USING ISOTHERMAL MICROCALORIMETRY FOR THE PREDICTION AND TESTING OF LONG-TERM PROPERTIES OF MATERIALS AND PRODUCTS

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Abstract

The use of isothermal microcalorimetry (MC) as a sensitive monitor for slow reactions is demonstrated in a number of examples. In Example 1 the spontaneous decomposition of a nitrate ester propellant is studied and the absolute degradation rate estimated. Example 2 illustrates how MC can be used for comparing the rate of oxidative ageing at different O_2 concentrations. Synergetic effects between oxygen and moisture in accelerated ageing of nitrile rubber are evaluated from a so-called 4-point test in Example 3. The last example shows a simple MC technique for rapid determination of moisture permeability through a polymeric sealant.

Keywords: degradation, microcalorimetry, moisture, oxidation, permeability

Introduction

Microcalorimetry (MC) has been used for more than 15 years in military shelf-life technology (SLT) for testing long-term stability and compatibility properties of various substances, including explosives, polymers and chemicals [1–4]. The extreme sensitivity together with a broad applicability makes MC one of our most powerful laboratory techniques in this field. MC data are interpreted either in terms of reaction rates (absolute method) or on a relative basis (comparative method) depending on the complexity of the chemical system and the purpose with the experiment. The comparative method plays an important role in the design of accelerated ageing programmes (so-called 'test tailoring') and for the conversion of ageing rates between different storage environments. Selected examples illustrating the use of MC both as an absolute and as a comparative method will be presented in this paper.

Experimental

All MC results in this work were obtained with a 2277 Thermal Activity Monitor (TAM) from ThermoMetric AB, Järfälla, Sweden. The instrument was equipped with 4 measuring cylinders of type 2277–201. TAM is a heat conduction microcalorimeter of twin type, originally developed at the Department of Thermochemistry at the University of Lund, Sweden. The measuring sensitivity is better than 1 μW

and the sample capacity typically ca. 1 g. A detailed survey of the design and properties of TAM calorimeters is given elsewhere [5].

Measurements were carried out either in sealed standard vessels (3 cm^3 glass vials or 5 cm^3 stainless steel ampoules) or in an open 5 cm^3 gas flow ampoule system (GFAS) of our own design [6]. GFAS was used in experiments requiring continuous relative humidity (RH) control. The flow rate of the carrier gas (air) was set to 60 cm^3 h^{-1}. In experiments with sealed vessels dry conditions were obtained by pre-conditioning the sample in the open vessel together with a powerful desiccant (Dehydrite) for approx. 24 h at the measuring temperature. Moist conditions (100% RH) were maintained by means of a micro-hygrostat [7] with pure water. Atmosphere control (different O_2/N_2 mixtures at 1 bar pressure) was effected by purging the sample for at least 3 min prior to sealing the vessel.

Examples

Absolute methods

Conversion of calorimetric data to absolute reaction rates (e.g. in mol s^{-1}) requires knowledge of the reaction enthalpy ΔH. For processes with well-defined initial and final states ΔH can be calculated theoretically provided that the enthalpy of formation is known for each individual reactant and product. An example of a complex chemical process for which a crude ΔH value can be obtained in this manner is the spontaneous decomposition of nitrate esters (nitrocellulose and nitroglycerine) used in propellant charges. The calculation is based on quantitative data from the analysis of the degradation products from prolonged storage at elevated temperatures. Table 1 summarizes such data for two different systems [8, 9]. The results are practically identical. Simple stoichiometry applied to the nitroglycerine (NG) data converts the gas volumes into moles from which ΔH is calculated from the heats of formation. The amount of H_2O (not analyzed quantitatively) is adjusted to fit the stoichiometry. The calculation yields $\Delta H = -435$ kJ mol^{-1} of nitrate ester ($-ONO_2$), a value in relatively good agreement with the heat of explosion of NG, -478 kJ mol^{-1}–ONO_2 [10]. We use the calculated enthalpy for routine estimations of degradation rates from heat flow rate data for most types of nitrate ester propellants. The relation between reaction rate dα/dt and heat flow rate dq/dt (in J s^{-1} g^{-1}) is given by the equation

