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International Journal of Pharmaceutics 192 (1999) 3–20
international journal of pharmaceutics
www.elsevier.com/locate/ijpharm

A discussion of the principles and applications of Modulated Temperature DSC (MTDSC)

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Received 28 January 1999; received in revised form 21 May 1999; accepted 21 May 1999

Abstract

The benefits of Modulated Temperature DSC (MTDSC) over conventional differential scanning calorimetry (DSC) for studying thermal transitions in materials are reviewed by means of examples. These include the separation of overlapping phenomena such as melting/recrystallization in semi-crystalline materials, the heat capacity variation and enthalpic relaxation at the glass transition, and transitions from the different components of a blend. In addition, examples are presented demonstrating the ability of MTDSC to detect subtle transitions more readily and without loss of resolution. The possibility of measuring heat capacity in quasi-isothermal conditions and the evaluation of the thermal conductivity of a material are explained. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Modulated temperature differential scanning calorimetry; Differential scanning calorimetry; Heat capacity; Glass transition; Melting/recrystallization; Thermal conductivity

1. Introduction: the limitations of DSC

Differential scanning calorimetry (DSC) is a thermal analysis technique which has already been used for several decades. It is applicable to a variety of materials including polymers, pharmaceuticals, foods and inorganics. DSC measurements provide qualitative and quantitative information as a function of time and temperature regarding transitions in materials that involve endothermic or exothermic processes, or changes in heat capacity. Some of the advantages contributing to the widespread usage of DSC are the ease of sample preparation, the applicability to both solids and liquids, fast analysis time and wide temperature range.

On the other hand, DSC does have some important limitations. It is often difficult to interpret the heat flow from a DSC experiment if multiple processes are involved over the same temperature range. In a single component material, different types of transitions can overlap such as, for example, melting and recrystallization in a semi-crystalline material and changes in heat capacity during the exothermic cure reaction of a thermoset. In a multicomponent material, transitions

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PII: S0378-5173(99)00267-7

of the different compounds can overlap. Moreover it is not always straightforward to identify the nature of a transition: an enthalpic relaxation peak superimposed on the heat capacity variation at the glass transition temperature can be so large that the transition is confused with a melting transition.

To increase the sensitivity (i.e. signal-to-noise) for the detection of a weak transition either the sample mass or the scan rate can be increased. For obtaining a better resolution in separating transitions occurring at close temperatures, either smaller samples are used or the scan rate is lowered. So increased sensitivity is always at the expense of the resolution and vice versa. Besides, the detection of weak transitions is also strongly influenced by the baseline curvature and stability. The determination of a small jump in heat capacity, for example, is much more difficult when it is superimposed on a curved baseline than if the baseline is straight. Often the baseline is not straight due to, for example, moisture evaporation from the sample, variations in thermal contact between the sample and the DSC pans during the scan and the overall baseline characteristics of the specific DSC cell.

Some quantities such as the absolute value of a material's heat capacity and its thermal conductivity cannot be determined straightforwardly with DSC and require multiple experiments. Moreover, the heat capacity cannot be determined in an isothermal experiment with DSC.

Modulated Temperature DSC (MTDSC) overcomes these limitations and therefore provides new insight into the material's properties. A number of instruments are available under the category of MTDSC. In this paper, we focus on the operation and use of the TA Instruments model, modulated DSC (MDSC); this is necessary in order to avoid confusion between the operating modes and signal nomenclature used for the various approaches. In this review paper, the basic principle of the MDSC technique is summarized and guidelines for the choice of the operating conditions are described. In the next section the advantages of MDSC over DSC are demonstrated by means of examples. Although most of the presented examples are in the field of polymeric materials, the described principles are of course also valid to other materials such as pharmaceuticals and food applications. To conclude, some guidelines are outlined for the choice of MDSC versus DSC. An extensive bibliography is provided including papers describing in detail the theoretical aspects of the MTDSC technique and also studies focussing on the investigation of a particular class of material or type of transition.

2. Operating principle of MDSC

In DSC the difference in heat flow between a sample and an inert reference is measured as a function of time and temperature as both the sample and reference are subjected to a controlled environment (pressure, purge gas). The imposed temperature program is either isothermal, or the temperature is varied linearly as a function of time. In MDSC a sinusoidal modulation is overlaid on the linear ramp as shown in Fig. 1a. This example is for a heating experiment but is analogous for cooling and isothermal experiments. As a result of the temperature modulation, the heating rate is no longer constant, but varies in a periodic (modulated) fashion (Fig. 1b). The average heating rate, corresponding to the rate for a conventional DSC experiment, is called the underlying heating rate. The modulated heating rate varies between a minimum and a maximum value; these are determined by the value of the underlying heating rate, the period (or frequency) and the amplitude of the superimposed temperature wave. Depending on the combination of these three parameters, the minimum modulated heating rate is positive (heat-only), zero (heat-isothermal), or negative (heat-cool).

