Combined microwave/conventional-heating calorimetry

D M Price, J G P Binner, M Reading & B Vaidhyanathan
IPTME, Loughborough University, Loughborough, UK

Abstract

A calorimetric device intended to study the 'microwave effect' – an apparent acceleration in kinetics or lowering of transition temperatures in inorganic and organic systems under the influence of microwave radiation – is being developed. Previous studies have often compared experiments where the thermal energy has been supplied using conventional heating and microwave power in different equipment. This leads to uncertainties in temperature measurement and calibration of the instrument which make direct comparison of results problematic at best. This work will introduce the design of a calorimetric apparatus which overcomes existing problems by using microwave-inert temperature sensors and the potential for combined microwave and conventional heating in the same apparatus. Novel to this work is the means to operate the device as a modulated temperature calorimeter so that heat capacity changes can be monitored independently of latent heat effects. Such an approach is capable of overcoming the problems discussed above and preliminary results will be presented which illustrate the utility of this method.

Introduction

Many investigators have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials. This has included apparent evidence for accelerated kinetics for a range of processes in ceramic, polymeric and organic systems; enhanced sintering of ceramic powder compacts, including lower sintering temperatures and reduced activation energies [1]. It is now generally, though not unanimously, accepted that a 'microwave effect' exists. The primary reasons for any remaining uncertainty are:

i. The inability to vary the energy source without simultaneously affecting a wide range of other variables. For example, whilst microwave heating experiments are performed in a microwave applicator the corresponding conventional experiments are typically carried out in a separate, radiant furnace of totally different specification (e.g. power level).

ii. Uncertainties associated with temperature measurement. Pyrometry is often used with microwave heating whilst thermocouples are used in the conventional experiments. When a single technique is used, it is usually a shielded thermocouple - although the presence of the metallic shielding is known to distort the local microwave field [2]. Finally, the surface temperature is usually measured. With conventional heating this will be the hottest part of the specimen, whilst with microwave heating it will be the coolest. This leads to difficulties in making a direct comparison of data.

In this work we propose a novel design of calorimeter which combines conventional and microwave heating in a single device. The temperature and heat flow monitoring system does not interact with the R.F. field and thus measurements can be made with a combination of energy inputs from 100% conventional to 100% microwave power.

Design Strategy

The components of the apparatus are be broken down into distinct units for further discussion. All but the microwave cavity itself have been built and tested at the time of writing.

Temperature and heat flow sensing

Two approaches for temperature and heat flow sensing have been explored:

i. Gas thermometry: Bond *et al.* have described the design and construction of a simple constant volume gas thermometer for temperature sensing in a microwave field [2]. We have extended this approach to incorporate a differential arrangement by using nested concentric cylinders of glass. The sample is contained within the innermost chamber and is completely surrounded by the first jacket which measures its temperature. A second jacket surrounds the first one and the pressure difference is used to measure the heat flux between the sample and the environment. This device was used as a titration calorimeter by monitoring the stepwise addition of 0.1 ml aliquots of 1 M aqueous NaOH to the cell containing 1 ml of 1 M aqueous HCl. Each addition of alkali results in evolution of heat (in total 0.0571 J [4]) which decreases at the end point of the neutralisation reaction (figure 1). The main drawback with this type of design is the time response of the high thermal mass cell, although the principle might be revisited for high temperature applications.

