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MICROWAVE THERMAL ANALYSIS – A NEW APPROACH TO THE STUDY OF THE THERMAL AND DIELECTRIC PROPERTIES OF MATERIALS

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Abstract

This paper describes a new instrument for performing thermal analysis using microwaves both as a form of heating and as a novel means of detecting thermally induced transformations in materials. Results are presented for a selection of processes including decompositions, dehydrations and phase changes. The capability of the instrument to be coupled with ancillary techniques such as EGA is also demonstrated.

Keywords: dielectric properties, microwave heating, thermal analysis

Introduction

Conventionally, thermal analysis experiments are carried out using linear heating and cooling rates in electrically heated furnaces. These have the disadvantage that, as the heat is applied externally, temperature gradients are formed within the sample so limiting the resolution obtainable. Various strategies have been adopted to address this problem including low heating rates, the use of small samples (typically 1 to 20 mg) and the development of Sample Controlled Thermal Analysis [1].

Microwave thermal analysis (MWTA) confers several advantages. Most importantly, it provides a unique means of detecting thermally induced processes (i.e. melting, decomposition, phase change, etc.) via changes in the dielectric properties of the material. These changes can be observed from the shape of the microwave power profile obtained whilst heating a sample at a linear rate. Microwaves heat by direct interaction with the sample (rather than by conduction of heat as in conventional thermal analysis) and can penetrate up to about 2 cm. This allows the study of samples with masses up to 0.5 g, as the uniform application of heat helps reduce temperature gradients, so providing sufficient material for subsequent analysis by other techniques.

Previous attempts to use microwaves (as a form of heating) in thermal analysis include the early work of Karmazin *et al.* [2, 3] who studied the dehydration of calcium hydrogen phosphate dihydrate and the decomposition of zinc acetate. More recently, Ravindran *et al.* [4] monitored the temperature of coal samples while they

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were irradiated but made no attempt to control the heating rate. The current work on the use of the microwave power profile as a means of detection is a development arising from preliminary studies [5] performed by one of the authors.

Theory

The extent to which a material is heated when subjected to microwave radiation depends on two critical parameters, the dielectric constant, ε', and the dielectric loss factor, ε''. The dielectric constant describes the ease with which a material is polarized by an electric field, while the dielectric loss factor measures the efficiency of conversion of the electromagnetic radiation to heat. Both ε' and ε'' vary with frequency, with latter reaching a maximum, as the dielectric constant falls, in the microwave band of the electromagnetic spectrum [6]. The ratio of the two gives the dielectric loss tangent:

$$\tan\delta = \varepsilon''/\varepsilon'$$

which defines the ability of a material to convert electromagnetic energy into thermal energy at a given temperature and frequency. The dielectric properties of a material are also dependent on its atomic/molecular geometry. Therefore, any thermally induced changes causing molecular or structural rearrangement will affect $\tan\delta$ so forming the basis of a means of detection.

To obtain the linear increasing temperature required for thermal analysis it is necessary to continuously adjust the microwave power as $\tan\delta$ alters smoothly, but nonlinearly, as a function of temperature. Changes in $\tan\delta$ caused by thermally induced transformations in the sample will necessitate a more abrupt increase or decrease in the microwave power to maintain the desired linear heating rate. These latter power changes appear either as a discrete step or a complex peak thus providing qualitative information on the associated process.

Experimental

The majority of workers utilising microwave heating in chemistry use *multimode* instruments. These are broadly similar to domestic microwave ovens in operation with microwaves being launched into a cavity where they reflect off the walls and through the sample at random angles. Typically, these devices use pulse-width modulation with on/off cycles in the order of seconds which does not allow the power to be adjusted with sufficient accuracy necessary for thermal analysis.

In this work a *single-mode* device is used with the microwaves launched coherently into a rectangular waveguide tuned to set up a standing wave. The sample is positioned so as to be at a peak maximum of the electric component of the microwave field. A continuously variable microwave generator permits the fine adjustment of power essential if controlled heating of the sample is to be achieved.

