3 shows the curve fits to these two sets of points. Figure 4 shows the calculated heating rates of the sample based on these corrections. Heating rates (extreme values) in the phenolic pyrolysis regime (400–600°C) ranged from 1700 to 3500°C/min. A representative sample heating rate of 2500°C/min (75°F/s) was chosen for the 1000°C/min (*TC*) data set. A similar process was performed on the 500 and 750°C/min (*TC*) data, and material heating rates of 650 and 1280°C/min were obtained, respectively. At heating rates below 500°C/min (*TC*), material heating rates were not significantly different from those of the thermocouple.

Figure 5 shows the most probable correction curves for the six other heating rates compared to the 1000°C/min (*TC*) data. Figure 6 shows the mean weight corrected weight remaining curves as a function of the thermocouple temperature and heating rate. Figure 7 shows the mean first derivative curves as a function of the thermocouple temperature and heating rate. Figure 8 gives the raw and corrected percent weight remaining curves for the 1000°C/min (*TC*) data. Figure 9 shows

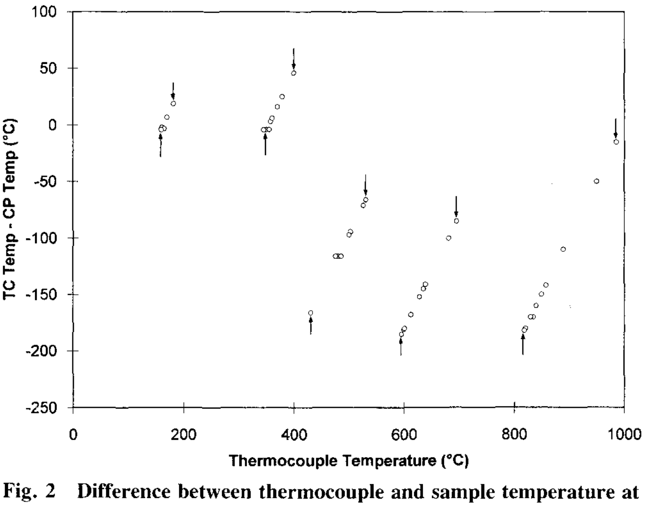

Fig. 2 Difference between thermocouple and sample temperature at 1000°C/min (*TC*).

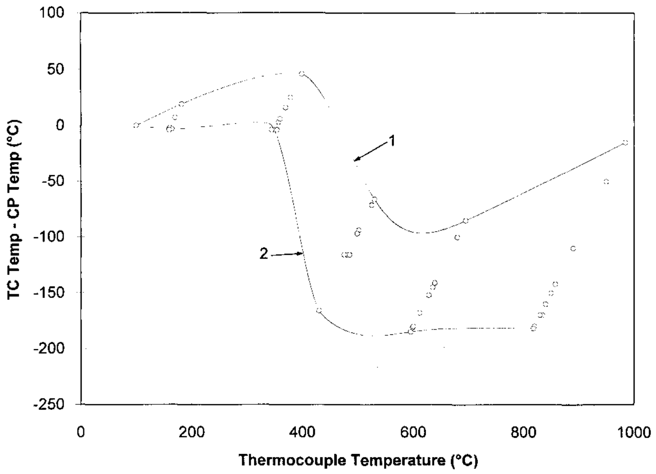

Fig. 3 Curve fits to extremes in 1000°C/min (*TC*) Curie point temperature correction data as a function of *TC* temperature.

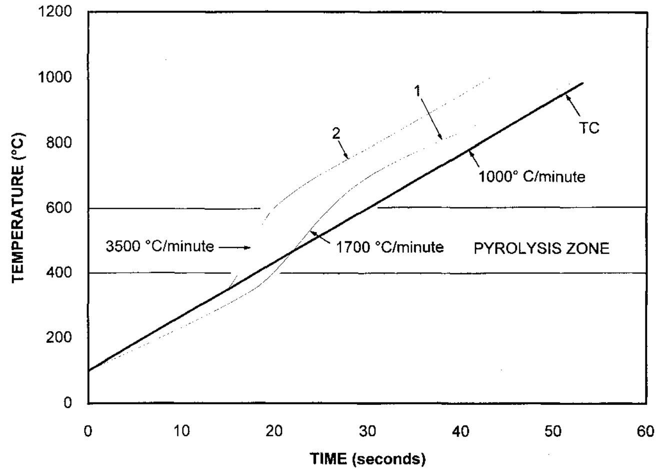

Fig. 4 Heating rates of the sample (extremes) and thermocouple based on Curie point correction data.

