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Development and applications of a sample controlled DSC system

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Abstract The development of a new sample controlled thermal analysis technique based on a heat flux DSC is described. The performance of the system is demonstrated by studies on the decomposition of sodium bicarbonate and the oxidation of a copper impregnated carbon. The ability of the technique to study reactions which take place without a change in mass is illustrated by the curing of an epoxy resin with a polyaminoamide hardener.

Keywords Sample controlled · DSC · Sodium bicarbonate · Carbon · Epoxy resin

Introduction

In conventional thermal analysis, it is often necessary to use slow heating rates and small sample masses in order to reduce the deleterious effects of thermal gradients or self-generated atmospheres on the experimental resolution. These limitations have led to the development of an alternative approach called sample controlled thermal analysis (SCTA) where the rate of change of a property of a sample is made to follow a pre-determined programme and this controls the heating of the sample [1].

The technique was pioneered independently in the 1960s by Rouquerol in France who developed a method for use at reduced pressures called Constant Rate Thermal Analysis [2] and by the Pauliks in Hungary who introduced an approach called Quasi-Isothermal Quasi-Isobaric Thermal Analysis [3, 4]. In a later development, Sorensen established the Stepwise Isothermal Analysis method [5].

SCTA techniques have been based largely on the measurement of changes in gas concentration or in mass, although the temperature difference technique developed by Smith in 1940 [6] could be considered as the first SCTA method. This method generally referred to as “Smith Thermal Analysis” used a differential thermocouple to establish a constant temperature difference between the sample and furnace wall. It is still being employed in a modernised form to study alloy systems [7].

Paulik et al. [8] modified the Derivatograph simultaneous TG-DTA apparatus to enable the rate of the reaction to be controlled by the derivative of the DTA signal. They described the application of this technique to the study of a range of inorganic samples with the main emphasis on dehydration and decomposition reactions [9–12].

The aim of this study is to develop an apparatus to enable the advantages of SCTA to be applied to differential scanning calorimetry, which is the most powerful and widely used of the thermal analysis methods. The equipment is based on a Du Pont 910 DSC cell. This was chosen not only for its sensitivity and baseline stability but also for its ease of interfacing to the in-house control and data processing system.

Instrumentation

The SCDSC system is based on a Du Pont 910 DSC cell which uses a constant an heat flux plate and is shown

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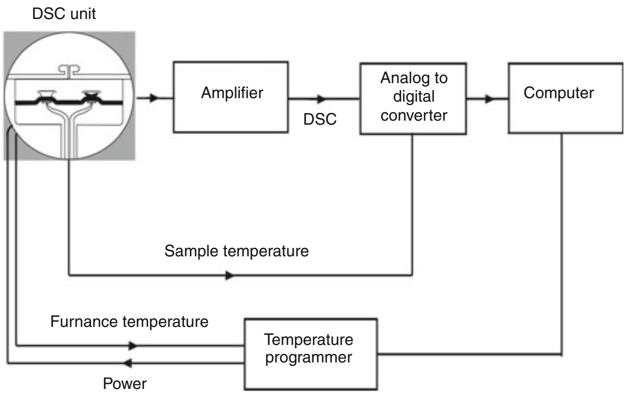

Fig. 1 Schematic diagram of SCDSC system

schematically in Fig. 1. The DSC signal is amplified using a microvolt DC-amplifier (Stanton Redcroft) and together with the sample, temperature is fed to a 22 bit USB analogue to digital converter (IOTech Data Shuttle USB/54) which also linearised the chromel–alumel sample temperature output. The furnace temperature is controlled by a digital temperature programmer (Eurotherm 818P) connected to the platinel control couple of the silver block DSC furnace. For sub-ambient work, a DSC refrigeration system has been used (TA Instrument RCS).

The data acquisition and control systems are a development of those used originally for sample controlled studies based on evolved gas techniques [13]. In addition to storing the DSC and sample temperatures, the reference temperature, furnace temperature and programmer set point temperature are also recorded.

The rate of heating is controlled directly from the DSC signal. A number of strategies relating the DSC signal to the rate of heating are available including constant reaction rate and stepwise isothermal analysis. For the initial experimental programme, an in-house technique called Proportional Heating has been used. The operation of the method depends on four main parameters. These are a maximum and minimum heating rate, a ‘target’ reaction rate and a function relating heating rate to reaction rate. When the reaction rate is zero, the heating rate is set to its maximum value. When the reaction rate is at, or above, the pre-set target level, heating rate is set to its minimum value. In between these limits, the heating rate is related to the reaction rate, by one of a number of possible functions. In this study, a linear relationship has been used with maximum and minimum heating rates of 5 and −5 °C min^{-1}. The choice of a negative value for the minimum heating rate means that the sample will be cooled if the specified target rate is exceeded.