$$\frac{d\alpha}{dt} = \frac{dq}{dt}\frac{M}{\Delta H} \tag{1}$$

where α is the reaction parameter ($0 \le \alpha \le 1$) and M the molar mass (ca. 100 g mol^{-1}–ONO_2 for nitrocellulose). An example of a measured curve for a standard double base propellant is shown in Fig. 1. The measurement was carried out with the temperature sequence 60–50–60–70°C without removing the sample from the calorimeter. The heat flow rate increases markedly with increasing temperature, as expected. By means of Eq. (1) the approximate degradation rate for
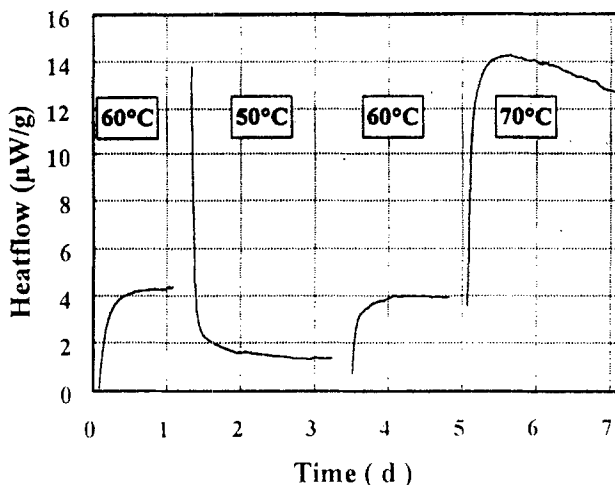
Fig. 1 *Heatflow* curve at 60 – 50 – 60 –70°C for a standard type of double base propellant in a sealed 3 cm³ glass vial. Sample mass: 2.19 g

each temperature has been determined to 0.0094, 0.032 and 0.10 year^{-1}, respectively. At the instrument 'sensitivity limit' 1 μW Eq. (1) yields dα/d$t\approx$0.007 year^{-1}, i.e. it is possible to determine the rate of a propellant degradation process that would continue for 100 years or more.

Comparative techniques

The MC technique is particularly useful for comparison of ageing rates under different external conditions. By performing separate measurements for each individual environmental factor a relation can be established between the reaction rate (heatflow), concentration ('severity') of the environmental factor and temperature (activation energy). This basic kinetic information allows conversion of ageing rates between different storage and/or testing conditions. The change in reaction rate when the temperature is altered from T_1 to T_2 is calculated as rate(T_2)=k_T·rate(T_1) where k_T is the temperature acceleration factor. k_T is related to the activation energy E_a through the modified Arrhenius equation

$$k_T = \exp\left(\frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right) \qquad (2)$$

E_a is normally calculated from a plot of ln(heat flow rate) *vs.* $1/T$, although the basic theory prescribes the use of ln(rate constant k). However, when dα/dt is sufficiently small (cf. the propellant example above) α is practically constant during the MC experiment (pseudo-zero order reaction). In these circumstances the rate and rate constant are proportional quantities.

Subsequent examples illustrate how MC can be used to study the influence of two common environmental factors, the oxygen concentration [O_2] and the relative

