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APPLICATION OF MODULATED TEMPERATURE DSC TO DISTILLATE FUELS AND LUBRICATING GREASES

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Abstract

In this work the usefulness of Modulated Temperature DSC (MTDSC) for characterizing petroleum products is illustrated with some typical examples of recent applications. Specifically, the reliability of the method is outlined on the basis of the freezing behaviour of distillate fuels and the thermal analytical characterization of lubricating greases. The results of experiments performed on the evaporation residue of distillate fuels, aimed at providing insights into the structure of degradation products, will also be presented. The experiments were carried out using a DSC 2910 module from TA Instruments Inc., upgraded with the MTDSC option. The samples were exposed to a cyclic heating profile which was generated by an underlying heating (or cooling) rate of 2°C min^{-1} while superimposing a sinusoidally varying time-temperature wave with an amplitude of ±0.5°C and a period of 40 s.

Keywords: diesel, distillate fuel, grease, Modulated Temperature DSC

Introduction

DSC has found widespread use as a reliable quality control tool for petroleum and related products [1]. It provides information on such diverse properties as phase transitions, crystallinity, reactivity, and stability.

MTDSC is an extension to conventional DSC which provides additional information about the reversing and non-reversing characteristics of thermal events, thereby improving the understanding of transitions seen in DSC experiments [2]. Moreover, MTDSC supplies more accurate heat capacity data [3], and can also directly monitor the apparent heat capacity during certain transitions as a function of temperature [4, 5].

It is the object of this paper to show that MTDSC analysis can easily be used to characterize petroleum products. It overcomes some of the limitations of conventional DSC by separating complex, overlapping transitions into more easily interpreted component.

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Principle of the measurement

In MTDSC the same heat flux DSC cell arrangement is used as in conventional DSC, but a cyclic heating profile is applied by the furnace to the sample and reference. Specifically, a sinusoidal temperature modulation is overlaid on the traditional linear heating ramp to yield a cyclic heating profile. The temperature increases at a rate which is sometimes faster, sometimes slower than the underlying heating rate. The actual variations in heating rate obtained depend on three experimental variables: the underlying heating rate, the amplitude of modulation, and the frequency of modulation [6]. The combination of the underlying heating rate with the more rapid instantaneous heating rate results in improved sensitivity without loss of resolution [4]. In the present investigation, the selected underlying heating rate, modulation amplitude, and modulation period resulted in an instantaneous heating rate varying between +6.7°C min^{-1} and –2.7°C min^{-1} (Fig. 1). The resultant raw experimental heat flow and heating rate signals for an experiment on *n*-dodecane are shown in Fig. 2.

Fourier transformation analysis of the modulated heat flow signal is used to continuously calculate an average heat flow value, which is equivalent to the total heat flow signal in conventional DSC, and to separate that total heat flow into its heat capacity-related (reversing) and kinetic (nonreversing) components [7, 8]. The reversing component of the heat flow is heating rate dependent, i.e. it follows directly the modulated heating rate, whereas the nonreversing component is dependent only on the absolute temperature. In MTDSC, the heat flow