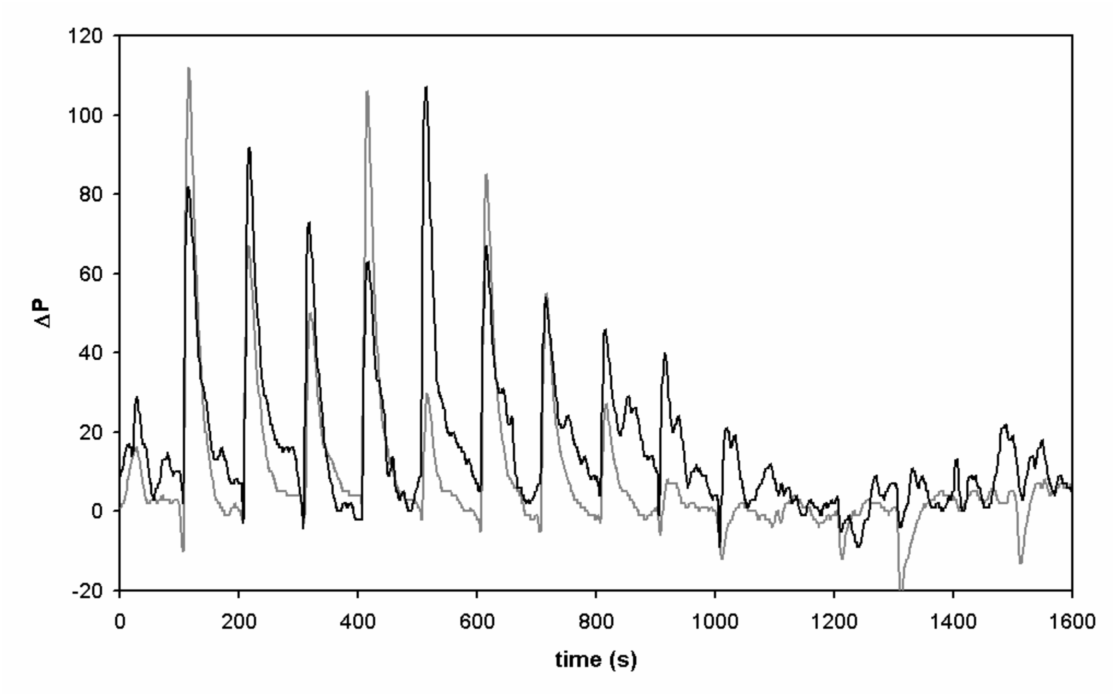

Figure 1. Calorimetric titration of 1 ml of 1 M HCl with 1 M NaOH. Alkali added in 0.1 ml steps every 100s (replicate measurements shown).

ii.. Fluoroptic thermometry: This relies on the principle that the decay time of a phosphorescent material excited with light depends on its temperature. Light from a xenon discharge tube is passed down an optical fibre onto a phosphor and the resulting emitted light is measured. The rapid time response of such sensors (<1 s) makes them ideal for our application and a differential arrangement of one or more sensors is a practical proposition for measuring heat flows. The maximum operating temperature of these probes is limited by the type of binder used to coat the probe with phosphor (300°C) and the ability of the electronics to monitor the decay curve (which becomes shorter with increasing temperature).

Conventional heating system

Previous workers have employed only pure microwave power to examine specimens although in some cases the sample has been mixed with or surrounded by a susceptor material which provides additional thermal energy to the sample via is own intrinsic absorption of R.F. energy [5-8]. There is little ability to control the ratio of conventional to microwave induced heating of the sample.

We propose to use a hybrid approach in which conventional heating is provided using a stream of heated gas injected into sample chamber. This affords a means of heating the sample without using a heated cavity itself. Furthermore, we can oscillate the temperature of the gas stream so as to construct a modulated temperature calorimeter [9] which will enable us to measure heat capacity quasi-isothermally [10] as the contribution to the sample's temperature by a constant microwave field is varied. Some preliminary results for a sample of poly(methyl methacrylate) are shown in figures 2 and 3. Figure 2 shows the modulation of the heated gas temperature and the corresponding response of the sample temperature. Although the data is noisy, the amplitude of the sample temperature can be determined over many cycles. Taking the ratio of amplitudes of the gas temperature to that of the sample allows the apparent heat capacity (which could be calibrated) to be determined. A plot of this parameter *versus* temperature is shown in figure 3 illustrating the detection of the glass-rubber transition of the polymer around 107°C consistent with the frequency dependent nature of this process [11].

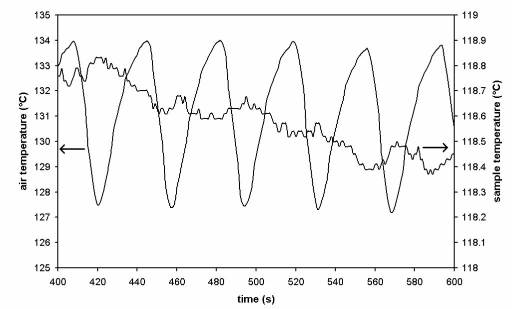

Figure 2. Time-temperature profile of gas stream and sample temperature.

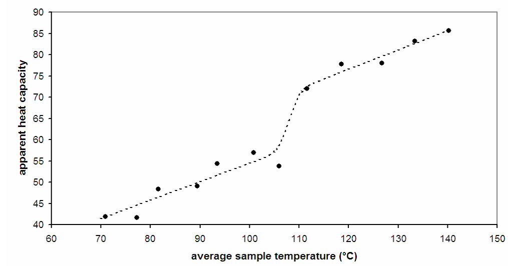

Figure 3. Apparent heat capacity of PMMA derived from data such as shown in figure 2 from a series of isothermal measurements.

