



THE USE OF MODULATED TEMPERATURE PROGRAMS IN THERMAL METHODS

M. Reading

IPTME, Loughborough University, Loughborough, Leicestershire LE11 3TU, United Kingdom

Abstract

Temperature modulation has long been used in various aspects of thermal methods. Historically, the principle areas of application have been the determination of kinetic parameters using variants of the temperature jump method and the measurement of heat capacity by AC calorimetry. More recently the introduction of temperature modulation in a variety of techniques has been used in combination with deconvolution algorithms to separate sample responses that are dependent on rate of change of temperature from those principally dependent on temperature. Finally, temperature modulation is important in the new field of micro-thermal analysis.

Keywords: dielectric analysis, kinetics, micro-thermal analysis, modulated temperature differential scanning calorimetry, modulated temperature, temperature jump, thermo-mechanical analysis

Introduction

The first question that must be addressed is what does modulation mean in the context of temperature programming. Here we will use the definition that it means the periodic perturbation of an underlying temperature program. The perturbation might be a square wave, a sine wave or some more complex wave function, but it must repeat a number of times during the course of the transition being studied. Modulations of this kind have been in use for some time in the study of kinetics and this is the first category of applications that will be considered here. AC calorimetry is based on measuring the amplitude of temperature variations caused by periodic heating of a sample either by exposure to light or electrical heating. This technique has been in use for over two decades and is the subject of the second category of applications. The third category deals with a collection of techniques where a response is elicited from a sample by using (usually) a rising temperature programme combined with a modulation. The data from the sample response is then analysed using a deconvolution algorithm designed to separate out that part of the response that is a direct function of heating rate from any other response that is occurring (and will usually be a direct function of temperature). The most widely used technique of this type is modulated temperature differential scanning calorimetry (MTDSC) where the heat capacity component,

which scales directly with heating rate, can be separated from other processes that are occurring. The final category will consider the uses of temperature modulation in the new field of micro-thermal analysis.

Kinetic studies

The temperature jump method was used in classical kinetic studies [2] before being applied in what we would recognise today as ‘thermal analysis’ [8]. In its simplest form the temperature is suddenly increased and the reaction rate immediately before and immediately after are measured. The analysis is based on the Arrhenius equation viz:

$$d\alpha/dt=f(\alpha)Ae^{-E/RT} \quad (1)$$

where α – the ‘extent’ of the reaction, t – time, $f(\alpha)$ – some function of extent of reaction, A – the pre-exponential constant, E – the activation energy, R – the gas constant, T – absolute temperature.

In Fig. 1 the temperature jump experiment is illustrated. Using the quantities defined in that figure, assuming negligible change in α over the interval of the jump and given

$$dM/dt \propto d\alpha/dt \quad (2)$$

where M – mass manipulation yields;

$$E=R\ln[(dM/dt_1)/(dM/dt_2)]/(T_2-T_1)/T_1T_2 \quad (3)$$

These jumps can be imposed in a continuous cycle thus enabling many values of E to be determined over the course of the reaction.

An alternative to the temperature jump method is the rate jump [6]. This is illustrated in Fig. 2. It relies on a control system that regulates the rate of mass loss rather than programming the temperature as a function of time. The rate of mass loss is cycled between a high and a low rate until the reaction is complete. Details of the techniques used to achieve this type of regulation can be found in [1, 4, 5, 13, 16, 19, 20, 39]. Although the controlled parameter is rate of mass loss, as this jumps from one value to another, a temperature jump is also achieved in each case. The method of calculation of the activation energy is exactly the same as for the temperature jump experiment and successive cycles again mean that values for the activation energy can be calculated as a function of extent of reaction [12]. The advantages of using the rate jump method compared to the temperature jump approach and have been discussed in a recent review [40]. Notwithstanding this, both methods are essentially an application of the same principle.