A schematic diagram of the microwave thermal analysis apparatus is shown in Fig. 1. It comprises a high stability, narrow-band 2.45 GHz generator (Sairem)

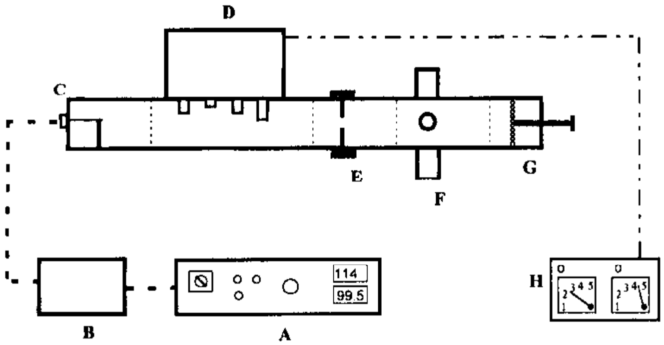

Fig. 1 Schematic cross-section of waveguide and principle associated components of the MWTA system. A – microwave generator, B – water-cooled dummy load, C – microwave launcher, D – 4-stub tuner, E – variable iris, F – 4-port sample section, G – plunge tuner, H – 4-stub control unit

whose power output can be varied in 1 steps to 300 W under computer control using a RS232C serial interface. From the generator the microwaves are passed via a water-cooled circulator, used to prevent reflected power from damaging the magnetron, to a launcher incorporated into a type 340 brass waveguide (internal dimensions 86 by 43 mm). The material to be analysed is situated in the sample section of the waveguide which has four circular ports, two vertical larger ports (diameter 50 mm) to allow insertion and removal of the sample, and two smaller horizontal ports (diameter 15 mm) to allow access for a temperature measurement device. These ports have cylindrical extensions of over twice their diameter to prevent microwave leakage.

The short circuit or 'plunge tuner' is used to alter the internal length of the waveguide to produce a standing wave with a maximum in the electric field in the centre of the sample section. A variable iris, consisting of a thin copper sheet with a rectangular orifice (50 by 25 mm), can be positioned over a range of 10 cm along the waveguide to produce multiple reflections of the microwaves thus maximising the power absorbed by the sample. An automated four-stub tuner comprising four cylindrical rods whose vertical positions in the waveguide are continuously altered to minimise the reflected power is also employed. It provides 'fine-tuning' to account for any small alterations in the system produced by changes in the dielectric properties of the sample as it is heated.

A variety of sample cells have been developed for this work. Typically, these have been constructed from either boro-silicate or silica glass depending on the temperature range used, but designs using ceramics have also been investigated. The dimensions and configuration of the cell used is largely determined by the type of experiment to be undertaken and designs, described in detail elsewhere [7], for performing MWTA experiments on sample masses from 5 to 500 mg have been constructed. Other, more specialised, cells for microwave assisted DTA and EGA have also been developed. Generally, the cells need a high degree of symmetry to prevent uneven distortions of the microwave field.

The suitability of a variety of temperature measuring devices was investigated, including optical pyrometers and IR fibre-optic probes. However, 0.5 mm diameter stainless steal sheathed thermocouples were eventually adopted as the principle form of temperature measurement. Our findings confirm those of Karmazsin *et al.* [8] in that thermocouples can be used in a single mode cavity with negligible microwave leakage providing that they are sufficiently thin, shielded and located perpendicular to the electric field. The thermocouple is positioned, via one of the side ports, through a suitable inlet in the sample cell directly in the material for good temperature measurement.

Data acquisition and control is performed using software written by the authors and runs under the Windows 95 (Microsoft) operating system on a 133 MHz IBM compatible PC. The software was developed using Visual Basic (Microsoft Visual Basic 4.0) with compiled routines written in C (Microsoft Visual C++ 1.52) incorporated to handle mathematically intensive tasks. The thermocouple(s) are read via a 16-bit ADC (Strawberry Tree, DynaRes-8-Ultra) which also is used to interface to other devices such as EGA detectors. The microwave power is set by commands sent from the computer to the generator via a RS232C serial connection.