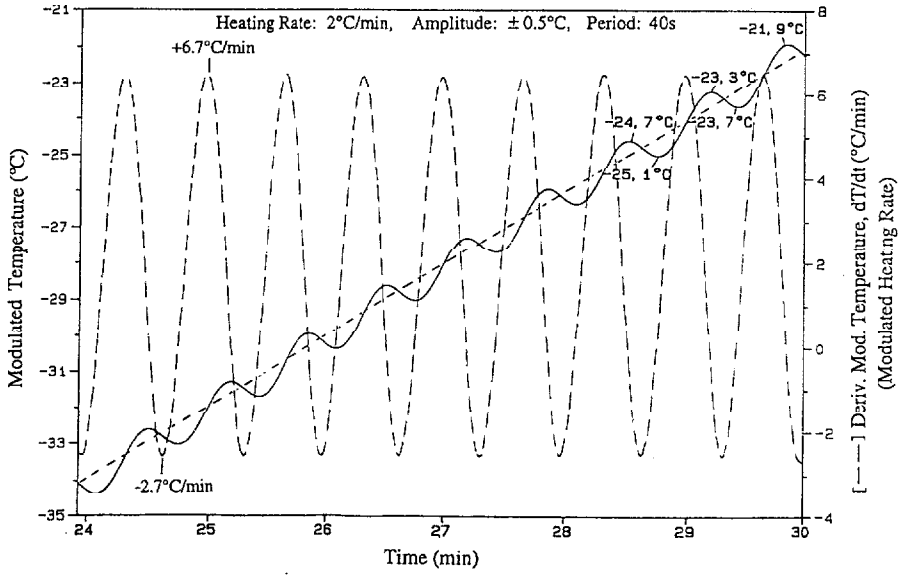

Fig. 1 MTDSC heating profile (cyclic heating/cooling)

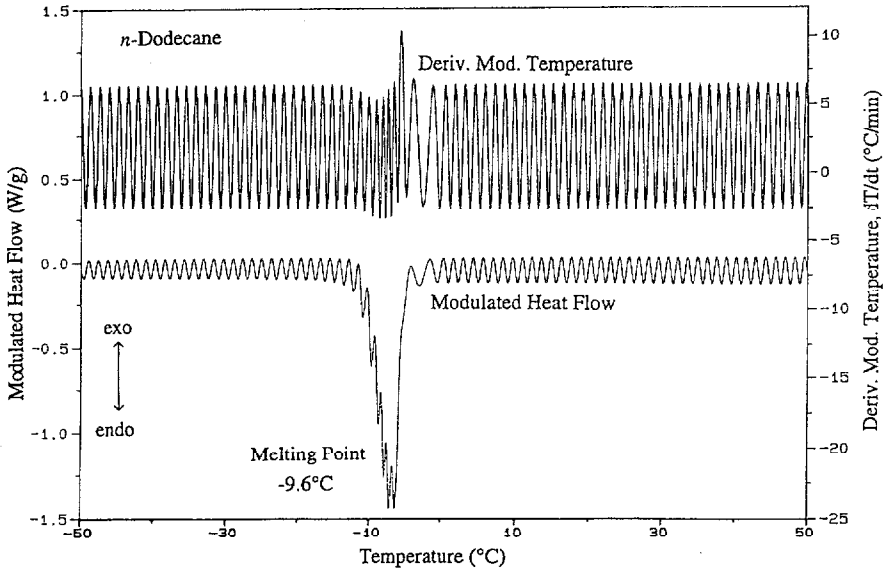

Fig. 2 MTDSC raw signals; experiment on *n*-dodecane (heating scan)

values during a scan are converted directly to heat capacity values at the indicated temperature by dividing the modulated heat flow amplitude with the modulated heating rate amplitude and then multiplying by the cell constant. The reversing heat flow is determined by multiplying this heat capacity by the average heating rate (adjusted for the direction of the heat flow). The nonreversing heat flow is determined as the difference between the total and reversing heat flows.

Experimental

Instrumentation and procedure

The experiments were performed using a DSC 2910 module from TA Instruments Inc., upgraded with the MTDSC option. A complete description of this device is given elsewhere [2]. An underlying heating (or cooling) rate of 2°C min^{-1}, an amplitude of modulation of ±0.5 °C and a period of 40 s were used throughout this investigation. Hermetically sealed aluminium crucibles of 40 µl volume available from Mettler Instruments were employed. Sample masses were 10–15 mg for both calibration and measurements. Rather large sample masses were chosen to maximize the size of the total and nonreversing signal. An empty sealed crucible was used as a reference. The measurements were carried out using liquid nitrogen coolant and nitrogen purge gas with a flow rate of 40 ml min^{-1}. The temperature calibration was carried out using the onsets of the transition

peaks for *n*-octane, 3-pentanone, *n*-dodecane, stearic acid and indium metal (melting points = –56.8, –39.0, –9.6, 70.0°C, and 156.6 °C, respectively).