More recently a sinusoidal modulation has been used [33]. The amplitude of the modulations in temperature and dM/dt are determined using a Fourier transform and the activation energy is calculated as follows:

$$E=(\langle T^2 \rangle + U^2)\ln((\langle dM/dt \rangle - V)/(\langle dM/dt \rangle + V))/2U \quad (4)$$

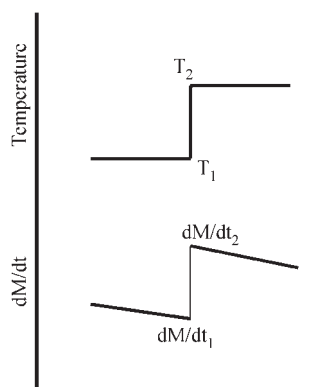


Fig. 1 The temperature jump experiment used with thermogravimetry

where $\langle \rangle$ designated the average over one or more cycles of the modulation, U – half the amplitude of the temperature modulation, V – half the amplitude of the dM/dt modulation.

Again values for the activation energy can be calculated as a function of extent of reaction.

All three methods are variations on the same theme and can be used to determine reliable values for activation energies provided they are used with care. In this context the problems discussed by Reading *et al.* [14]. With regard to the influence of product gas pressure influencing apparent activation energy should be noted. The worst combination of circumstances is low temperature and high product gas pressure and this may occur in these experiments because the high product gas pressure associated with the fast reaction rate may still be present during the slower rate when the temperature is stepped down. This might lead to erroneous results. If this problem can be avoided then temperature modulation is a valuable tool for determining activation energies especially in complex systems.

AC calorimetry

AC calorimetry has been used since 1962 [3]. A useful review of AC calorimetry has been provided by Hata [9]. In this technique one side of a sample is heated by either incident light or by an electric heater while temperature changes are measured on the other side. Sawtooth or sinusoidal modulations are used and the amplitudes of the temperature changes are measured using a lock-in amplifier. With appropriate calibration, these can then be related to heat capacity. A phase signal can generally also be measured in this type of experiment which then leads to the possibility of calculating a complex heat capacity with an in phase (real) and out of phase (imaginary) component.

This type of experiment is useful for measuring changes in heat capacity as a function of temperature. It has found applications for measuring with high precision transitions such as three dimension magnetic phase transitions, two-dimensional

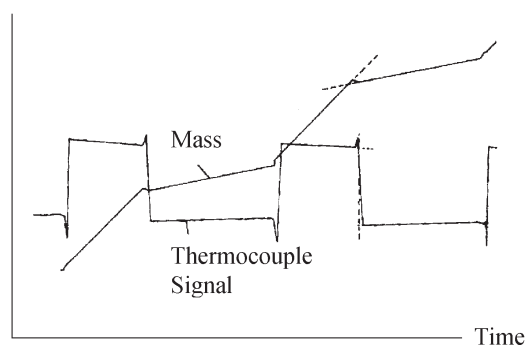


Fig. 2 The rate jump method used with thermogravimetry

antiferromagnetic phase transition or gel to liquid transitions in liposomes. However, this type of measurement is insensitive to the heat flows that arise as a consequence of chemical reactions, crystallization events, loss of volatile material etc. and can usually not be used to measure quantitatively latent heats for first order transitions

A differential AC calorimeter has been constructed [10]. In principle a differential configuration might enable both the heat capacity and heat flows for chemical reactions etc. to be measured simultaneously. However, the design and use of the calorimeter described by Dixon *et al.* did not achieve this. It functioned simply as an AC calorimeter and provided only heat capacity as a function of temperature.

A power compensation DSC has been used with a modulated isothermal temperature program to measure a complex heat capacity [7] (in fact it was only ever used to make one measurement). In normal use a DSC, of course, has the potential to measure heat flows associated with chemical reactions and similar processes. However, the demodulation system coupled to the DSC in this experiment measured only the amplitude and phase of the response to the temperature modulation and, therefore, only determined complex heat capacity. Consequently this device must also be classified as an AC calorimeter.

Modulated temperature programs used with deconvolution procedures

Reading used a modulated rising temperature program with a DSC and collected the complete heat flow signal which comprises the modulated component plus a quantitative measure of all processes that gave rise to a heat flow into or out of the sample during the experiment. This was combined with a deconvolution process designed to exploit the modulation to separate different types of contribution to the total heat flow [17, 18, 21, 23–25, 28–32, 35, 36, 38] by separating the response of the sample into a response to the underlying temperature ramp and its response to the modulation.