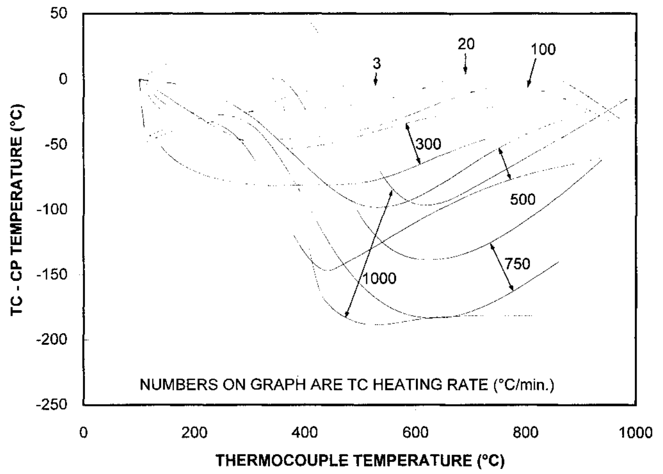

Fig. 5 Curie point correction data as a function of heating rate and thermocouple temperature.

the corrected sample data for the seven other heating rates compared to the 1 and 2 corrected 2500°C/min data. The kinetic effects at low heating rates (0.25–300°C/min) are clearly evident. However, there appears to be a transition between the 300–1280°C/min data, with the pyrolysis events of the latter occurring at lower temperatures than were observed with the former. The 2500°C/min data then appears to proceed in a kinetically driven manner, i.e., delayed to higher temperatures, from the 1280°C/min data.

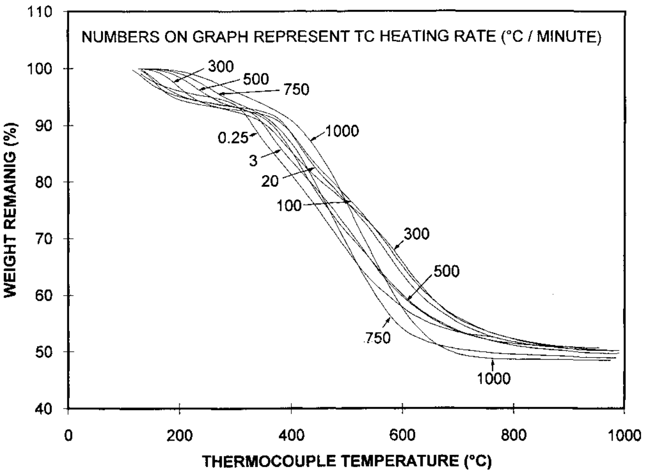

Fig. 6 Mean weight corrected *TG* curves as a function of *TC* temperature.

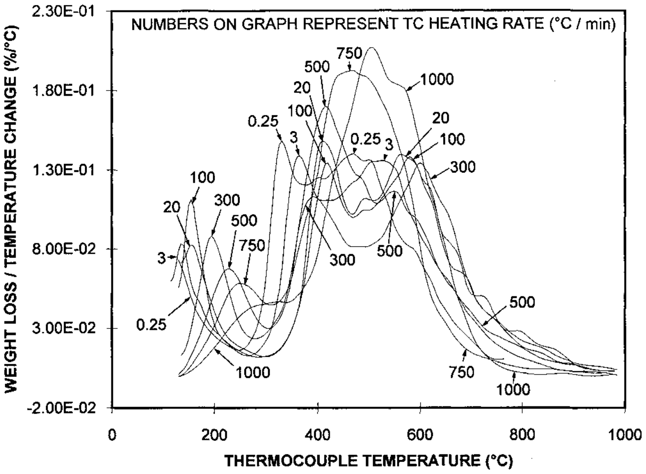

Fig. 7 Average weight-corrected derivative *TG* curves as a function of *TC* temperature.