Microwave heating system and calorimeter design

A schematic diagram of the microwave cavity and calorimeter cell is shown in figure 4. We have chosen to employ a cylindrical TM_{010} cavity fed by a conventional rectangular TE_{10} waveguide. Moveable, motor-driven end caps to the top and bottom of the cavity are incorporated to assist with tuning. The heated gas stream enters and exit through chokes in these assemblies. The sample temperature will be measured via a fluoroptic probe as described earlier. This part of the apparatus is currently under construction.

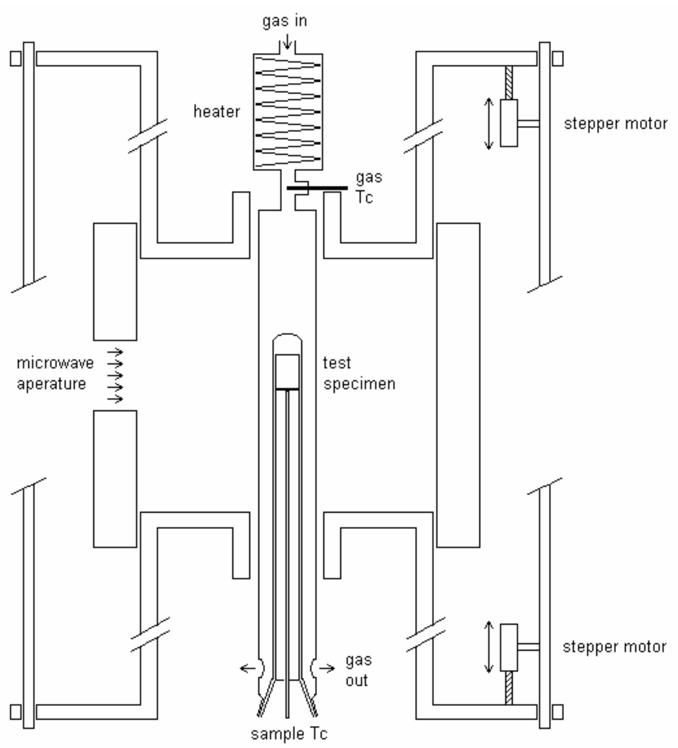

Figure 4. TM010 cavity and sample holder design (schematic).

Conclusions

This paper outlines the design and construction of a hybrid microwave and conventionally heated modulated temperature calorimeter. Preliminary results that illustrate the proof of concept of component parts of the apparatus have been presented and the authors are confident that the finished equipment will be able to answer many of the questions surrounding the 'microwave effect'.

References

1. Bykov Y.V., Rybanov K.I. and Semenov V.E., *J Phys. D*, **34** (13) R55-R75 (2001)
2. Pert E., Carmel Y., Birnboim A., Olorunyolemi T., Gershon D., Calame J., Lloyd I.K., Wilson O.C., *J. Am. Ceram. Soc.*, **84** [9] 1981-1986 (2001)
3. Bond G., Moyes R.B., Pollington S.D. and Whan D.A., *Meas. Sic. Technol.*, **2** 571-572 (1991).
4. Stark J.G. and Wallace H.G., *Chemistry Data Book (S.I. Edition)*, John Murray, London (1970).
5. Parkes G.M.B., Barnes P.A., Charsley E.L and Bond G., *Anal. Chem.*, **71** 5026-5032 (1999).
6. Parkes G.M.B., Barnes P.A., Charsley E.L and Bond G., *J. Thermal Anal.*, **56** 723-731 (1999).
7. Parkes G.M.B., Bond G., Barnes P.A. and Charsley E.L., *Rev. Sci. Instrum.*, **71** [1] 168-175 (2000).
8. Parkes G.M.B., Barnes P.A., Bond G. and Charsley E.L., *Thermochim. Acta*, **356** 85-96 (2000).
9. Royall P.G., Craig D.Q.M., Reading M., Lever T.J., J. Thermal Anal. Cal., **60** [3] 795-805 (2000).
10. Sullivan P.F. and Seidel G., *Phys. Rev.*, **173** [3] 679-685 (1968).
11. Birge N.O., *Phys. Rev. B*, **34** [3] 1631-1642 (1986).