The instrument was calibrated at a heating rate of 5 °C min^{-1} using the fusion of standard samples of *p*-nitrotoluene, benzil, indium, tin, lead and zinc (LGC Limited). The DSC signal was linearised for enthalpy by means of the in-house software. Regular calibration checks were made using indium. The DSC and SCDSC experiments were performed with the samples in open aluminium pans (TA Instrument Tzero) in an atmosphere of flowing nitrogen or air at a flow rate of 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. The samples were balanced for heat capacity with an equivalent amount of fused alumina powder in order to achieve minimum deflection on initial heating.

One problem with sample controlled techniques is the difficulty of making baseline corrections since the baseline for a given experiment is specific to both the sample and to the experimental conditions. The authors have addressed this by building in a facility to replay the temperature programme for an experiment. This enables a baseline to be determined under the same experimental conditions as for the sample. Thus, the experiment can be replayed with the reaction product or with empty pans.

Instrument performance and applications

The performance of the system is illustrated by studies on the thermal decomposition of sodium bicarbonate to form sodium carbonate. A typical DSC curve obtained at 5 °C min^{-1} is given in Fig. 2. The small peak preceding the main decomposition reaction has been attributed to the decomposition of surface bicarbonate [14]. Figure 3 shows an SCDSC experiment on sodium bicarbonate and illustrates the excellent temperature control obtained. It can be seen that after the onset of the main reaction, the sample initially had to be cooled to avoid exceeding the set reaction rate. This behaviour in sample controlled studies of decomposition reactions is considered to be typical of a nucleation and growth or autocatalytic mechanism [15]. Thus, sample controlled techniques can provide information on the nature of the reaction which cannot be deduced readily from thermal analysis curves obtained under linear heating conditions. The DSC and SC-DSC curves are

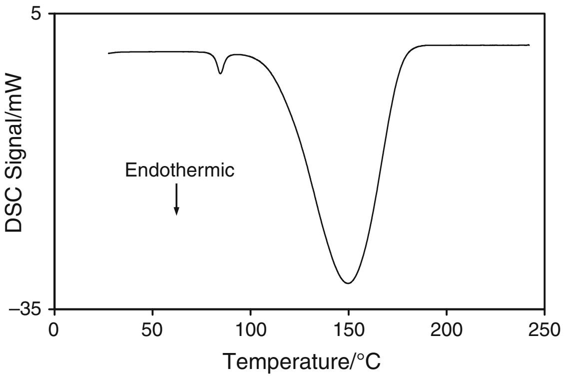

Fig. 2 DSC curve for sodium bicarbonate (Sample mass, 20 mg; heating rate, 5 °C min^{-1}; nitrogen atmosphere)

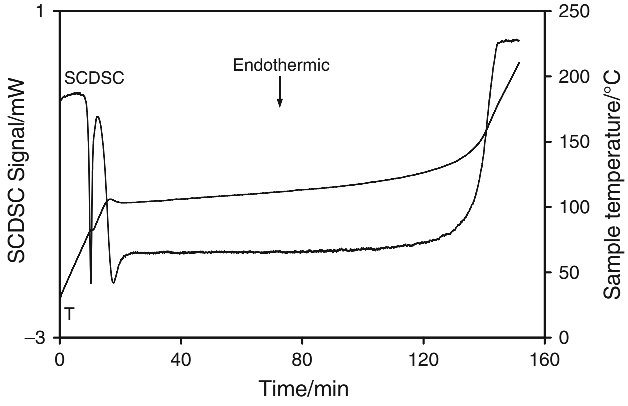

Fig. 3 SCDSC curve for sodium bicarbonate (Sample mass, 20 mg; heating rate, ± 5 °C min^{-1}; nitrogen atmosphere)