For the heating scans, the samples were quickly cooled to the initial temperature (–110°C) without collecting data. After giving the entire system time to stabilize by holding isothermally for 10 min at this temperature with the selected modulation period and temperature amplitude, the data storage was turned on and with continued liquid nitrogen feeding the underlying heating started. The heating was stopped at the desired final temperature (+50°C, except for the grease sample: +220°C). The cooling scans were performed in the same way from +50 down to –110°C.

Results and discussion

Freezing behaviour of distillate fuels

The low temperature operability is an important quality factor, in particular for oil fuels which are used in winter and are stored in outdoor tanks. Since petroleum fuels are not generally individual chemical substances with well-defined solidification temperatures but mixtures of various hydrocarbons with different molecular weights, their transitions occur over a temperature range. Rapid and accurate determination of the transition temperatures is important both for the final products and for controlling the refining process. The low temperature properties of distillate fuels provide one area where conventional DSC is potentially a very valuable research tool and sometimes more convenient than the standard methods [9, 10]. MTDSC, however, yields additional information not available from conventional DSC.

Figures 3 and 4 illustrate the ability of MTDSC to detect the last stages of crystallisation of a heating oil and a diesel fuel oil. The conventional DSC curve (total heat flow) obtained for the heating oil sample exhibits a broad transition due to the crystallisation of the different compounds in the fuel. Only the cloud point – the temperature at which a cloud of wax crystals first appears in an oil upon cooling – can be clearly identified in this curve: +1.0°C. The reversing heat flow signal, however, shows the freezing end at –18.0°C, which can be used as an estimate of the pour point – the lowest temperature at which the oil is observed to flow when cooled. The diesel fuel sample exhibits in the reversing signal a cloud point of –15.0°C and a pour point of –45.0°C.

Since instrument baseline variations are non-reversing phenomena, MTDSC has improved signal/noise ratio in the reversing signal which further increases the ability to observe subtle transitions. Any change in the reversing signal baseline is due to a change in measured heat capacity. Replicate measurements gave an overall standard deviation of about ±2°C. Both values were confirmed by the

standard methods ISO 3015 (Petroleum products – Determination of cloud point) and ISO 3016 (Petroleum products – Determination of pour point).

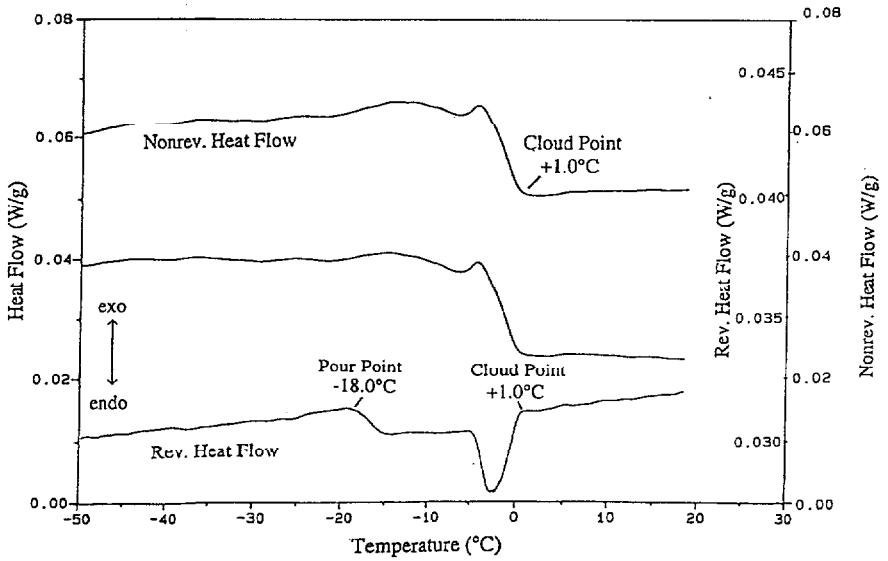

Fig. 3 Freezing behaviour of a customary heating oil (cooling scan)