Three basic types of heating experiment can be performed.

a) Constant power. A fixed microwave power level is set between 0 and 300 W and the sample temperature is monitored as a function of time. This is the simplest form of experiment which can reveal changes in tanδ with temperature.

b) Linear power. The microwave power is ramped at a pre-set rate (e.g. 2 W min^{-1}) and the sample temperature monitored.

c) Linear heating. The microwave power is altered as required to maintain a pre-set heating rate. Experiments using up to three heating/cooling ramps with variable length isothermal periods can be performed and controlled heating has been achieved with rates between 0.5 and 50°C min^{-1}. Performing linear heating experiments using microwaves is considerably more difficult than is the case with conventional furnaces. This is because the sample is heated directly and has both a relatively low thermal mass and a changing, perhaps rapidly so, ability to couple with the microwave field. A sophisticated algorithm incorporating a 3-term PID routine has been developed to provide the temperature control necessary to allow the power profile to be used as a method for investigating physiochemical changes in the sample.

All the experiments described below were performed under static air except for the EGA experiment which used helium (BOC) with a flow rate of 30 $\text{cm}^3\ \text{min}^{-1}$ and hot-wire katharometer (thermal conductivity detector) to monitor carbon dioxide. A cold-trap prior to the katharometer was used to remove any evolved water.

Results and discussion

The temperature profiles for a 60 mg of boron nitride (Aldrich) heated in a borosilicate cell using three different constant power experiments are shown in Fig. 2. Boron nitride was selected as it couples strongly with microwaves and is thermally inert over a wide temperature range. It can be seen that the sample temperature for the lowest power experiment (curve a, 120 W) rises only slowly before levelling off

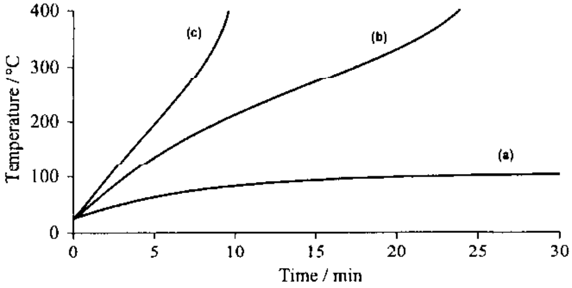

Fig. 2 Heating of 60 mg of boron nitride using power levels of a) 120 W, b) 135 W and c) 165 W

to attain an equilibrium of approximately 80°C. In contrast, the sample temperature for the highest power experiment (curve c, 165 W) rises in an approximately linear manner until around 300°C where the rate of temperature increase becomes progressively more rapid. The temperature profile for the middle power experiment (curve b, 135 W) is intermediate between that for a) and c). The rate of temperature rise appears to be slowing up to approximately 200°C, but at higher temperatures the rate starts to increase again. These results demonstrate that the relationship between applied microwave power and temperature are complex as the tanδ of a material itself increases with temperature. This increased coupling can lead to a 'thermal runaway' effect depending on the initial temperature and the counteracting effect of heat losses to the surroundings.

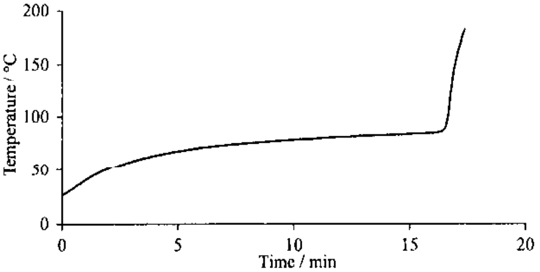

Fig. 3 Temperature profile obtained for the melting of benzil (α,α-dimethoxy-α-phenylacetophenone) using a constant power of 105 W

The temperature profile of a 250 mg sample of benzil (α,α-dimethoxy-α-phenylacetophenone, BDH, laboratory grade) heated in a boro-silicate cell in static air using a constant power of 105 W is shown in Fig. 3. Initially the temperature rises slowly and levels off in a similar manner to curve a) in Fig. 1. However, after approximately seventeen minutes the temperature rises rapidly, increasing by over 100°C in approximately one minute. This sudden jump in temperature is caused by the increase in tanδ as the material melts, and demonstrates the potential sensitivity of MWTA for the study of certain reactions involving fusion.