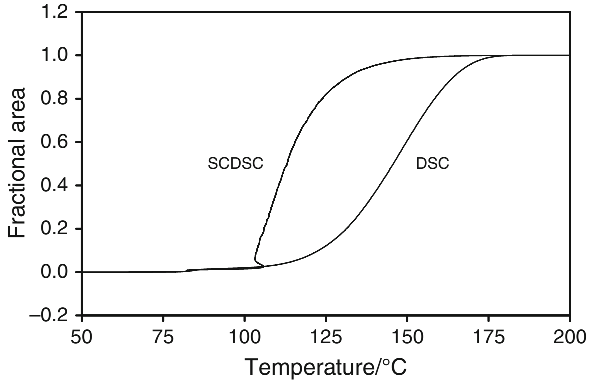

Fig. 4 Comparison of the fractional extent of reaction versus temperature plots for DSC and SCDSC experiments on sodium bicarbonate (sample mass, 20 mg; heating rate; DSC, 5 °C min^{-1}; SCDSC, ± 5 °C min^{-1}; nitrogen atmosphere)

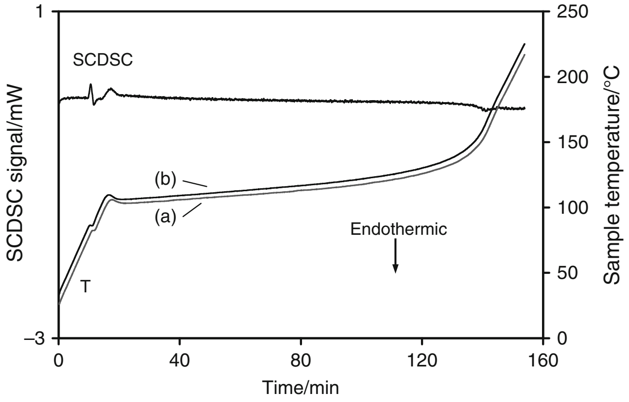

Fig. 5 SCDSC empty pan baseline obtained using replayed temperature profile from the sodium bicarbonate experiment shown in Fig. 3. *a* sodium bicarbonate SCDSC temperature profile. *b* replayed temperature profile (for clarity this has been displaced by +3 °C)

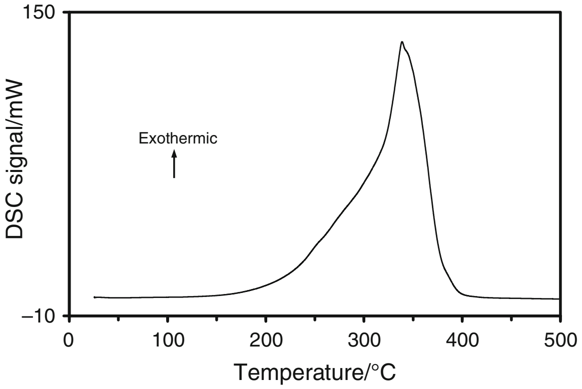

Fig. 6 DSC curve for a copper impregnated carbon (sample mass, 5 mg; heating rate, 5 °C min^{-1}; air atmosphere)

compared in Fig. 4 and show the significantly reduced temperature range over which decomposition takes place using SCDSC.

Figure 5 shows the temperature plot from the SCDSC experiment on sodium bicarbonate and the replayed temperature plot which can be seen to have closely followed the original. The DSC empty pan baseline obtained in the replayed experiment is also plotted and demonstrates the good baseline stability of the SCDSC system. This is particularly important since the heating programme is controlled by the magnitude of the deviation of the DSC signal from the baseline.

The second example is oxygen activation studies on a copper impregnated carbon formed by the pyrolysis of a copper doped carboxy methyl cellulose sample in nitrogen at 400 °C [16]. In common with a number of activated carbon precursors, this system is very reactive and gives rise to highly exothermic reactions when heated in air. This is illustrated by the DSC curve obtained using a sample mass of 5 mg (Fig. 6). The gasification reaction using aerial oxidation can therefore be difficult to control. This can result in overheating and excessive burn-off leading to a non uniform product [16].

An SCDSC experiment on the doped carbon in air is given in Fig. 7. This shows that a well controlled low temperature oxidation reaction has been obtained and that in order to achieve this, a low rate of heating has been used in the final stages. The chosen target rate has extended the oxidation reaction over a period of more than 2 h effectively eliminating self-heating problems. Thus, the technique offers the possibility of producing products of predetermined pore structure and surface area [16].