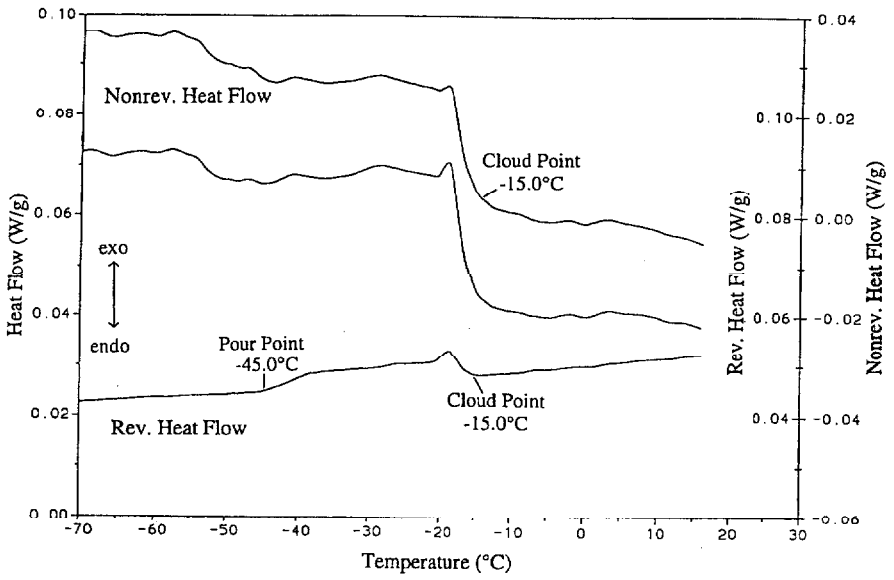

Fig. 4 Freezing behaviour of a customary diesel fuel (cooling scan)

Characterization of the evaporation residue of distillate fuels

One of the benefits of MTDSC is its ability to separate the reversing glass transition from the nonreversing transitions, thereby revealing thermal transitions not observable by conditional DSC.

