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STANDARDISATION IN THE INDUSTRIAL R&D LABORATORY

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Within industrial thermal analysis applications there is an increasing requirement for more rigorous standardisation to ensure that the data obtained can be reproduced within any other laboratory, using the same procedures. Fundamental to all Quality Accreditation programmes is the need to generate 'equivalent data'. The paper highlights TA applications where this is not achieved despite the use of standard calibration procedures, where true calibration is difficult to establish due to hardware/software design limitations or the absence of proven and traceable reference materials. Lack of standardisation can have important commercial or legal consequences for both instrument manufacturer and end-user.

Keywords: standard calibration procedures, DSC, DMA, TMA

Introduction

Standardisation of techniques within thermal analysis (TA) laboratories is not a new phenomenon; there have been countless methods and standard reference materials (SRM) established over the years for basic setting-up, calibration and use of such instrumentation. More recently, however, there has been a significant movement towards a more rigorous approach to many of the aspects of standardisation within industrial thermal analysis laboratories. A very strong influence in this respect has been the need to comply with the requirements of Quality Accreditation programmes e.g. BS5750 [1], ISO9000 [2], GLP [3], NAMAS [4], in which key features are traceability, reproducibility and the fundamental requirement to achieve 'equivalent data'.

For any single industrial TA laboratory, reproducibility of data has always been a number one priority. Monitoring industrial processes, or the materials from these processes, makes it essential to be able to discriminate between real changes and those that merely result from variations in test conditions. Comparative data are likely to be reproducible when they are obtained using a single instrument, but results may be different from those obtained for identical specimens examined using the same procedures, on an alternative instrument. This is then the failure to produce 'equivalent data'. The effect is surprisingly common and is a particularly important consideration in large industrial companies where the same analysis procedures are being used, on a range of instrumentation, perhaps on a global scale. Here, the material specification being monitored by the TA technique may be changed only because of the error in analysis; this has significant commercial implications. Standardisation of the instrumentation would reduce or eliminate such problems.

Differential Scanning Calorimetry

The following examples demonstrate some of the problems experienced by the authors and colleagues and the corrective procedures established over the last fifteen years. Computerisation has, within the same timescale, facilitated analysis but has also been a contributory factor in the variability of data.

For example, it may come as a surprise to many TA users that the same type of instruments, connected via identical computer systems, may give output temperature differentials of 10°C even though the precision quoted is ±0.1°C. For the majority of thermal analysts a DSC instrument, set up according to the manufacturers' specification, would produce precise, accurate and reproducible data. This is largely true for heating, but, as will be shown, is not always true when cooling. The latter is important for monitoring the temperature at which a polymer might crystallise, a wax might begin to separate in an oil or grease, a fat might solidify — processes which the industrial scientist would wish to resolve to a few degrees Celsius.

Table 1 Test results for nylon evaluation using different DSC-7 systems (T_p melting peak endotherm, T_c crystallisation exotherm)

	Instrument 'W'		Instrument 'B'		Instrument 'R'	
Polymer sample	T_p/ °C	T_c/ °C	T_p/ °C	T_c/ °C	T_p/ °C	T_c/ °C
Nylon 1	264.4	236.4	263.6	230.5	264.0	233.4
Nylon 2	263.7	225.0	262.0	218.2	263.5	221.4
Nylon 3	221.3	190.3	221.2	183.5	221.6	187.2

NB: after constructing the 'calibration' plots, the calculated corrections required were: Instrument 'W' +0.5°C; Instrument 'B' +6.1°C; Instrument 'R' +3.5°C. After applying these corrections to the T_c values the results were as follows. Nylon 1: Instrument 'W' 236.9°C; Instrument 'B' 236.6°C; Instrument 'R' 236.9°C

Figure 1 shows the recrystallisation of various nylon compounds [5], the basis of a test specification used to assess the quality of compounding or to monitor effects of homogeneous or heterogeneous nucleation. Differences in the peak of the crystallisation exotherms, T_c, are small and a typical test specification might be ±3°C. Table 1 shows a series of results obtained on three such compounds evaluated by identical methods on three different Perkin Elmer DSC-7 systems, set up and calibrated to the manufacturers' recommended specification. As can be seen, peak temperatures of the endotherms for melting, T_p, are reasonably consistent.

