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THERMOPLASTIC POLYMERS QUALITY CONTROL
DSC baseline optimisation for heat of fusion measurements

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Abstract

A technique is proposed for improving the accuracy of the heat of fusion of semicrystalline polymers by DSC. The results of three commercially available instruments are compared.

Keywords: baseline, DSC, heat of fusion, polyethylene

Introduction

Thermal analysis techniques are not widely applied for the characterisation of plastic and composite materials used in telecommunication networks and equipments [1, 2]. Among thermoplastics, polyolefin cable insulation and sheathing play an outstanding role from a quantitative point of view and there are nowadays several manufacturing plants in Italy. Due to the necessity to assess the conformity and the technical 'quality level' of different lots of product, at the end of '70s in technical specifications were introduced DSC (differential scanning calorimetry) measurements like melting peak temperature, heat of fusion and oxidative induction time. In the '80s computerisation enlarged the possibilities of control and data manipulation so that measurements and evaluations were speeded up. However measurement accuracy did not increase at the same extent due to the introduction of new variables. As far as melting parameters are concerned, significative spread of heat of fusion values has sometimes been experienced; this is primarily caused by the existence of different methods of defining parameters for curve integration [3, 4] and also by the variability among different instruments.

The present paper describes a technique for improving accuracy in heat of fusion determinations and reports comparative data obtained by 3 different DSC instruments.

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Experimental

Instruments

Experiments were carried out using 3 different DSC analysers:

– Mettler DSC 30 (temperature range −170°C– +600°C) controlled by an IBM workstation-software TA 72 PS 5

– Mettler DSC 820 with liquid nitrogen cooling option (temperature range −150°C– +700°C), controlled by a TAS 811 workstation-software vers. 2.03

– Perkin Elmer DSC 7 with sub-ambient accessory (temperature range −170°C– +700°C) controlled by a Digital workstation-software UNIX series vers. 2.21

Instrument calibrations were carried out according to respective manufacturer instructions, keeping into account guidelines detailed in relevant standards [5–7]. For heat of fusion calibration a NBS-NIST certified Indium reference material was used. Heating rate, purge gas and flow rate conditions were identical for calibrations and tests to prevent any inconsistency.

Material

Polymer sample was a black LDPE under the form of pellets used for outer cable sheath; specimens were cut by the use of a microtome or of a razor blade and weighed with ±0.01 mg precision by the use of Mettler ME 30 electronic microbalance.

Characterization of the sample

About 10 mg of sample was weighed in an aluminium pan; then a lid was applied taking care to minimise any free space between polymer sample and the crucible. No hole was made in the lids of sample and reference crucibles. A 30–60 cm^3 min^{-1} N_2 gas flow and a heating rate of 10°C min^{-1} were used during tests. Starting temperature was about 120°C lower than the expected melting point and end temperature was about 30°C higher than completion of melting.

In order to keep into account the 'thermal history' of the sample, only the first melting cycle was considered; this is an important point in product quality level assessment and represents a major difference with respect to ASTM D 3417–83 where preliminary melting and cooling cycles are recommended to destroy any 'memory effect' of the sample.

Results and discussion

The determination of heat of fusion from the area of a DSC peak can be performed after establishing a baseline to bound the area which is to be integrated.

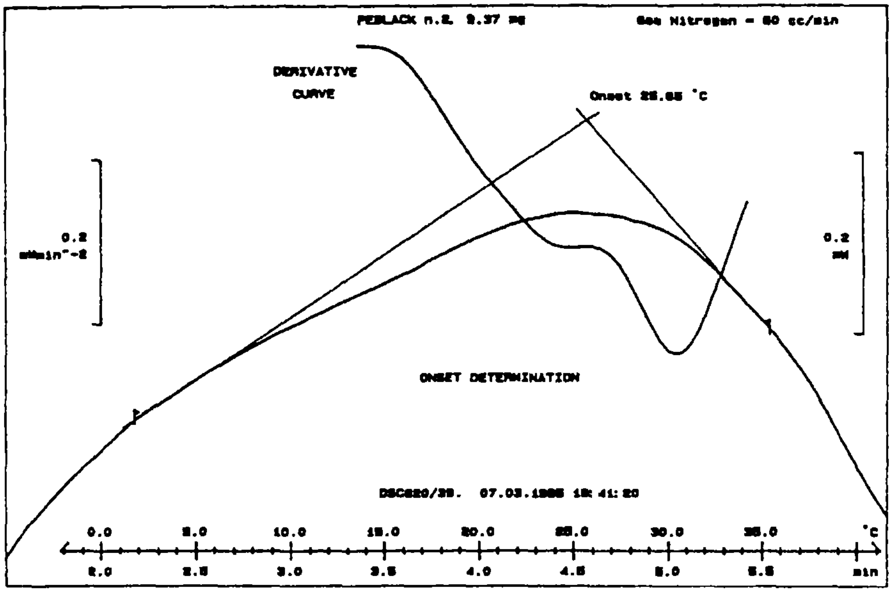

Fig. 1 Onset determination by the use of DSC derivative curve (Mettler DSC 820)