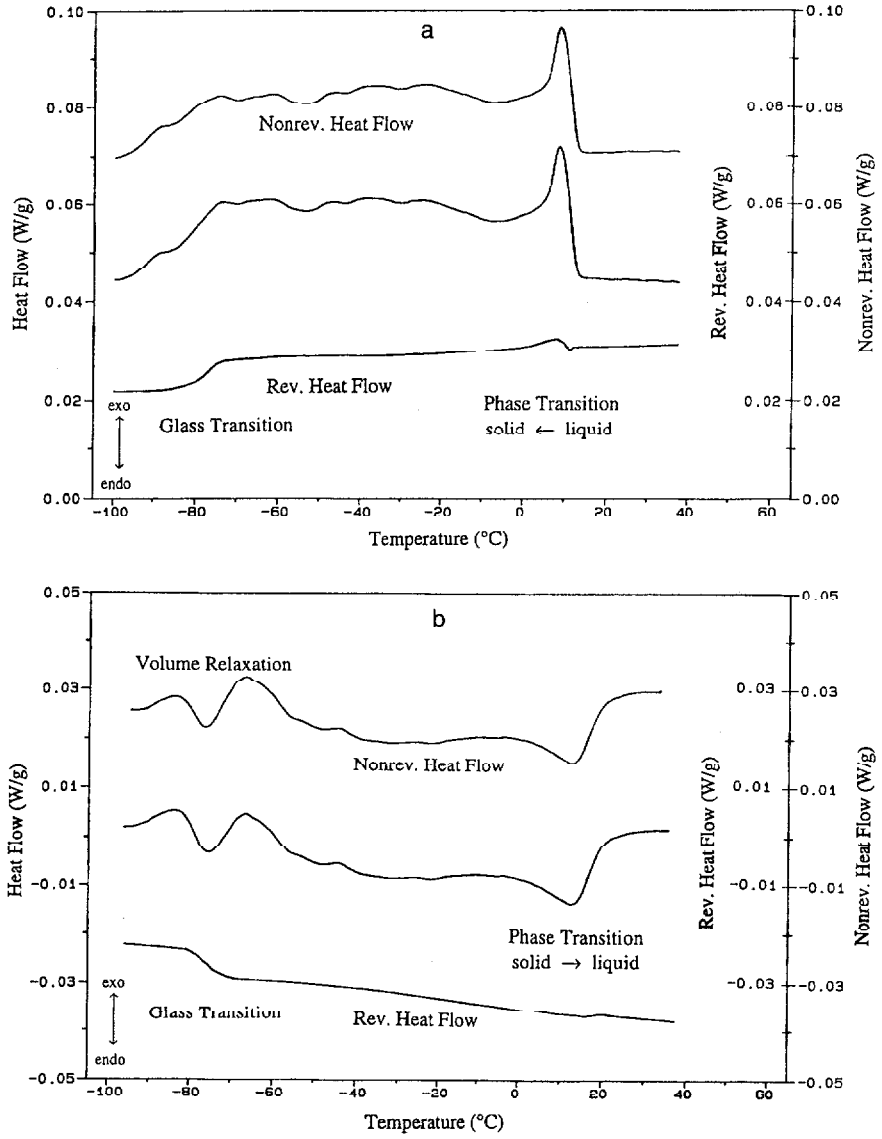

Fig. 5 Results from an MTDSC experiment on an evaporation residue of a diesel oil containing ageing products. (a, top), cooling scan; (b, bottom), heating scan

An illustration of how this capability can be useful is given in Fig. 5 for an evaporation residue from a diesel fuel containing non-volatile resinous material. These degradation products, commonly called gums, are deleterious to fuel quality, and can often cause undesirable effects such as tank corrosion, clogged filters and fuel lines, and blockage of engine components [11]. The content of existent gum in diesel fuels is usually evaluated at EMPA by a slightly modified method of European Standard EN 5 [12], which involves evaporating a measured quantity of fuel under controlled conditions of temperature and flow of steam. The primary purpose of the test is the measurements of the oxidation products formed in the sample prior or during the test procedure. However, the unwashing gum content, which is the resulting residue without any further treatment, is also indicative of purposely blended nonvolatile additives as well as contamination of fuel by higher boiling oils or particulate matter.

During cooling, exothermal effects corresponding to the solidification of the oil residue are observed at a temperature of +10°C (Fig. 5a). This process is mainly nonreversing. Upon continued cooling, that part of the oil matrix which cannot crystallize transforms into a glassy state. The glass transition, seen as a sudden decrease in heat capacity in the reversing curve at approximately –75°C, indicates the presence of an amorphous structure, as expected for resinous material. The abrupt fall of the total heat flow signal, which is probably the result of partly prevented crystallization due to the drastically reduced molecular mobility of the frozen matrix [13], almost completely masks the glass transition. The