During a conventional scanning calorimetry experiment, when a chemical reaction starts, there are two contributions to the heat flow: a heat flow contribution from the heat capacity that depends on $heating\ rate = C_p dT/dt$; a heat flow contribution from the chemical reaction that depends on $temperature = Pf(\alpha)Ae^{-E/RT}$, where P – a constant of proportionality between reaction rate and heat flow.

Thus for a conventional DSC experiment we can write:

$$dQ/dt = C_p dT/dt + Pf(\alpha)Ae^{-E/RT} \tag{5}$$

Adding a temperature modulation:

$$T = T_0 + \beta t = B \sin(\omega t)$$

where T_0 – initial temperature, β – underlying heating rate, B – amplitude of the temperature modulation, ω – the angular frequency of the modulation, $dT/dt = \beta + B\omega \cos(\omega t)$.

Introducing the modulation to Eq. 5:

$$dQ/dt = C_p \beta + \langle Pf(\alpha)Ae^{-E/RT} \rangle \dots \text{the average or underlying response} \tag{6a}$$

$$+ C_p B \omega \cos(\omega t) + C \sin(\omega t) \dots \text{the response to the modulation} \tag{6b}$$

where C – the amplitude of modulation of the heat flow due to the chemical reaction caused by the temperature modulation

Under most circumstances, when applied to polymer transitions, C is small enough to be neglected thus *the response to the modulation is dominated by the heat capacity of the sample*. This then provides a simple route to separating out the two different contributions as follows:

$$\langle dQ/dt \rangle = C_p \beta + \langle Pf(\alpha)Ae^{-E/RT} \rangle \tag{7}$$

where $\langle dQ/dt \rangle$ can be calculated simply by averaging the modulated heat flow over one or more periods (as this suppresses the modulation). This provides the signal a conventional (unmodulated) DSC experiment would have provided.

A Fourier transform is used to determine: A_{HF} – the amplitude of the modulation of the heat flow; A_{HR} – the amplitude of the modulation to the heating rate

Assuming $C=0$

$$A_{HF}/A_{HR} = C_p \tag{8}$$

Thus C_p can be determined from the modulation. From this:

$$\langle dQ/dt \rangle - \beta C_p = \langle Pf(\alpha)Ae^{-E/RT} \rangle \tag{9}$$

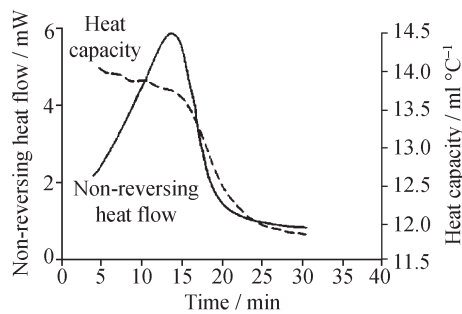


Fig. 3 MTDSC result for an epoxy cure showing the glass transition occurring underneath the cure exotherm

Thus we are able to separate out the two different types of contribution to the heat flow, the heat capacity contribution, $=\beta C_p$, usually called the reversing signal, and the chemical reaction, $=Pf(\alpha)Ae^{-E/RT}$, usually called the non-reversing signal. This is illustrated in Fig. 3 which shows how a glass transition (a change in heat capacity) can be separated from a cure exotherm.

It is not necessary to assume, as we have above, that $C=0$ and the measured phase lag between dT/dt and dQ/dt can be used to calculate this quantity and provide a more accurate estimate of C_p . In this, and other respects, the above is a simplified explanation of this technique which provides many advantages over conventional DSC. The reader is invited to read the literature for a more detailed account [15, 18, 28, 31, 32, 36, 38].

