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A NEW APPROACH TO DSC CALIBRATION IN WAX/POLYMER BLENDING

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DSC analysis of wax/polymer blends is carried out between 270 and 420 K. Calibration for melting point and enthalpy is normally carried out using indium (melting point 430 K), which is unsatisfactory for these materials. IUPAC organic standards covering this range tend to sublime and their onset temperatures are variable. Pure alkanes have similar thermal characteristics to wax/polymer blends and some have been well characterised by adiabatic calorimetry. They are being investigated as alternative secondary calibration standards to give more accurate thermal characterisation of wax/polymer blends. Also, *n*-triacontane can be used to check DSC resolution.

Keywords: DSC calibration, wax/polymer blends

Introduction

Wax/polymer blends are manufactured for a range of uses (e.g. hot melt adhesives, laminates, coatings, casting waxes and rubber additives). They vary in composition, depending on their use, from a simple blend of paraffin wax and microcrystalline wax to complex blends of waxes. polyethylene, polypropylene, resins, and other additives (Fig. 1). The thermal properties of wax/polymer blends are very important to their industrial applications, and therefore DSC analysis is an essential tool in controlling quality, matching competitors blends, product development and raw materials characterisation.

Over the past 25 years the problems associated with the DSC analysis of waxes and wax/polymer blends has been investigated [1–4]. It has been found that the influence of experimental conditions and thermal pretreatment on the final results are of prime importance. This has led the ASTM Committee D-2 to produce the Standard Test Method for Measurement of Transition Temperatures of Petroleum Waxes by DSC [5]. However we have found several problems associated with this ASTM method, including the insufficiency of the minimum temperature (para. 11.2) for some low melting point materials and problems as-

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sociated with calibration (para. 9). The first point is easily resolved. The second point is addressed by this paper for the DSC melting curve data.

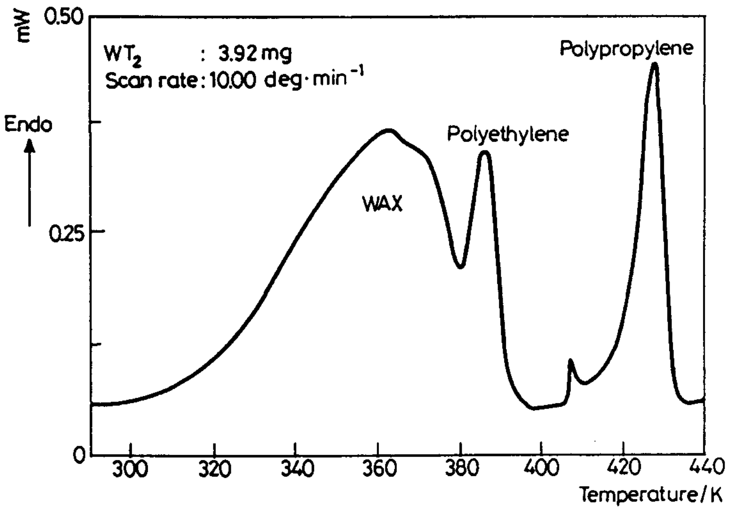


Fig. 1 Wax / polymer blend

Experimental

Materials

Indium high purity standard from Perkin Elmer Ltd. Diphenylacetic acid, benzoic acid and naphthalene from the Laboratory of the Government Chemist, Tedington, Surrey, U.K. Alkane standards from Aldrich, Polyscience Corporation and Supelco. Cyclohexane (hplc grade) from Merck.

DSC conditions

A Perkin Elmer DSC 4 with Intercooler 2, plus perspex hood over top of DSC (flushed with dry nitrogen to reduce condensation on DSC head) was used. Dry nitrogen flow through the DSC head was kept constant at 20 ml·min^{-1} (pressure 360 kPa) using a mass flow controller. The temperature and enthalpy response of Perkin Elmer DSC's have been shown to be dependant on the temperature of the controlled cooling accessory [6]. Therefore the Intercooler 2 was switched on 90 minutes before use to allow the DSC head to equilibrate and the same conditions were used for calibration.

The DSC method used is based on ASTM D 4419-90. Normally between 2 and 6 mg of sample is weighed into an aluminium pan (depending on whether it is a standard, a raw material or blend) and this is sealed with a lid. A thermal precycle is carried out from 250 to 20 K beyond the temperature where the melting curve meets the baseline (final peak temperature T_f), at a scan rate of 10 deg·min^{-1}. The DSC is automatically cooled to 250 K at the same rate. This removes any thermal history associated with the sample. When the DSC has reached equilibrium at 250 K, the cycle is repeated to obtain the DSC data and curve.