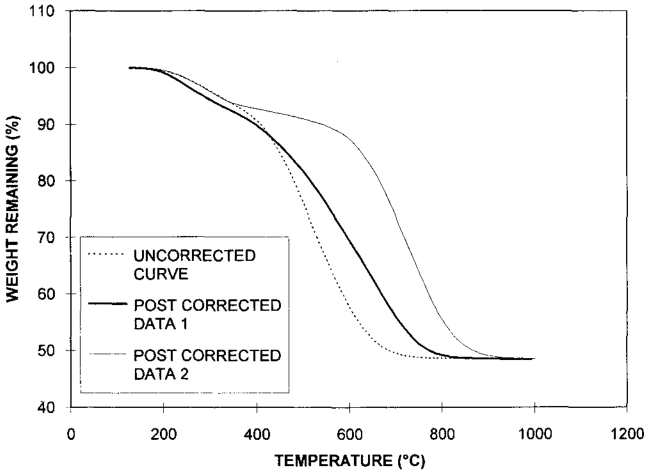

Fig. 8 Weight corrected and weight and temperature corrected weight loss data for 1000°C/min (*TC*).

Figure 10 gives the percent of post-100°C-hold weight remaining at 950°C as a function of the material's representative heating rate. The 95% confidence interval associated with each material heating rate data set is shown on the graph. Whereas, there is no apparent change in the char yield of the material over the range of low heating rates examined, 0.25–300°C/min, at heating rates in excess of 300°C/min there is a statistically significant, although small, reduction in char yield with increasing heating rate.

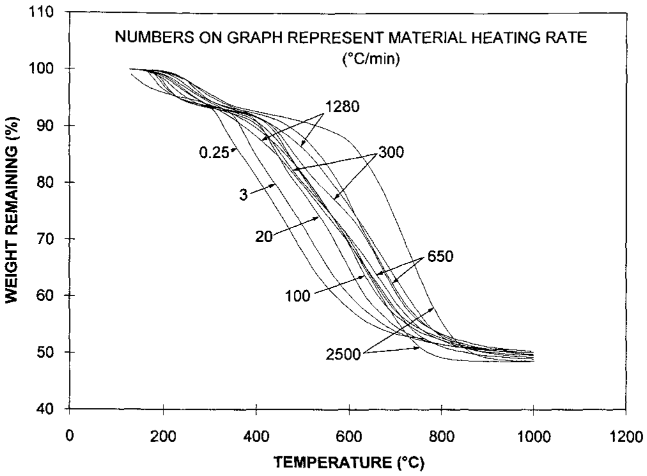

Fig. 9 Weight and temperature corrected weight remaining data as a function of material heating rate.

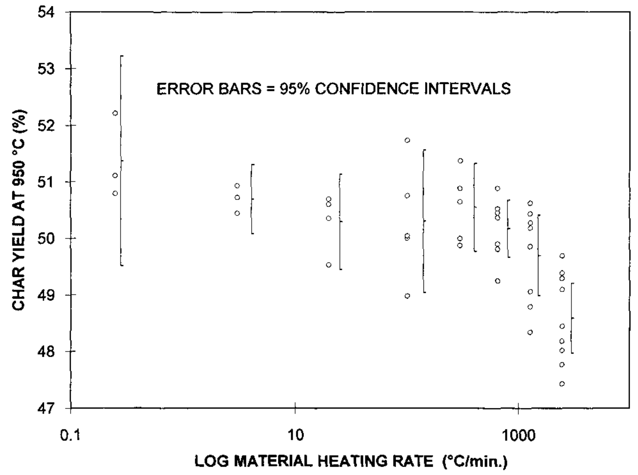

Fig. 10 Percent weight remaining at 950°C of SC 1008 resin heated at various heating rates in an inert (Ar, 1 atm) environment.