A procedure exactly analogous to that described above has also been applied to thermomechanical measurements to separate coefficient of thermal expansion, which also follows dT/dt , from irreversible processes like shrinkage or creep [37]. A temperature modulation has been used to separate pyroelectric effects, which are proportional to dT/dt , from other dielectric effects [11]. This technique focused on the amplitude and phase of the modulation, rather than, as described above, separating the underlying signal from the response to the modulation as its starting point. Nevertheless, it can be seen that the basic concept of using modulation to separate different types of response has wide applications.

Temperature modulation in micro-thermal analysis

Micro-thermal analysis is a new technique in which the passive probe in an atomic force microscope (AFM) is replaced by a small resistive heater at the tip [22, 26, 27, 34, 40, 42–45]. This resistance can serve not only to heat the tip but also to measure temperature. Local thermal analysis is possible by placing the tip on a selected area and ramping the temperature using a modulated temperature program. By using a reference probe a form of power compensation differential calorimetry is possible. This then provides the micro equivalent of an MTDSC experiment. Imaging is also possible using temperature modulation. The tip is rastered over the surface while a constant amplitude sinusoidal temperature modulation is maintained and the electric power required to do this is measured. This provides an image which, amongst other variables, is based on thermal diffusivity. The depth penetrated by the thermal wave is determined by the frequency of the modulation, thus it is possible to ‘look’ into the sample to different depths. The possibility exists of combining images at different frequencies to form a tomographic three-dimensional image of its structure.

Another consequence of modulating the temperature of the tip is that local expansion occurs. As the height of the tip is monitored by a light lever, this expansion can be detected and an image based on thermal expansion can be constructed [45].

Overview

In the past, and increasingly in the future, modulating temperature programs can provide very valuable additional information. All techniques can benefit from this but

only measurements made on small samples can follow the temperature modulation thus the future for modulated temperature experiments lies with small samples. This is one more reason why the emergence of micro-thermal measurements is important. The future of modulated temperature thermal methods looks challenging but interesting and full of potential.

References

- 1 C. S. Smith, *Trans. Am. Inst. Min. Metal. Eng.*, 177 (1940) 236.
- 2 M. Eigen, *Discussions Faraday Soc.*, 17 (1954) 194.
- 3 Y. A. Kraftmakher, *Zh. Prikl. Mekh. & Tekh. Fiz.*, 5 (1962) 176.
- 4 J. Rouquerol, *Bull. Soc. Chim. Fr.*, 1964, 31.
- 5 J. Paulik and F. Paulik, *Anal. Chim. Acta*, 56 (1971) 238.
- 6 F. Rouquerol and J. Rouquerol, *Proc. 3rd ICTAC*, Vol. 1, H. G. Wiedermann (Ed.), Birkhauser, Basel–Stuttgart 1972, p. 373.
- 7 H. Goldbrecht, K. Hamann and G. Willers, *J. Physics E: Scientific Instruments*, 4 (1971) 21.
- 8 J. H. Flynn and B. Dickens, *Thermochim. Acta*, 15 (1976) 1.
- 9 I. Hatta and A. K. Ikushima, *Japanese J. Application Phys.*, 20 (1981) 11.
- 10 G. S. Dixon, S. G. Black, C. T. Butler and A. K. Jain, *Analytical Biochemistry*, 121 (1982) 55.
- 11 L. E. Garn and E. J. Sharp, *J. Appl. Phys.*, 53 (1982) 12.
- 12 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, *J. Thermal Anal.*, 29 (1984) 775.
- 13 M. Reading, *Thermochim. Acta*, 135 (1988) 37.
- 14 M. Reading, D. Dollimore and R. Whitehead, *J. Thermal Anal.*, 37 (1991) 2165.
- 15 M. Reading, D. Elliott and V. L. Hill, *Proc. NATAS*, 1992, 145.
- 16 ‘Controlled Rate Thermal Analysis and Beyond’, M. Reading, *Thermal Analysis – Techniques and Applications*, Ed. E. L. Charsley and S. B. Warrington, Royal Society of Chemistry 1992.
- 17 M. Reading, D. Elliott and V. L. Hill, *J. Thermal Anal.*, 40 (1993) 949.
- 18 M. Reading, *Trends in Polymer Science*, 1 (1993) 8.
- 19 ‘Application of Thermal Analysis to Kinetic Evaluation of Thermal Decomposition’ D. Dollimore and M. Reading, *Treatise on Analytical Chemistry*, Part 1 Vol. 3. Ed. J. D. Winefordner, John Wiley & Sons 1993.
- 20 M. Reading and D. Dollimore, *Thermochim. Acta*, 240 (1994) 117.
- 21 M. Reading, A. Luget and R. Wilson, 238 (1994) 295.
- 22 N. S. Lawson, R. H. Ion, H. M. Pollock, D. J. Hourston and M. Reading, *Physica Scripta*, T55 (1994) 199.
- 23 M. Song, A. Hammiche, H. M. Pollock, D. J. Hourston and M. Reading, *Polymer*, 36 (1995) 3313.
- 24 D. J. Hourston, M. Song, A. Hammiche and M. Reading, *Polymer*, 37 (2) (1996) 243.
- 25 M. Song, A. Hammiche, H. M. Pollock, D. J. Hourston and M. Reading, *Polymer*, 37 (1996) 5661.
- 26 A. Hammiche, M. Reading, H. M. Pollock, M. Song and D. J. Hourston, *Review of Scientific Instrumentation*, 67 (1996) 4268.
- 27 A. Hammiche, D. J. Hourston, H. M. Pollock, M. Reading and M. Song, *J. Vacuum Science and Technology*, B14 (1996) 1486.
- 28 A. A. Lacey, C. Nikolopoulos and M. Reading, 50 (1997) 279.