Indium calibration

Indium is generally used for DSC calibration in wax/polymer analysis without any thought to its relationship to these materials. As a sole calibrant it is beyond the melting point range of most wax polymer blends and should be used in conjunction with a low temperature melting point calibrant such as cyclohexane (Fig. 2). Indium is a monomolecular metal of high thermal conductivity and low thermal lag. Whereas waxes and polymers are macromolecular, have low thermal conductivity and high thermal lag [7, 8]. This can lead to a significant temperature gradient within a thick wax/polymer sample, giving a broader peak with it

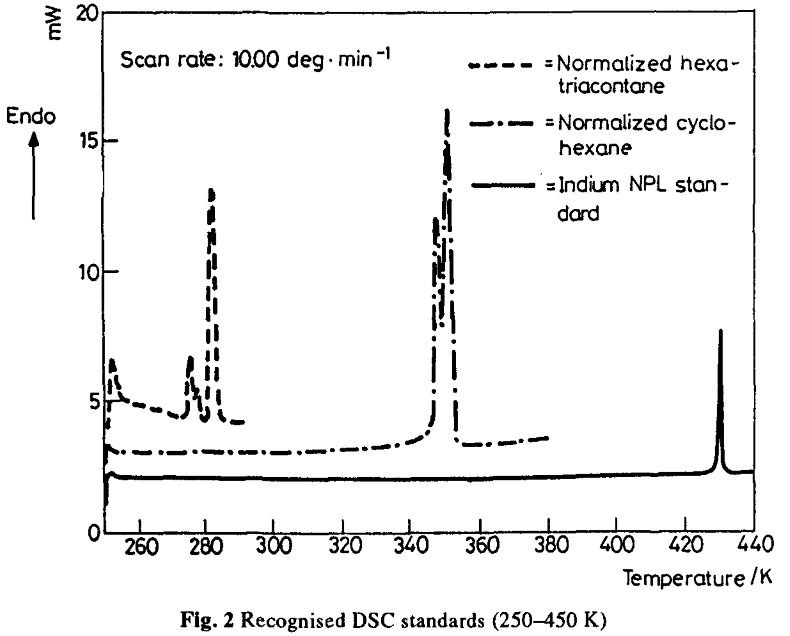


Fig. 2 Recognised DSC standards (250–450 K)

shifted to a higher temperature [9]. Therefore the sample has to be thin, which gives a low weight (3 to 6 mg).

Also it has been shown that power compensating DSC instruments have a temperature gradient in the bottom of the sample holder which leads to different temperature readings over the base of the sample holder [10]. This means that the sample must be evenly distributed over the pan base of the DSC pan, which requires a large weight for indium (over 10 mg).

Indium has a low enthalpy, whereas waxes and polymer have a relatively high enthalpy. This means that the calibration is not carried out comparatively at a similar enthalpy level.

Other DSC calibration standards

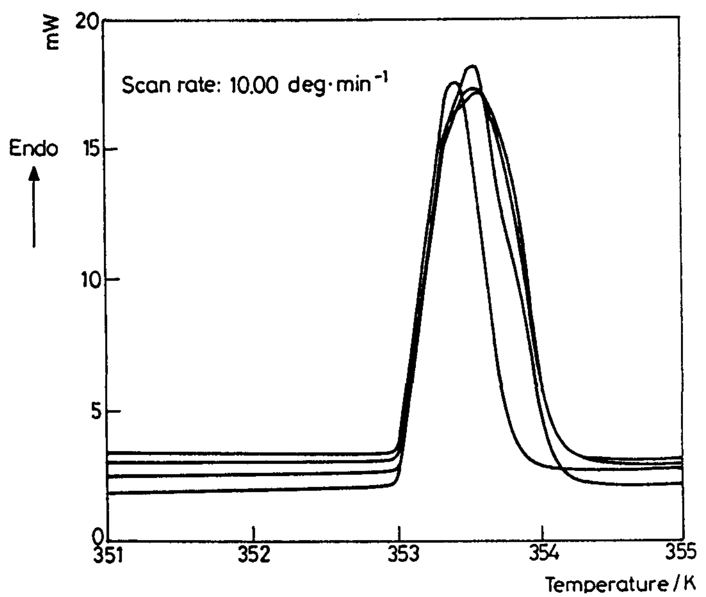
Cyclohexane is an accepted ICTA standard [11] with a low melting point (280 K), but it is difficult to handle due to its volatility (it has to be refrigerated before use). 1,2 dichloroethane, a useful low temperature ICTA standard, has now been classified by the EEC as a dangerous chemical [12] and can no longer used in an open laboratory.