The resultant heat flow between the sample and reference in a DSC or MDSC experiment is described by the general equation:

$$\mathrm{d}Q/\mathrm{d}t = C_\mathrm{p}b + f(T, t) \tag{1}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the resultant heat flow, C_p is the heat capacity of the sample, b is the rate of temperature change (dT/dt) and $f(T, t)$ is the heat flow from kinetic processes.

For an MDSC experiment, the resultant heat flow is periodically varying and termed the modu-

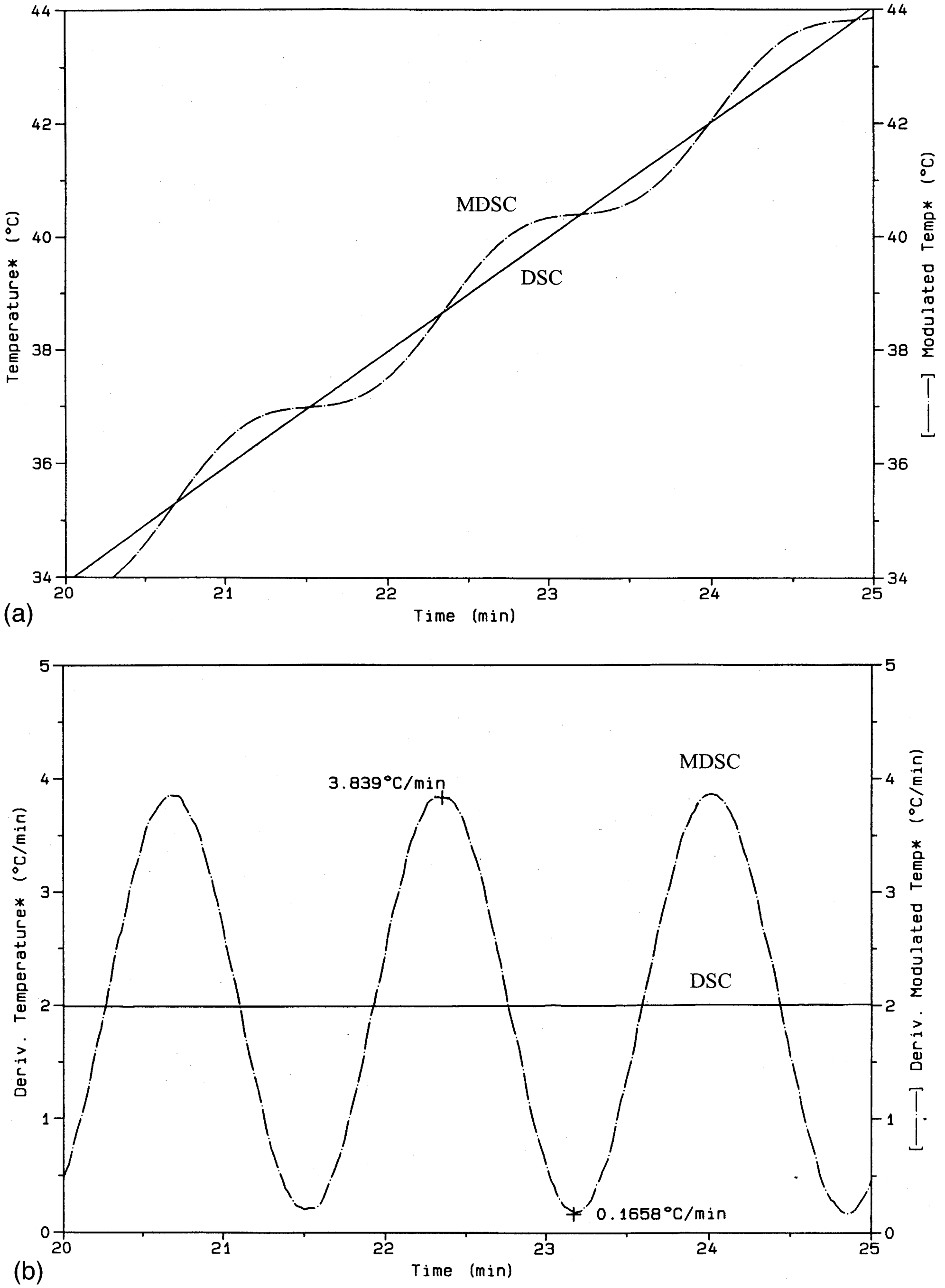

Fig. 1. (a) Temperature as a function of time for a typical DSC and MDSC experiment. (b) Heating rate as a function of time for a typical DSC and MDSC experiment.

lated heat flow. An example of an MDSC experiment on quenched polyethylene terephthalate (PET) is depicted in Fig. 2: the modulated heating rate (stimulus) as well as the modulated heat flow (response) are shown.