However, the same cannot be said for the recrystallisation temperatures, T_c, which vary by almost 7°C. This is not uncommon for cooling data obtained from

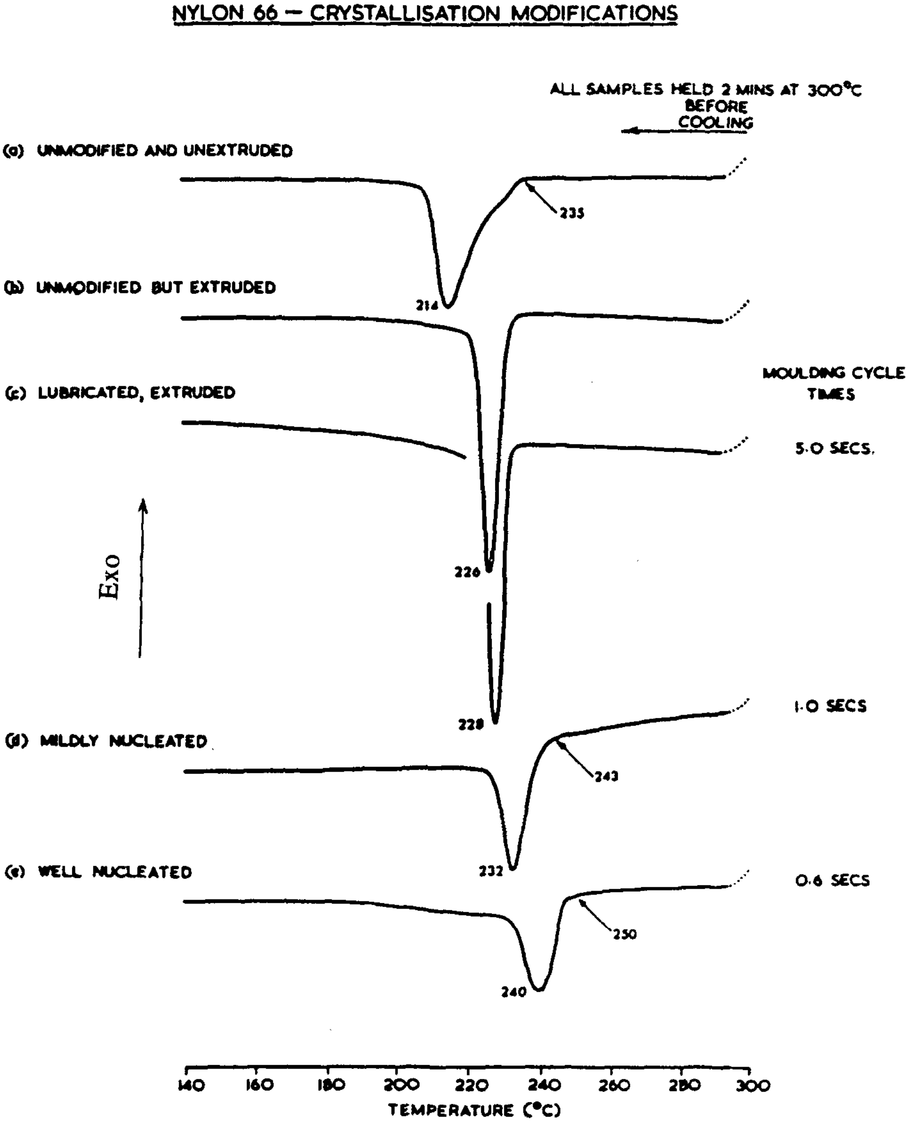

Fig. 1 Crystallisation exotherms for various nylon 6:6 compounds

DSC-7 systems; differentials up to 11°C have been measured on other polymeric samples. Variations of this magnitude, without standardisation corrections, can make a nonsense of any test specifications for DSC evaluations that involve cooling.