- 29 D. J. Hourston, M. Song, A. Hammiche, H. M. Pollock and M. Reading, *Polymer*, 381 (1997) 1.
- 30 M. Song, H. M. Pollock, A. Hammiche, D. J. Hourston and M. Reading, *Polymer*, 383 (1997) 503.
- 31 K. J. Jones, I. Kinshott, M. Reading, A. A. Lacey, C. Nikolopoulos and H. M. Pollock, *Thermochim. Acta*, 305 (1997) 187.
- 32 M. Reading, *Thermochim. Acta*, 292 (1997) 179.
- 33 R. L. Blain, *Proc. North American Thermal Analysis Society* (Ed. R. J. Morgan), 1997, 485.
- 34 H. M. Pollock, A. Hammiche, M. Song, D. J. Hourston and M. Reading, *J. Adhesion*, 67 (1998) 217.
- 35 M. Reading and R. Luyt, *J. Therm. Anal. Cal.*, 54 (1998) 535.
- 36 M. Reading, *J. Therm. Anal. Cal.*, 54 (1998) 411.
- 37 M. Price, *Thermochim. Acta*, 315 (1998) 11.
- 38 'Differential Scanning Calorimetry', P. Haines, C. Keatch and M. Reading, *Handbook of Thermal Analysis*, Ed. M. Brown, Elsevier 1998.
- 39 'Constant Rate Thermal Analysis and Related Techniques', M. Reading, *Handbook of Thermal Analysis*, Ed. M. Brown, Elsevier 1998.
- 40 D. M. Price, M. Reading and T. J. Lever, *J. Therm. Anal. Cal.*, 56 (1999) 673.
- 41 M. Song, D. J. Hourston, M. Reading and H. M. Pollock, *J. Therm. Anal. Cal.*, 56 (1999) 991.
- 42 D. M. Price, M. Reading, A. Hammiche, H. M. Pollock and M. G. Branch, *Thermochim. Acta*, 332 (1999) 143.
- 43 P. G. Royall, D. Q. M. Craig, D. M. Price, M. Reading and T. J. Lever, *Int. J. Pharmaceutics*, 192 (1999) 87.
- 44 D. M. Price, M. Reading, A. Hammiche and H. M. Pollock, *Int. J. Pharmaceutics*, 192 (1999) 85.
- 45 A. Hammiche, L. Bozec, M. Conroy, H. M. Pollock, G. Mills, J. M. R. Weaver, D. M. Price, M. Reading, D. J. Hourston and M. Song, *J. Vac. Sci. Technol.*, B 18 (2000) 3.