From the general equation, it follows that the resultant heat flow is composed of two components: one component is a function of the sample's heat capacity and rate of temperature change, and the other is a function of absolute temperature and time. In conventional DSC only the sum of the two components is determined and is called the total heat flow. In MDSC the total heat flow and the two individual components can be distinguished as the heat capacity component (C_pb) or reversing heat flow and the kinetic component ($f(T, t)$) or non-reversing heat flow.

All of these signals are calculated from three measured signals: time, modulated temperature, and modulated heat flow. The total heat flow in MDSC is calculated from the average of the modulated heat flow; this average corresponds to the total heat flow in a conventional DSC experiment at the same underlying heating rate. In conventional DSC, C_p can be calculated from the difference in heat flow between two runs on an identical sample at two different heating rates. In MDSC, C_p can be determined in a single experiment because of the periodical variation in heating rate: the heat capacity is calculated from the ratio of the modulated heat flow amplitude and the modulated heating rate amplitude by discrete Fourier transformation. The reversing heat flow is then calculated by multiplication of C_p with the negative heating rate b. The kinetic component or non-reversing heat flow is the arithmetic difference between the total heat flow and the reversing heat flow. The total, reversing, and non-reversing heat flows for the MDSC experiment of quenched PET (Fig. 2), are plotted in Fig. 3. The advantages of the splitting of the total heat flow into a reversing and non-reversing component will be discussed in section 4.

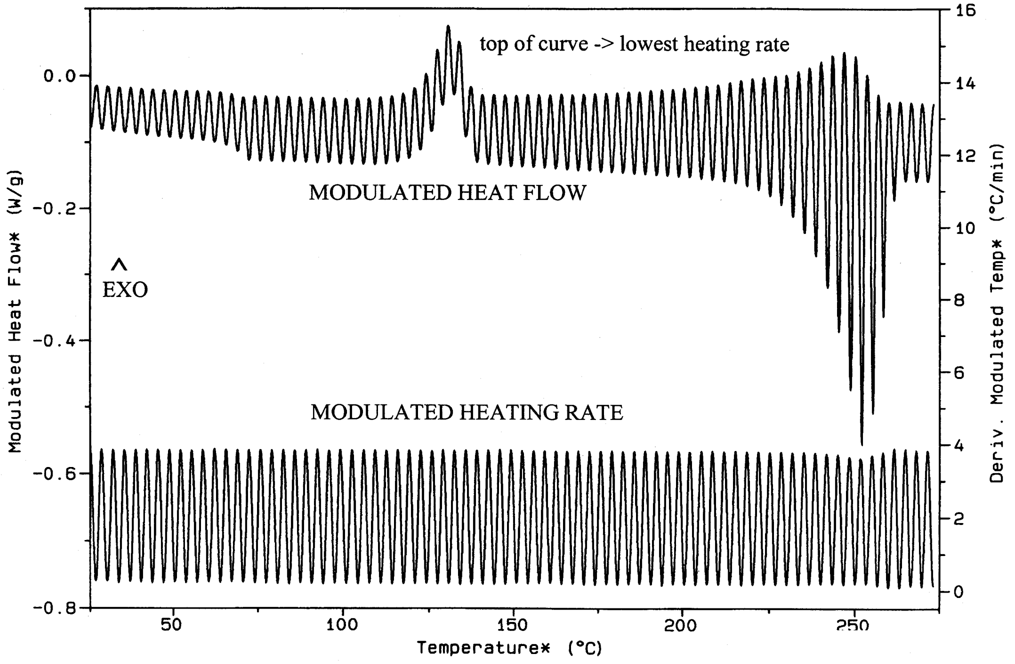

Fig. 2. Modulated heating rate (input) and modulated heat flow (output) for the MDSC heating experiment of a quenched PET sample.