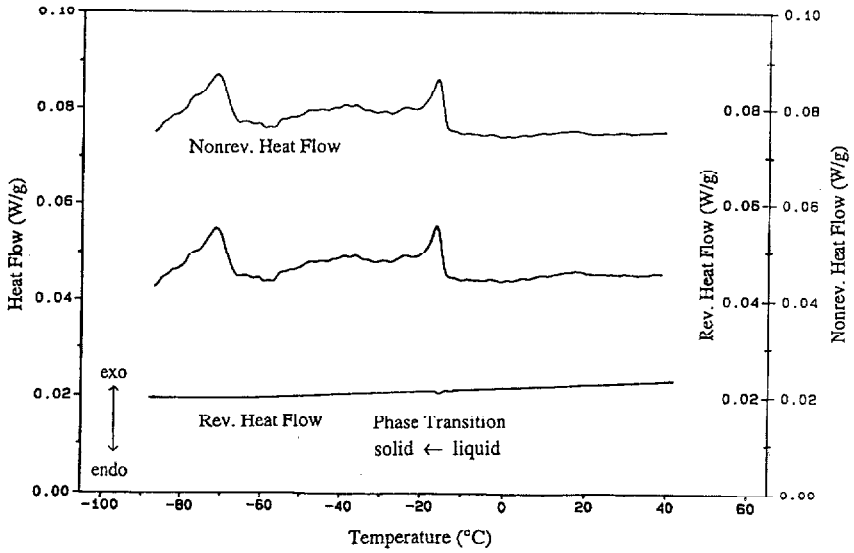

Fig. 6 Results from an MTDSC experiment on an evaporation residue of a diesel oil containing a pour point depressant (cooling scan)

enthalpy related to this process does not affect the reversing signal recorded by MTDSC, i.e. the evaluation of the heat capacity itself.

On heating (Fig. 5b) the glass transition is not seen in the total heat flow from conventional DSC because the small change in heat capacity is obscured by an endothermic relaxation (a thermal history effect), which is a nonreversing phenomenon. Conversely, MTDSC can separate this structural relaxation from the glass transition. The reversing signal displays a neat baseline, where the change corresponding to the T_g is easily detectable. The crystalline melting exhibit only nonreversing behaviour under the experimental conditions chosen.

To show whether MTDSC can be applied on the evaporation residue of distillate fuels to distinguish degradation products of the fuel from chemical additives, a pour point depressant was added at room temperature to a diesel fuel that showed very little gum forming tendency. This additive consisted of about 50% polymeric active ingredient plus 50% solvent and its dosage was 1000 mg kg^{-1}.

The solidification peak of the evaporation residue is now smaller in comparison with that of the aged fuel and appears at lower temperature (–10°C, Fig. 6). On further cooling, a second crystallization process is seen at about –70°C. This exotherm is probably due to the freezing of the depressant molecules trapped in the frozen fuel residue. Because of the large difference in molecular mass between the fuel residue and the additive, they tend to form a non-ideal solution on freezing and to crystallize independently. Both exothermic events were not observed in the reversing heat flow signal. Nor did a glass transition occur in the temperature range investigated. Presumably, the amount of polymer contained in the evaporation residue is not sufficient to manifest a glass transition above –100°C.

Characterization of greases

Greases are typically 80–90% lubricating oils with an added gelling agent and high temperature thickeners. They are formulated for use in severe service environments and multipurpose applications. Therefore, the specifications usually require a wide operational-temperature range. The soap melt and the glass transition define the temperature limit of their application. MTDSC can be particularly helpful in establishing the operational-temperature range as seen in Figs 7 and 8. By conventional DSC the glass transition is often difficult to measure because the heat capacity change at T_g is overshadowed by an endothermic volume relaxation peak. MTDSC, on the other hand, can detect this rather weak glass transition because of the technique's increased sensitivity and ability to sufficiently separate overlapping transitions so as to allow quantitative interpretation. For both greases investigated, four transitions are observed: the glass transition, wax dissolution, soap melt, and decomposition. In the reversing heat flow signal the glass transition is clearly seen but not the wax dissolution. The

soap melting peak of the lithium stearate grease contains both reversing and non-reversing components, whereas in the MoS_2 grease the nonreversing component is predominant.