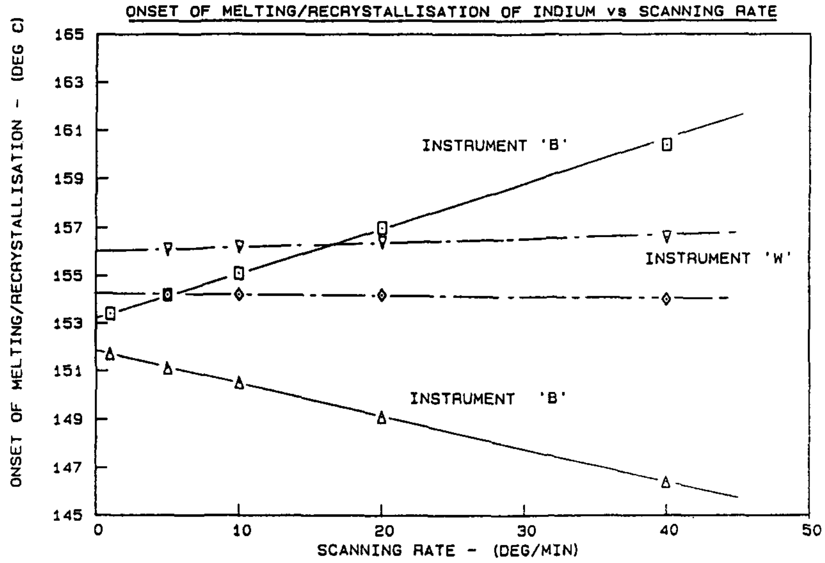

Fig. 2 Thermal lag characteristics of two Perkin-Elmer DSC-7 systems

The cause of this problem is related mainly to software and 'firmware', but is also known to vary with the age and condition of the sensors. The fundamental differences between two of the DSCs, W & B, are plotted in Fig. 2. This shows how the onset temperatures, recorded on the endotherms and exotherms for an Indium SRM when heating and cooling, vary as a function of heating or cooling rate. For instrument W the software/firmware combination has significantly modified the effects of thermal lag; instrument B on the other hand has virtually unmodified lag characteristics. The only region of reasonable agreement is on the heating curves at 20 deg·min^{-1}, a calibration point common to both. The interpretation and corrections derived from such data are shown schematically in Fig. 3 and discussed in Appendix 1. Whilst there is no absolute justification for this correction procedure it provides a first step towards obtaining 'equivalent data' as shown in the corrected data of Table 2. Interestingly, it then also aligns with corrected data from other DSC systems. Close examination of Fig. 2 might also suggest that isothermal temperature measurement (rate = 0) is also subject to error.

Important points arise from this. It is better to establish for oneself the full specification for an instrument rather than believe all the manufacturer's quoted

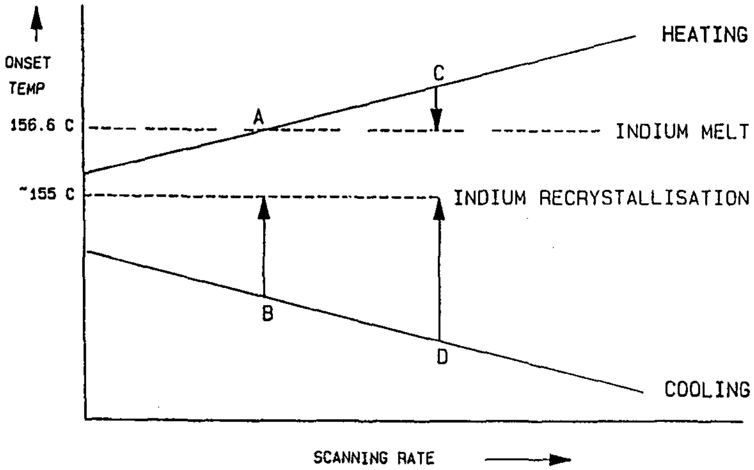

Fig. 3 Schematic representation of Perkin-Elmer DSC-7 correction parameters in the heating and cooling modes for indium (see discussion in Appendix 1)

figures. In this context it is seen to be essential to identify a reproducible 'cooling standard', perhaps a liquid crystal which has little or no intrinsic supercooling. It again demonstrates the need for more rigorous standardisation and the importance of inter-laboratory testing in monitoring likely errors. Within the European Community, the Community Bureau of Reference (BCR) located in Brussels, is actively examining the quality of standardisation which currently exists in all types of laboratory; inter-laboratory comparisons are a key part of this.