A major advantage of SCDSC is that it may be used to study reactions which take place without a mass change. This is illustrated in Fig. 8 which shows the curing of an epoxy resin with a polyaminoamide hardener (Araldite Precision) carried out under sample controlled conditions. This experiment is compared with a DSC experiment carried out on the same sample mass at 5 °C min^{-1} in Fig. 9 and again illustrates the reduced temperature range over

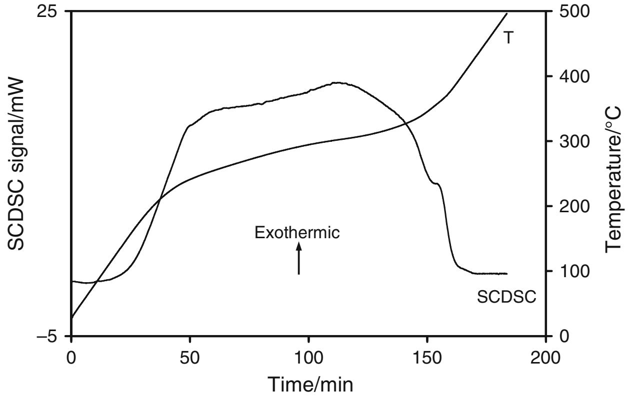

Fig. 7 SCDSC curve for a copper impregnated carbon (sample mass, 5 mg; heating rate, ± 5 °C min^{-1}; air atmosphere)

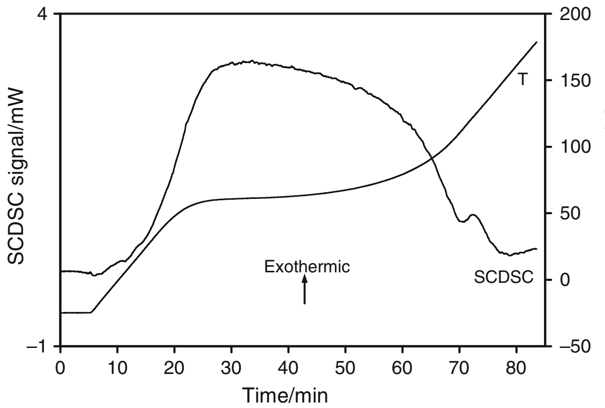

Fig. 8 SCDSC curve for an epoxy resin (sample mass, 33 mg; heating rate, ± 5 °C min^{-1}; nitrogen atmosphere)

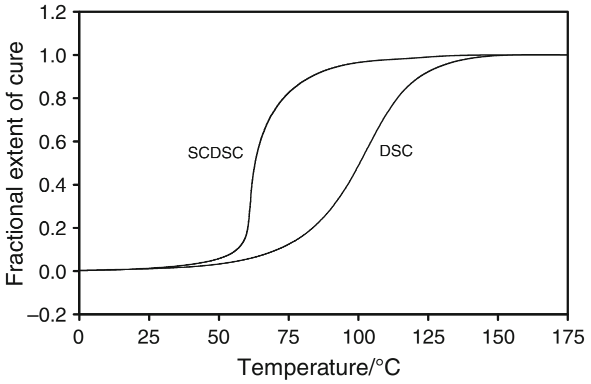

Fig. 9 Comparison of the fractional extent of cure versus temperature plots for DSC and SCDSC experiments on an epoxy resin (sample mass, 33 mg; heating rate; DSC, 5 °C min^{-1}; SCDSC, ± 5 °C min^{-1}; nitrogen atmosphere)

which a reaction takes place under sample controlled conditions. The use of SCDSC should allow the development of temperature profiles to enable samples to be cured at a selected rate.

Other areas for future study include investigation of the fusion of energy storage materials and pyrotechnic systems based on mixtures of metal powders and inorganic oxidants. In particular, work is being carried out on the very reactive zirconium-potassium perchlorate system where SCDSC has enabled the reaction to be studied at a slow controlled rate thus enabling samples to be extracted at intervals for chemical analysis.

Conclusions

A new system has been developed which for the first time has enabled the benefits of sample controlled thermal analysis to be extended to the widely used technique of DSC. This is based on a Du Pont 910 heat flux DSC cell which has been interfaced to an in-house control and data processing system. The rate of heating is controlled directly from the DSC signal and the excellent temperature control obtained using the new system is illustrated by studies on the decomposition of sodium bicarbonate and on the oxidation of a copper impregnated carbon.

The problem of making baseline corrections to sample controlled experiments has been addressed by the implementation of a facility to replay the temperature programme for an experiment. This enables a baseline to be determined under the same experimental conditions as for the sample. This facility will also be a value in enabling a suitable buoyancy correction to be applied in SCTG experiments.

The new technique has extended the range of reactions that fall within the scope of SCTA, particularly those taking place without a change in mass. This has been demonstrated by studies on the curing of an epoxy resin. It is anticipated that SCDSC will be of particular value in the study of metal-oxidant pyrotechnics where an ignition reaction can take place under linear heating conditions.

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