humidity RH, on the degradation rate. Oxidative degradation of polymers is frequently tested with MC in our laboratory. The degradation is assumed to follow the auto-oxidation mechanisms proposed for hydrocarbons [11] based on radical reactions with initiation, propagation and termination steps. Figure 2 summarizes heat-flow curves at 60°C and different $[O_2]$ (0, 10, 15, 20, 30, 50, 75 and 100%) for a standard type of vinyl ester matrix material used in fibre-reinforced laminates. All measurements were carried out in sealed ampoules with well-dried samples (ca. 0% RH) finely grated to obtain a larger reactive area. Curve (1) represents the actual heat flow rate for the $[O_2]=0\%$ sample (pure N_2) while all other curves show the deviation from (1) for the respective $[O_2]$ level. The heat flow rate increases with $[O_2]$, as expected, but also the oxygen-free sample contributes markedly to the signal through internal (e.g. post-curing) processes. The slow increase in heat flow rate with time (for all curves 2–8) reflects the build-up of an O_2 concentration gradient from the surface into the bulk of the material [12]. Figure 3 shows the oxygen dependence expressed as 1/heat flow rate vs. $1/[O_2]$ in accordance with the kinetic model for auto-oxidation [13] that predicts a linear relation between $1/(O_2$ consumption rate) and $1/[O_2]$. The graph is based on heat flow rate values at $t = 16$ h in Fig. 2. It is used e.g. for estimating the oxidation acceleration factor k_{OX}, i.e. the relative change in oxidation rate between two $[O_2]$ levels. k_{OX} is useful in the 'tailoring' of accelerated environmental test programmes for specimens with more than one ageing mechanism. By proper choice of $[O_2]$ level the total acceleration factor for oxidation ($k_{OX} k_T$) can be fitted to the acceleration factors of other (O_2-independent) reactions. This technique stems from the so-called EAP (Equalized Ageing Processes) method [14]. Even for pure oxidative ageing $[O_2]$ is frequently utilized as an acceleration parameter. Bulky specimens, for example, should preferably
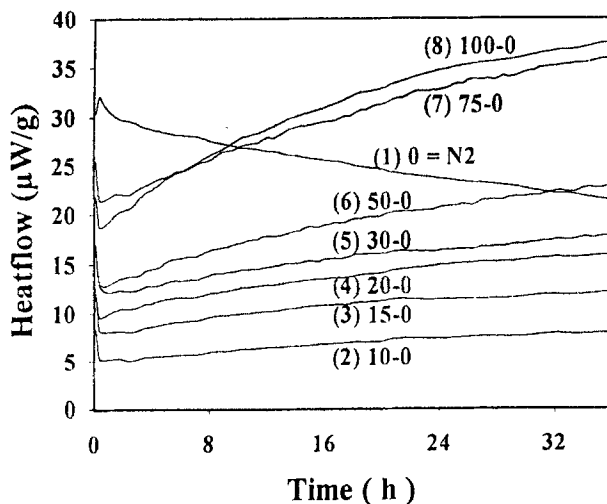

Fig. 2 *Heatflow* curves at 60°C for a finely grated, pre-dried vinyl ester polymer in atmospheres with different $[O_2]$. Note that curves (2) through (8) show the deviation from (1), i.e. they represent pure oxidation at the respective $[O_2]$ level
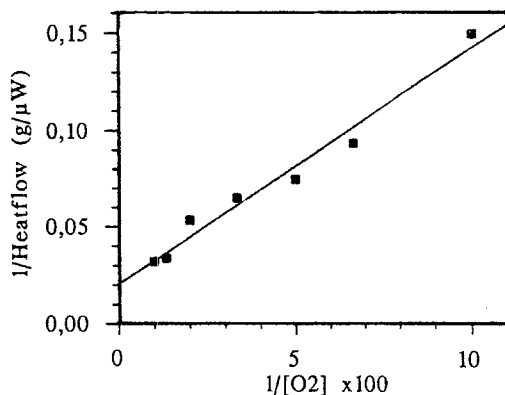
Fig. 3 Linear plot of reciprocal *heatflow* as a function of $1/[O_2]$. The plot is based on *heatflow* values at $t = 16$ h for the vinyl ester sample in Fig. 2

be aged with the smallest possible temperature acceleration in order to minimize deformation of the oxidation profile [15]. According to Fig. 3, $k_{OX} \approx 2.5$ for the replacement of air (20%) by pure O_2 (100%). This is roughly the same acceleration as obtained by a 10°C temperature shift. Forced ageing of the vinyl ester can thus be carried out at, say, 50°C instead of 60°C if air is replaced by pure oxygen.

MC offers a rapid and convenient means for screening possible synergetic effects between O_2 and moisture in the so-called 4-point test. This test is based on four identical samples in sealed vessels pre-loaded with different atmospheres: (1) Dry N_2, (2) dry O_2, (3) 'wet' N_2 and (4) 'wet' O_2. The term 'wet' refers to any specified non-zero *RH*-level, controlled either by pre-conditioning or a micro-hygrostat. O_2 may represent pure O_2 or some specific mixture of O_2 and N_2. Dry conditions imply pre-dried samples in dry gas. The 4-point test is exemplified in Fig. 4 for a