Dynamic mechanical methods

Dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) are techniques which have become very widely used commercially. The former is particularly well suited to the aerospace industry, an area in which analysis requires high levels of standardisation. Yet, experience has indicated that both these techniques have inherent design problems which can produce difficulties in obtaining 'equivalent data'. In most cases the furnaces and specimen dimensions are relatively large, which present problems with thermal transfer, temperature distribution and monitoring. Reproducibility and equivalence of data are generally only possible at very slow heating rates, <2 deg·min^{-1}, but many examples of control data have been produced which were obtained at rates of 5°C or even 10 deg·min^{-1}. Some aspects relating to this were comprehensively studied and presented by J. L. Thomason [6]. The authors, and colleagues within ICI, have been trying to standardise such equipment, but one major drawback has been the absence of adequate, well defined or documented Standard Reference Materials

(SRM), or standardisation techniques. Interestingly, we have had contact from users in the aerospace industry who have arrived at the same conclusion. Results so far have not been encouraging and in addition to the well established variables, we have identified some additional problems when using liquid nitrogen cooling accessories (LNCA). Temperatures recorded for the same molecular transitions on an internal reference standard (PMMA), have shown differences of 10°–15°C when using or not using the LNCA in the test procedure, and even without this complication it is rarely possible to achieve agreement between instruments of better than 5°C. This becomes commercially relevant, for example, when judging the degree of cure of an epoxy composite using a difference in glass transition (T_g) specification of the same order. The causes of poor reproducibility of data are fairly well understood, and largely stem from temperature variations across much of the specimen, often enhanced by localised cooling in the clamp region [6]. In one dielectric system in ICI, changing the mass of the upper plate also shifted the results by 10°C, despite the temperature sensing device being located in the same position relative to the specimen. These problems can only be eliminated when acceptable SRMs are established.

Table 2 Variation in melting peak endotherm (T_p) or crystallisation peak exotherm (T_c) values for nylon samples

Polymer	T_p/°C		T_c/°C		T_c/°C	
			Before correction		After correction	
sample	Range	Diff.	Range	Diff.	Range	Diff.
Nylon 1	263.6–264.4	0.8	230.5–236.4	5.9	236.6–236.9	0.3
Nylon 2	262.0–263.7	1.7	218.2–225.0	6.8	224.3–225.5	1.2
Nylon 3	221.2–221.6	0.4	183.5–190.3	6.8	189.6–190.8	1.2

Thermomechanical methods

Thermomechanical analysis also uses specimens which make temperature distribution effects significant. Specimen lengths may be generally of the order of 5–15 mm and the temperature can vary by >10°C over that length, depending on the relative position within the furnace. Location within the furnace can be particularly relevant for thin film or fibre-like materials. Another interesting feature in more than one fibre attachment for TMA systems is that the metal clamps are mounted in such a way that they form part of the actual specimen, and the data produced are therefore in error by an amount dependent on the relative length of specimen to metal clamps and the relative differences in expansion coefficient of the two materials.

One aspect which is critical in TMA, yet is overlooked or cannot be easily checked by the user, is the force exerted on the probe. This is important since the specimen deformation at a given temperature is often critically dependent on the local forces or pressure exerted on the specimen, particularly in low-modulus materials. A standard means of checking the nominal force is required, which will also show how the actual force on a specimen might change with relative probe displacement.

Conclusions

The problems highlighted here are not considered complex, yet for those individuals who are attempting to 'standardise' test equipment and methods, i.e. obtain consistent data from a variety of sources, they can introduce a significant level of frustration. In the industrial laboratory it will not be possible to evaluate materials satisfactorily if the basic instrumentation is considered the largest single variable. The need for greater reproducibility and equivalence of data will be an ongoing feature for everyone, particularly for those involved in accreditation schemes within large industrial networks. Manufacturers of instrumentation, academics and industrial scientists must work together to achieve the higher levels of standardisation anticipated.

References

1 BS5750 is a product of the British Standards Institution and is published in various parts as follows. BS5750 Part 1: 1987 – Quality Systems, specification for design/development, production, installation and servicing. BS5750 Part 2: Specification for production and installation. BS5750 Part 3: Specification for final inspection and test. BS5750 Part 4: 1990 – Guide to BS5750.