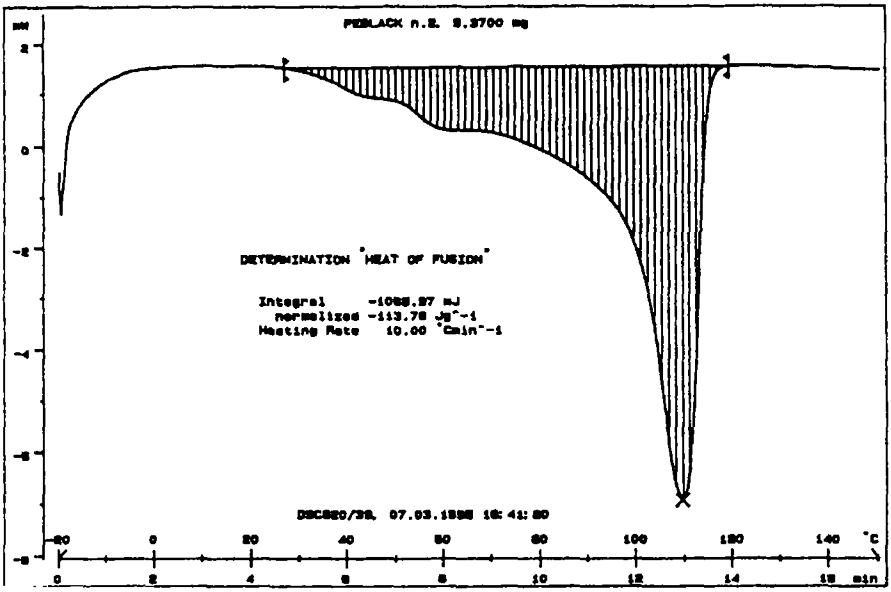

Fig. 2 DSC curve and extrapolated baseline for heat of fusion calculation (Mettler DSC 820)

This can easily be done by linear extrapolation of the baselines before and after the 1st order DSC transition, when the extrapolations meet to form a straight line, i.e. when there is insignificant change in heat capacity during the transition [8]; if this is not the case, the proper heat of transition can be obtained by using a step function baseline [9].

In polyolefins for cable materials, the effect of change in heat capacity is usually negligible and a straight baseline can be used. However, due to the relatively low melting temperature, some difficulties have been encountered in baseline extrapolation before DSC transition; in fact when additives like waxes are present, baseline rising occurs at temperature appreciably lower than the beginning of DSC peak. This phenomenon is often overlooked because initial temperature of DSC scans is relatively high (e.g. room temperature for LDPE polymers) with respect to the beginning of melting peak temperature.

For optimal determination of starting point temperature from which to extrapolate a baseline before DSC transition, two precautions are currently adopted in our laboratory:

- the initial scanning temperature is chosen at least 120°C below DSC transition
- the derivative DSC curve is used to calculate the 'onset temperature' i.e. the departure of thermal curve from horizontal baseline.

In Figs 1 and 2 examples of graphical treatment of data are reported. According to this test procedure, typical results of 10 replicates are summarised in the following Table:

	Mettler DSC 30	Mettler DSC 820	Perkin Elmer DSC 7
Heat of fusion/J g^{-1}*	113.5±0.9	114.1±0.7	114.0±0.5
R.S.D./%	0.8	0.6	0.5

* Reported values for purely crystalline LDPE are 140.6–277.1 J g^{-1} [10]

For the same DSC, standard deviation values range from 0.5 to 0.9 J g^{-1} while total standard deviation calculated on the basis of 30 determinations carried out by the 3 different DSC, is 0.8 J g^{-1}. These values can be considered satisfactory since ASTM D 3417–88 reports that duplicate measurements of heat of fusion should not differ by more than 4.2 and 8.4 J g^{-1} respectively in 'repeatability' and 'reproducibility' conditions. Experimental data allow therefore the conclusion that the proposed method yields good results.

Conclusion

The integration of DSC curves starting from an extrapolated onset temperature avoids one of the principal causes of inaccuracy and variability among different laboratories, in the calculation of heat of fusion changes. The proposed calculation can be easily performed with modern thermoanalytical instruments provided with sub-ambient cooling option and interfaced with computers. This technique has been extensively applied to polyolefins but can be used also for other semicristalline thermoplastic materials to improve the accuracy of heat of fusion determinations and to obtain reliable data for conformity and quality level assessment.

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