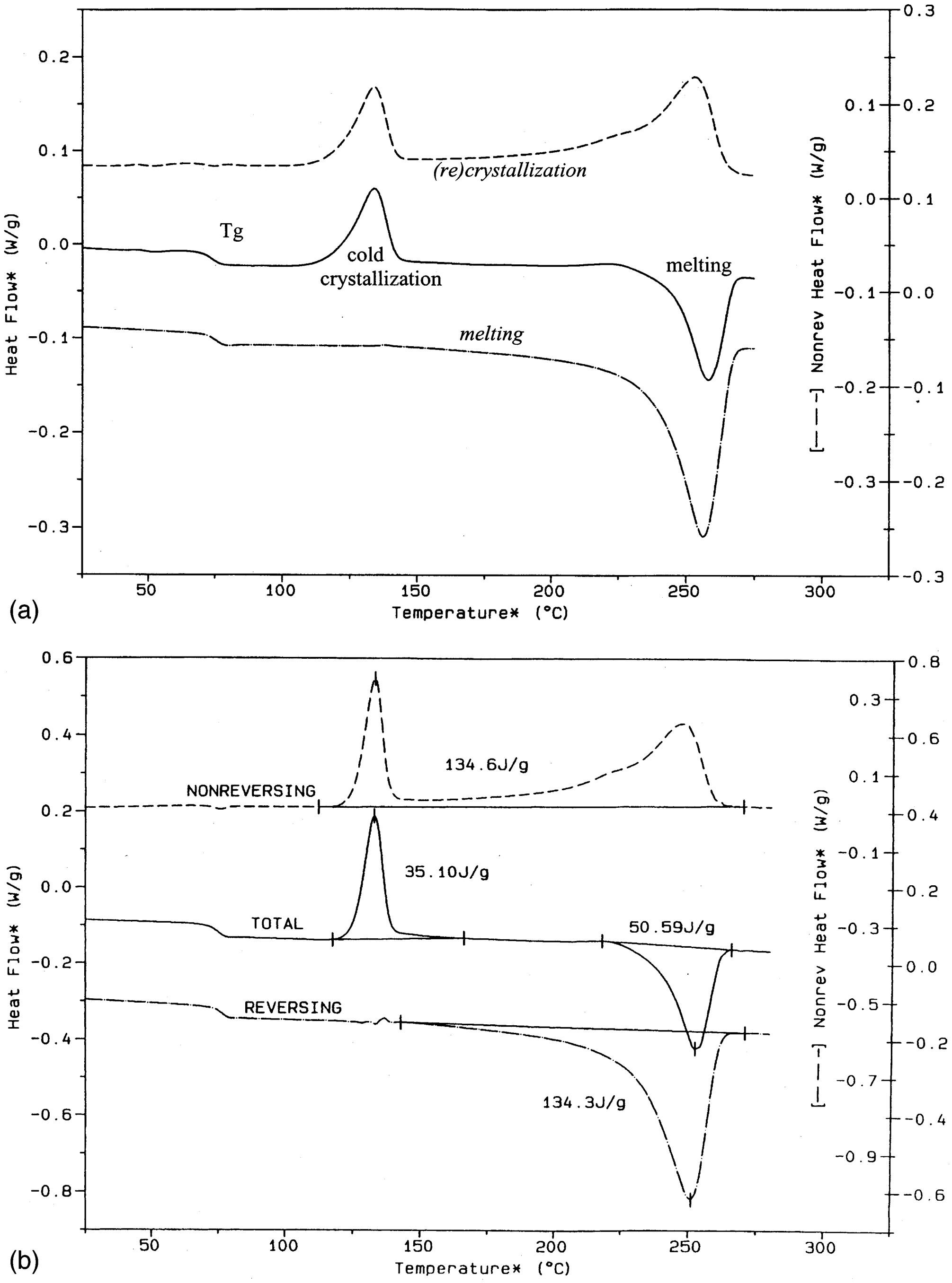

Fig. 3. (a) Deconvoluted signals (total heat flow, reversing heat flow, non-reversing heat flow) for the MDSC heating experiment of a quenched PET sample. (b) Calculation of the initial crystallinity of a quenched PET sample; result from total heat flow: 50.6 – 35.1 J/g = 15.5 J/g; result from reversing and non-reversing heat flow: 134.3 – 134.6 J/g ≈ 0 J/g.

3. Experimental procedures

For the examples given in subsequent sections of the paper, the experiments were performed using a TA Instruments DSC 2920, with MDSC® option and a refrigerated cooling system (RCS). The heat flow was calibrated using indium, and the heat capacity by means of a sapphire standard. The latter is the only additional calibration step that MDSC requires over DSC.