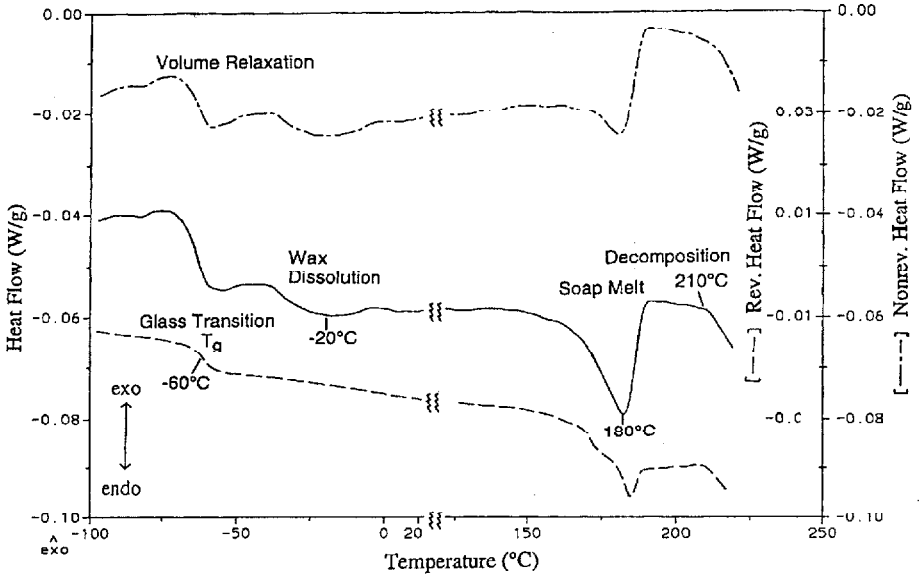

Fig. 7 Characterization of a lithium stearate grease by MTDSC (heating scan)

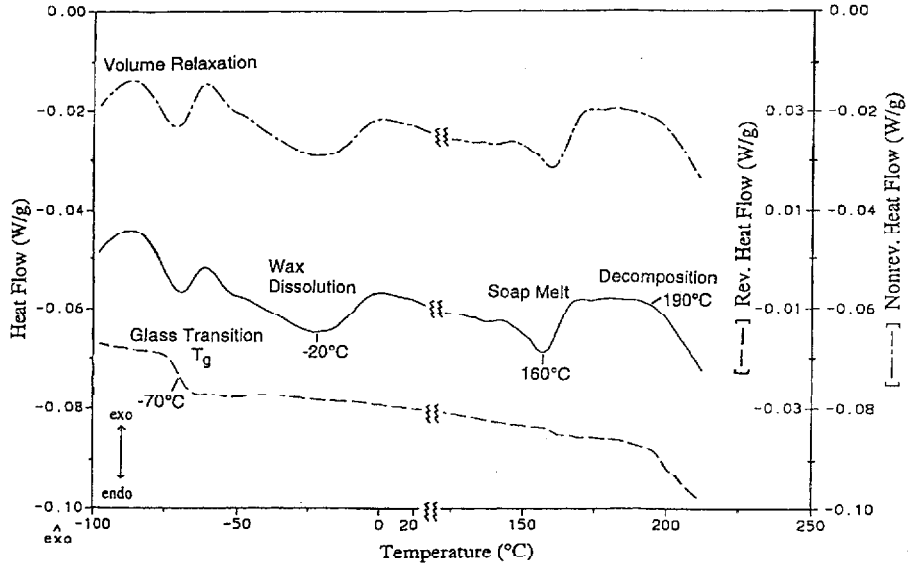

Fig. 8 Characterization of a MoS_2 grease by MTDSC (heating scan)

Conclusions

On the basis of these measurements, MTDSC proved to be a suitable technique with which to characterize petroleum products. The improved resolution compared with conventional DSC as well as its ability to disentangle overlapping phenomena make it valuable for both quality control purposes and research studies.

Although further work must be carried out, there are some encouraging indications that MDSC will ultimately enable, for example, the detection of additives or degradation products in the evaporation residue of fuels. It may also provide a simple way to achieve information about the difference in the quality of greases regarding their final application.

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