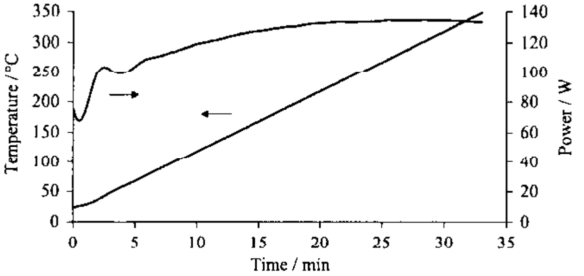

Fig. 4 Power and temperature profiles for 60 mg of boron nitride showing the achievement of a linear heating rate of 10°C min^{-1}

The power profile obtained when heating a 60 mg sample of boron nitride in a boro-silicate cell at 10°C min^{-1} is shown in Fig. 4. It can be seen that, apart from some initial small variations at the onset of the experiment, the power profile required to maintain the linear heating rate is smooth and featureless. Note how the power levels off, and even begins to fall slightly, at higher temperatures, again due to the effect of increased coupling with increasing temperature described above.

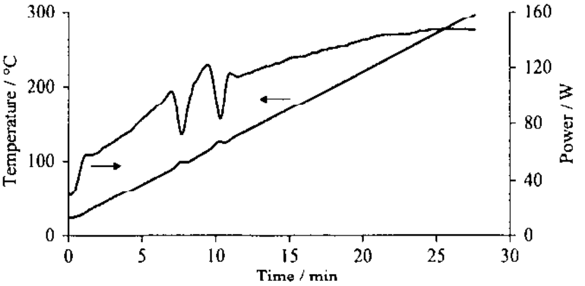

Fig. 5 Power and temperature profiles obtained with a 15 mg sample of copper sulphate pentahydrate heated at 10°C min^{-1}

The power profile obtained when heating a 15 mg sample of copper sulphate pentahydrate (Aldrich) in a boro-silicate cell at 10°C min^{-1} is shown in Fig. 5. The overall power profile is of a similar shape to that for boron nitride shown in Fig. 4, but with two pronounced events which occur centred on 90 and 120°C. These changes in the power profile arise in response to the effect of the two dehydration stages which occur at these temperatures. At first sight the power profile in this region might suggest that, as the power level needs to fall to maintain the heating rate, the dehydration stages are somehow exothermic. However, a more detailed examination shows that prior to each downward peak there is a small *increase* in the power caused by the requirement to put energy into the system to drive the endothermic dehydration processes. We provisionally attribute the subsequent large *decrease* in the power arises, not from the energetics of the processes, but because either liquid water is released or there is an intermediate stage with loosely bound water which couples very strongly with the microwave field. The latter explanation is more probable for the second event at 120°C, where the presence liquid water is unlikely. The power increases again after each dehydration stage because as the water is lost through evaporation the overall tanδ of the partially hydrated material falls. The loss of the fifth molecule of water, typically seen as a broad peak around 220°C with conventional DTA, has only a very small effect on the power profile. This is presumably because the water is lost directly as steam at this temperature and suggests that the dielectric properties of the monohydrate are very similar to that of the anhydrous material.

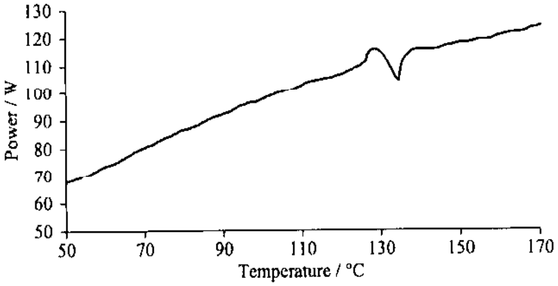

Fig. 6 Power profile plotted as a function of temperature showing the phase change in a 10 mg sample of potassium nitrate heated at 10°C min^{-1}