Discussion

The extrapolation of low heating rate data to higher use heating rates has been employed in the study of combustible solids,[28] unstable materials,[29] propellants,[30,31] and ablatives.[12,32] However, several authors have concluded that kinetic parameters calculated from slow rate data cannot be used to predict the rates of reactions at higher heating rates.[8,11,15,16,33,34]

In general, kinetic parameters *Ea*, *n*, and *A* or *Z* are obtained using slow rate or isothermal data and some form of the Arrhenius equation. These kinetic parameters are then employed to extrapolate to higher rates using the governing equation. Numerous methods have been developed and used to obtain these constants. They include differential,[12,35,36] integral,[37–42] ratio,[43] difference,[44] graphical,[45] numerical,[46] maximum point,[47–49] and parameter jump[50] techniques. One of the limitations of most of these methods is that the basic governing equation was developed to describe a single reaction. The kinetic parameters (*Ea*, *n*, and *A*/*Z*) obtained from such a system have specific chemical and physical meaning.

The pyrolysis of phenolic materials, however, involves multiple reactions.[31,32,50–56] More than 40 molecular species have been identified from the thermal decomposition of these materials.[10,12,21,23,48,49,51–57] Intermediate products in the decomposition of phenolics to volatiles are known to exist.[10,12,23,56,58,59] Furthermore, there appears to be no agreement in the literature as to whether these reactions are consecutively or simultaneously occurring and whether product competition is involved.[6,60–65] Some studies have reported a change in the type and quantity of pyrolysis products produced as the heating rate is varied.[9,23,66,67] Still others have found higher weight losses (lower char yield) with higher heating rates.[9,11] However, this has not universally been the case.[18] Finally, some researchers have reported that the kinetic parameters change with heating rate[9,17,68,69] and percent conversion.[6,12,15] For all of these reasons the use of a single set of kinetic parameters and the Arrhenius equation, in addition to generally having been found not capable of predicting pyrolysis reaction rates, is theoretically unjustified.

As a consequence, several researchers have attempted to develop more theoretically sound models. Models have been developed that describe the decomposition process as a set of parallel[70–76] and serial reactions[77] or account for the requirement of multiple bond breakage.[78] Still others have used techniques that employ conversion dependent activation energies[12,75,79,80] or a distribution of activation energies.[71,81–92] Finally, a method using time-temperature superposition that was initially developed to describe curing processes[93–96] has been extended to decomposition reactions.[74,97]

Figure 11 was created in order to compare the results of this study to the findings of others. This figure shows the temperatures at which SC 1008 experienced 50% of its total pyrolysis weight loss. Extremes in the data are plotted to show the boundaries of the data. Other values reported in the literature on cured neat and composite-based phenolics along with the reference from which the data was obtained are shown for comparison. It should be recognized that chemical formulation and processing conditions of the resin can play a major role in the decomposition kinetics of phenolics.[20,46,73,98,99] A significant number of additional data points at slow but undefined rates can be found in a paper by Learmonth.[20]

Figure 11 indicates that there appears to be a nonlinear relationship between the 50% weight loss temperature and heating rate at low heating rates. Much of the scatter in the data is undoubtedly due to the diversity of materials studied. At higher heating rates, i.e., somewhere between 300–1280°C/min, there was a discontinuity in the data. The temperature at which 50% of the pyrolysis weight loss occurs shifts to a lower temperature. At still higher heating rates, the 50% pyrolysis weight loss temperature once again increases with heating rate. Figure 9 shows this shift for the temperature corrected mean weight-averaged curves. Further evidence of this shift can be found in Fig. 7 where the typical three-hump response of the material at low heating rates changes to a two-hump response beginning with the 500°C/min (*TC*) derivative *TG* curve. This curve displayed a reduction in the height of the third peak and an increase in the height of the second. At heating rates of 750°C/min (*TC*) and above, the third peak is absent. The first peak in the response of this