The Perkin Elmer DSC 4 Manual refers to the use hexatriacontane (melting point 349 K) as a calibration standard [13]. This is a pure alkane melting in the middle of the wax/polymer blend DSC range, and it is well characterised for melting point and enthalpy (Fig. 2). As a DSC calibrant compared with indium, it gave very reproducible and accurate results, as well as being easy to prepare.

IUPAC temperature calibration reference materials

As an alternative to indium several IUPAC temperature calibration reference materials [14], in the relevant temperature range, were used as comparative standards with indium. These were naphthalene (melting point 353 K), benzoic acid (melting point 395 K) and diphenylacetic acid (melting point 420 K), obtained as certified reference materials (calibrated by adiabatic calorimetry) from the U.K. Laboratory of the Government Chemist.

When using these standards we had problems with shifts in the peak temperature and changes in enthalpy (Fig. 3). On inspection of the DSC pans after use, it was found that the samples were subliming up the sides of the pans. Therefore these standards could not be treated in the same way as wax/polymer blends (with preheating). P. A. Barnes *et al.* were found to have reported this previously [15]. Another problem associated with these standards is that they are supplied as powders, which should be melted first to remove any thermal lag effects.



Alkane standards

From the investigations into the use of hexatriacontane, it appeared that alkane standards could be potentially better for the DSC analysis of waxes and polymers. Many alkane standards have been well characterised using calorimetry [13, 17 to 19]. They are similar in structure to the components of waxes and polymers, as well as having similar thermal properties. Also they can be thermally cycled, similar to wax/polymer blends. Alkane standards can now be obtained in high purity up to hexacontane (melting at 372 K), which covers a large part of the DSC range (Fig. 4). For the past year they have been used in our laboratory as secondary standards and have proved reliable.

Also *n*-triacontane shows two clearly separate peaks (Fig. 4), the first melt peak being due to a change in crystal structure [20]. This can be used to check the resolution of the DSC over the instruments lifetime, or to compare the resolution of different DSC instruments under the same test conditions.

These standards are now being more extensively checked and also new, low molecular weight polymers are being tested as DSC heating standards. It is hoped to report these results in the near future.

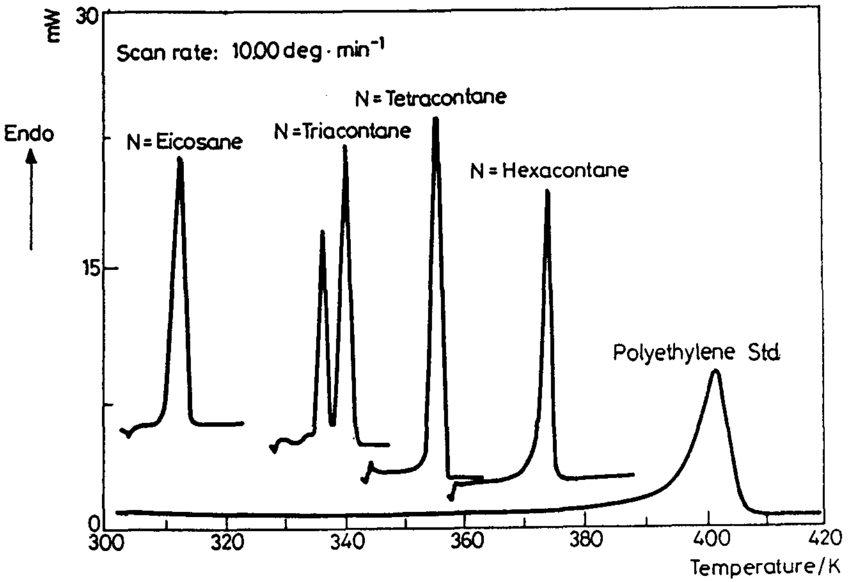


Fig. 4 Normalised series of alkane standards

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Zusammenfassung — Mittels DSC wurden Wachs/Polymer-Mischungen im Temperaturbereich von 270 und 420 K untersucht. Die Kalibrierung für Schmelzpunkt und -enthalpie wurde normal unter Verwendung von Indium (Schmelzpunkt 430 K) durchgeführt, was für diese Materialien unzureichend ist. Organische IUPAC-Standards, die diesen Bereich abdecken, neigen zu Sublimation und deren Einsatztemperaturen sind variabel. Reine Alkane haben ähnliche thermische Merkmale wie Wachs/Polymermischungen und einige wurden mittels adiabatischer Kalorimetrie gut charakterisiert. Sie werden als alternative Sekundär-Kalibrierstandards getestet, um eine präzisere Charakterisierung von Wachs/Polymermischungen zu erhalten. Zur Überprüfung der DSC-Auflösung kann auch *n*-Triakontan verwendet werden.