The power profile plotted as a function of temperature obtained from a 10 mg sample of potassium nitrate (Aldrich AnalaR) heated at 10°C min^{-1} in a boro-silicate cell is shown in Fig. 6. The phase change at 130°C is revealed by a complex peak which we provisionally interpret as follows. Initially, the power increases due to the endothermic nature of the phase change. When the phase change is complete the power is at a level higher than is required to maintain the set heating rate and the power falls quickly before returning to its 'baseline' value. The power 'undershoot' does not appear to be due to poor control as it has been observed for other, but not all, solid-solid phase changes. Possibly in this case the transition stage between phases has a greater value of tanδ. The fact that the power profile before and after the phase change lie on a smooth curve would suggest that there has been no overall significant change in the dielectric properties of the material.

The decomposition of 125 mg of a 1:1 w/w mixture of sodium hydrogen carbonate (BDH) and copper hydroxycarbonate (BDH) heated at 10°C min^{-1} is shown in Fig. 7. Two profiles are shown as a function of temperature. The upper profile shows the power level required to maintain the set heating rate, while the lower profile is the output from a katharometer. The power profile is interesting as it shows two distinct kinds of process which can be revealed by MWTA. The first event centred on 150°C corresponds to the decomposition of the sodium hydrogen carbonate. The power profile shows a complex peak, similar to that seen for the phase change de-

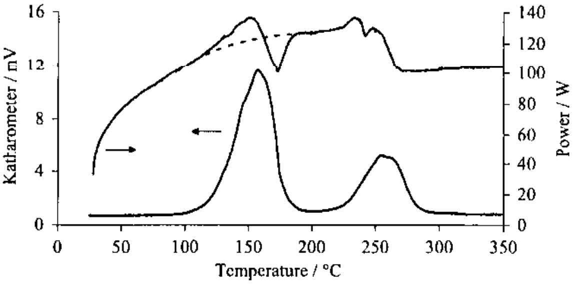

Fig. 7 Power and katharometer profiles plotted as a function of temperature showing the decomposition of 125 mg of a 1:1 mixture of sodium hydrogen carbonate and copper hydroxycarbonate heated at 10°C min^{-1}

scribed above, which suggests that the process is endothermic but with little overall change in dielectric properties between starting material and product. The corresponding katharometer peak shows the expected evolution of carbon dioxide for this process and, at first sight, it may appear that gas is being evolved prior to any changes in the applied power. However, with the aid of a constructed baseline (shown as a dotted line) corresponding to the power profile should no event have occurred, it can be seen that the initial deviation in the applied power does indeed correlate with the onset of the katharometer peak.

The second event centred on 250°C corresponds to the decomposition of the copper hydroxycarbonate. The power profile here is markedly different from that shown by the sodium hydrogen carbonate. There is an initial increase in the power due to the endothermic nature of the decomposition, but this is followed by an overall fall in the power which remains even after the process has reached completion (as revealed by the katharometer). This 'step' in the power arises because the product of the decomposition, copper oxide, couples more strongly with the microwave field than the hydroxycarbonate starting material.

A small downward peak can be clearly seen in the overall step change in the power profile for this latter process. This event has been consistently observed for this particular copper hydroxycarbonate and corresponds to some, currently unexplained, process barely visible on the katharometer trace.

Conclusions

The results presented in this paper demonstrate that, by the use of a suitable control algorithm, it is possible to achieve the controlled heating necessary for thermal analysis using microwaves. Under these conditions it is possible to use the shape of the power profile as a novel probe to characterise the changes in dielectric properties of a material as a function of temperature.

MWTA has been shown to be applicable to a wide range of processes including decompositions, phase changes and dehydrations, and the flexibility to couple the instrument with ancillary techniques such as EGA has been demonstrated. In some materials the change in tanδ may be relatively large compared to the parameter (i.e. mass loss or energy change) detected by other thermal analysis techniques and so be the basis of enhanced sensitivity.

Future work will focus on the potential for quantitative as well as qualitative analysis [9], and the scope for performing differential techniques, such as DTA, using microwave heating. We have also demonstrated the potential of other, more advanced, heating strategies such as modulated microwave TA which are being further developed.

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