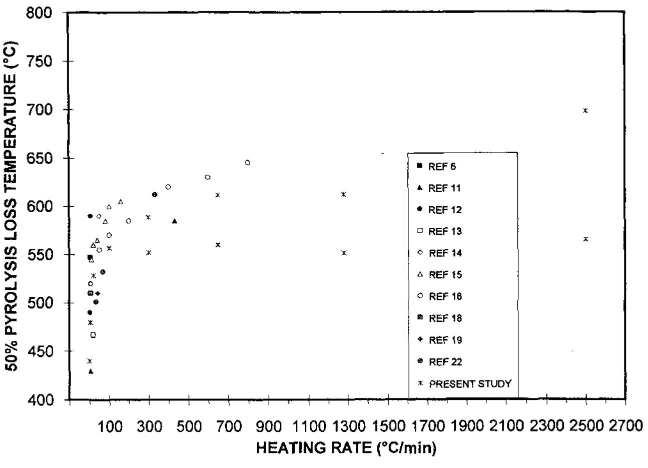

Fig. 11 Comparison of data from the present study and those from the literature on phenolic-based materials.

material is probably due to the evolution of high-temperature volatiles, e.g., bound water and phenol. It would appear from this data that the mechanism of the pyrolysis reaction changes as the heating rate is increased above 300°C/min.

An empiricist who employs new equipment and procedures should always suspect the fidelity of his data until there is sufficient evidence to exclude procedural aberrations. There are three pieces of evidence, in addition to those stated in the previous paragraph, that suggest these findings are not procedural artifacts, but in fact, a true reflection of the material's behavior. First, these findings have been corroborated with a second phenolic-based material (unpublished data). Second, there is a smooth progression in the temperature of the derivative weight loss first peak with heating rate (Fig. 7), i.e., the shift seen in the pyrolysis weight loss peak is not seen in the low-temperature weight loss peak. Finally, in a subsequent study on the dehydration and decarboxylation of calcium oxalate monohydrate using identical procedures, no shift of the weight loss curves was observed over the same range of heating rates (unpublished data).

Other researchers have attempted to measure the weight loss of phenolic-based materials at high heating rates. Boyle et al.[9] measured the gas pressure that developed in a closed container as 200-μm powdered carbon phenolic was heated at 7000°C/s. Temperature was monitored with an optical pyrometer. They interpreted the pressure that develops in the container of fixed volume as indicative of the moles of gas generated. The sample mass as a function of time was determined by digitizing the pressure curve within the limits of the starting mass (1–3 mg) and the mass of the char weighed after cooldown. In order to make this interpretation, they assumed that the average molecular weight of the mixture of gas species did not change with time/temperature, that the ideal gas law applies, that the pressure measured was not transport limited, that condensation on the room temperature pressure container was insignificant or occurred at a fixed rate, that there were no pressure effects on volatilization, that at the time of maximum pressure all the sample had been pyrolyzed, and that the average temperature of the gas was 295 K. Finally, at these extremely high heating rates, very small lags in the temperature measurement system can lead to significant errors in the interpretation of the data. It was not clear from the report whether the exact lag times had been determined.

Baer et al.[8] measured the weight loss behavior of a phenolic-acrylonitrile butadiene-boric acid film at 4200°C/min. Samples were heated at fixed rates to a desired temperature, then quickly quenched with a blast of cold nitrogen. Weight loss was determined by weighing the heated sample after it had cooled to room temperature and comparing this value to the starting weight. Temperature of the stainless-steel sample supporting foil was measured with an infrared thermometer. In addition to the limitations introduced by cooling down the sample and having to reweigh, there is some question in this author's mind as to the uniformity in temperature experienced by the film-like sample.

Still others have reported data at very high heating rates (1000–100,000°C/min) for other polymer systems,[66,76,100,101] most of which have entailed thin films deposited on electrically heated wires. Instead of residual weight measurements, evolved gas analysis was used to measure the rate of the pyrolysis reactions.

The usefulness of the data in the present study relates primarily to the fact that weight measurements were recorded directly and dynamically as the material was being heated. This eliminated the errors inherent in cooldown and indirect measurements of the sample mass.

Conclusions

The thermogravimetric response of 75-μm powdered samples can be reproducibly obtained at heating rates in excess of 2000°C/min.

At heating rates above 300°C/min, the char yield of the material is reduced by a small but statistically significant amount as the heating rate is increased.

The mechanism of the rate-dependent pyrolysis weight loss of cured SC 1008 resin appears to change as the heating rate is increased above 300°C/min. Pyrolysis mass loss shifts to lower temperatures as the heating rate increases and the reaction mechanism changes.

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