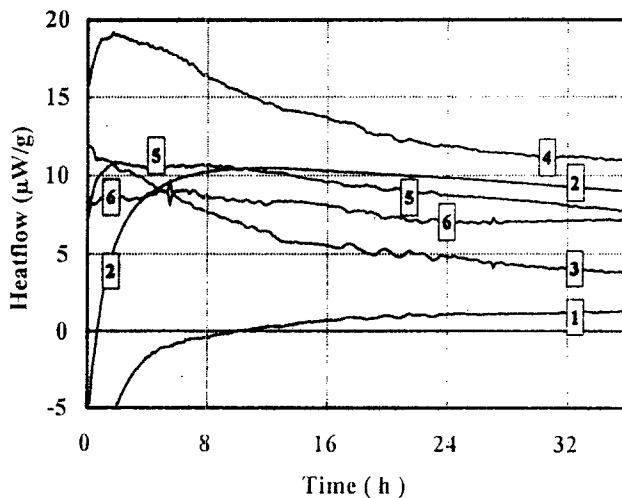
Fig. 4 *Heatflow* curves for a 4-point test of nitrile rubber at 70°C

standard type of nitrile rubber. The dry samples (1) and (2) both display an initial, weak endothermic behaviour due to evaporation of volatile additives in the rubber. In the wet (100% RH) samples (3) and (4) the corresponding process is distorted by a superimposed (exothermic) contribution from water absorption by the sample. Heat flow rate curves (5) and (6) obtained by subtracting curve (1) from (2) and (3) from (4) represent the oxidation rate under dry and wet conditions, respectively. The wet system yields a slightly lower heat flow rate signal than the dry which indicates a weak inhibiting influence by the humidity on the oxidation rate, at least in very moist environments. Oxygen and humidity are in other words not perfectly independent environmental factors for the nitrile rubber. For moderate RH variations, however, the synergetic tendencies can most likely be neglected.
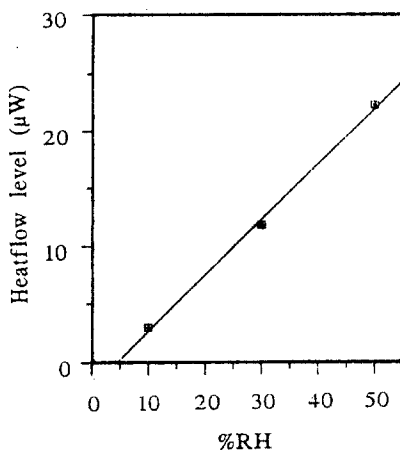

Fig. 5 Linear plot of the *heatflow* level as a function of ΔRH for a moisture permeability experiment with the sealant Loctite 242 at 70°C

Physical processes

Moisture permeability through polymeric materials (foils, o-rings, sealants, tubing walls, etc.) is an example of a physical process suitable for MC studies [6]. Permeability properties are essential, e.g. in applications where a material shall be used to protect moisture-sensitive components during long-term storage. An anaerobic sealant (Loctite 242) is chosen to exemplify the experimental technique. The sealant is allowed to cure in a small gap (0.2 mm) of a 10 mm diameter cylindrical sample support (stainless steel) filled with anhydrous $Mg(ClO_4)_2$ (Dehydrite ca. 0% RH). The support is then inserted in the GFAS at 70°C and a fixed RH. The RH difference (ΔRH) across the sealant gives rise to a moisture transport that eventually reaches a steady state. Calculation of the permeability coefficient Π is accomplished by the equation

$$\Pi = \frac{dq/dt}{\Delta RH} \frac{\Delta x}{A \Delta H} \tag{3}$$

where dq/dt is the steady state *heatflow* at ΔRH, A and Δx the permeation area and distance, respectively (here $6.47 \cdot 10^{-6}$ m^2 and $2.0 \cdot 10^{-3}$ m) and ΔH the enthalpy of the reaction

$$2H_2O(g) + Mg(ClO_4)_2 \rightarrow Mg(ClO_4)_2 \cdot 2H_2O$$
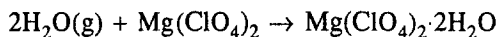
experimentally determined in our laboratory to approx. -65 kJ mol^{-1} H$_2$O(g). Routine permeability testing is usually carried out with several consecutive *RH* steps which eliminates the heat contributions from possible chemical reactions in the sample. The resulting *heatflow* levels are plotted *vs.* ΔRH and the slope $(dq/dt)/\Delta RH$ is calculated and inserted in Eq. 3. Data in Fig. 5 for Loctite 242 yields an almost perfectly linear plot with slope $=4.83 \cdot 10^{-7}$ J s^{-1}%R $\hat{H}$, corresponding to a permeability coefficient $\Pi = 2.30 \cdot 10^{-9}$ mol s^{-1} m^{-1} %RH^{-1}.

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