2 ISO9000 – 1987: Quality Management and Quality Assurance Standards – Guidelines for Selection and Use. Issued by the International Organisation for Standards. Comprises ISO9001–ISO9004.

3 GLP – Good Laboratory Practice. Principles established by various national authorities (FDA, DOH), based on OECD document 'Good Laboratory Practice in the Testing of Chemicals', published 1982. Mutual acceptance agreements exist between UK and USA, UK and Japan.

4 NAMAS – National Measurement Accreditation Service is operated by the UK National Physical Laboratory. Main documents are M10 and M11. Provides laboratory accreditation, traceable to national and international standards.

5 D. R. Beckett, Plastics and Rubber: Materials and Applications, Sept. 1976.

6 J. L. Thomason, Royal Society of Chemistry Thermal Methods Group Meeting, UMIST January 1989.

Zusammenfassung — Bei industriellen Anwendungen von TA werden in immer höherem Maße eine strengere Standardisierung gefordert, um sicherzustellen, daß die erhaltenen Daten von anderen Laboratorien unter Anwendung der gleichen Verfahren reproduziert werden können. Grundlegend für jedes Qualitäts-Akkreditionsprogramm ist die Notwendigkeit der Generierung "äquivalenter Angaben". Vorliegende Arbeit legt TA-Anwendungen dar, wo dies trotz dem Einsatz von Standard-Kalibriermethoden nicht gelang, weil die Durchführung einer wahren Kalibrierung wegen begrenzter Hardware- und Softwaremöglichkeiten zu schwierig war oder erprobte und verfolgbare Referenzsubstanzen fehlten. Fehlende Normung kann sehr wichtige kommerzielle oder gesetzliche Folgen sowohl für Hersteller als auch für Anwender von Instrumenten haben.

Appendix 1

An interpretation of the calibration corrections for the Perkin Elmer DSC-7.

Figure 3 shows the relationship between the onset temperatures for the melting endotherms (heating), and crystallisation exotherms (cooling) of indium with rate of temperature change. The linear gradients are due to the effective thermal 'lag' in the DSC system. As the rates increase, this lag becomes increasingly significant. The two horizontal 'baselines' represent the true onset of melting --- ---, or of recrystallisation ------- i.e. 156.6° and ~155°C respectively. The 1.5°C differential is largely due to the supercooling of indium at or very close to, zero rates of temperature change. The basis of the DSC correction is to match the experimentally observed temperatures to these true baseline values, for a given rate.

The majority of Perkin-Elmer instruments are set up in such a way that the characteristic relationship will be as shown in Fig. 3. A brief explanation of these plots are given below, using four points A, B, C & D.

A – Heating

Here the measured onset has been 'adjusted' to coincide exactly with the zero heating rate value, i.e. at this heating rate no correction is required. This is essentially a result of calibrating the instrumental temperature axis at the most commonly used heating rate.

B – Cooling

At the same rate as point A, but, as can be seen there is a temperature differential between the observed value and the true value for the onset. Hence a correction is required. The cooling corrections are generally larger as a result of the calibration mentioned for point A. The latter procedure has the effect of shifting the curves downwards relative to the 'baselines'. If the point B occurs at δT degrees below 155°C at a given cooling rate then in an experiment, using the same rate, the real temperature would be the recorded temperature, T°, say, plus δT. The correction, δT, is always positive for cooling.

C – Heating

At faster heating rates the increased 'lag' in the system will mean that, at points above A, a negative correction will be required i.e. the indicated temperature recorded for a transition will be higher than the true temperature. Real temperature = $T - \delta T$. (NB. below A, the correction will be positive.)

D – Cooling

At faster cooling rates the magnitude of the correction, δT, will increase but will always be positive. This indicates that, at very high cooling rates (>100 deg·min^{-1}), the effective temperature differential in the system will be very significant. The above will be compounded by the difficulty of removing the heat from large samples and results will only be valid if the 'control' light stays on i.e. programmed cooling rate does not exceed the natural cooling rate of the DSC cell. This demonstrates how different the real temperature may be to that which is indicated by the instrument.