The samples were analyzed in crimped aluminum pans or hermetically sealed aluminum pans with an ordinary lid or lid with pinhole. The reference was an empty pan of identical type as the sample pan and of equal weight (matched within ± 0.1 mg). Care was taken to prepare thin samples (typically 10 mg), with a flat surface to optimize the thermal contact with the pan.

The heating rate was 5°C/min or lower (2°C/min being a typical value), 40–100 s for the modulation period (60 s typically) and ± 0.03–3°C for the amplitude. The combination of heating rate and period was always chosen so that there were at least four modulation cycles during the transition of interest. For studying melt/recrystallization phenomena the parameters were depicted so that the modulated heating rate ranged from zero to a positive value (no cooling involved). For studying subtle transitions, a larger amplitude (> ± 1.0°C) was used, while for the study of transitions close in temperature, a smaller amplitude (< ± 0.5°C) was used. Stepwise quasi-isothermal measurements were performed by keeping the underlying temperature constant for a certain time, then increasing the temperature by 1–2°C, and repeating this procedure throughout the whole transition of interest. Due to the modulation of temperature, the actual heating rate in the quasi-isothermal segment is not zero, but varies between a small negative value and an identical but positive value. This allows for a measurement of heat capacity with an underlying heating rate of 0°C/min.

4. Discussion of MDSC results

The interpretation of a DSC curve is often difficult if different transitions occur in the same temperature range. In some cases these overlapping processes can be distinguished with MDSC since they are split in the reversing and non-reversing heat flow. Since the reversing component is related to the sample's heat capacity a glass transition event is detected in the reversing heat flow. On the other hand processes such as enthalpic relaxation, crystallization, evaporation, decomposition, and cure are resolved into the non-reversing heat flow. For a melting transition the interpretation is not straightforward. Melting can occur in the reversing heat flow as well as in the non-reversing heat flow, and moreover the fraction of melting in both of these signals depends on the experimental conditions (underlying heating rate, modulation period, modulation amplitude, sample thickness).

A first example of the additional information obtained from MDSC is illustrated in Fig. 3a (quenched PET). The conventional DSC signal (equivalent to the total heat flow from the MDSC experiment) subsequently shows the glass transition, the cold crystallization exotherm, and the melting of the formed crystals. In the region between crystallization and melting the heat flow seems to return to its baseline. However, when looking at the reversing and non-reversing components, it becomes clear that in this region endothermic melting (displayed in the reversing heat flow) and exothermic (re)crystallization (displayed in the non-reversing heat flow) compete, resulting in a net 'zero' effect in the total heat flow. In this example, the experimental parameters are chosen to provide a heat-isothermal modulated heating rate profile. At the moment that the modulated heating rate is zero, the heat flow is entirely due to kinetic processes (see the general heat flow equation, with $b = 0$). The heat flow at the lowest heating rate (zero in this case) is in fact the top of the modulated heat flow signal (Fig. 2). The kinetic process of (re)crystallization during heating can thus also be verified from the top of the modulated heat flow in Fig. 2. This example illustrates the ability of MDSC to gain more insight into the crystalline structure of semi-crystalline polymers. Moreover, from the total heat flow it is difficult to calculate the initial crystallinity (i.e. crystallinity at room temperature, prior to heating) of the sample, because it is not clear how to choose the baseline for peak integration. In essence one needs to compare the enthalpies of crystallization and melting. From the choice made for the total heat flow in Fig. 3b one would deduce a non-zero value for the sample's initial crystallinity. However, peak integration of the reversing and non-reversing heat flows is much less dependent on the choice of the baseline; summation of the endothermic and exothermic effect in these respective heat flows accounts for the initial crystallinity of the sample being zero, which is to be expected for an appropriately quenched PET sample.

A second example is the study of the glass transition of an epoxy resin (Fig. 4). With samples that have been stored just below their glass transition temperature, or have been cooled at a rate very different from the subsequent heating rate, an enthalpic relaxation peak is present in the glass transition region. This relaxation peak can be so large that it hides the variation of the heat capacity at T_g and the transition can be misinterpreted as a melting transition (total heat flow). The reversing and non-reversing heat flow signals separate the change in C_p at T_g from the enthalpic relaxation (Fig. 4) and greatly simplify interpretation of the transition.

A third example is the study of a blend material of three components: high density polyethylene (HDPE), polycarbonate (PC), and PET. Blending of materials is an important tool in improving their end use properties. Interpretation of the DSC signal of a blend, however, can be very complicated if the respective component transitions overlap, as in the total heat flow of the example in Fig. 5. When looking at the reversing heat flow, the T_g of the PET and PC can be

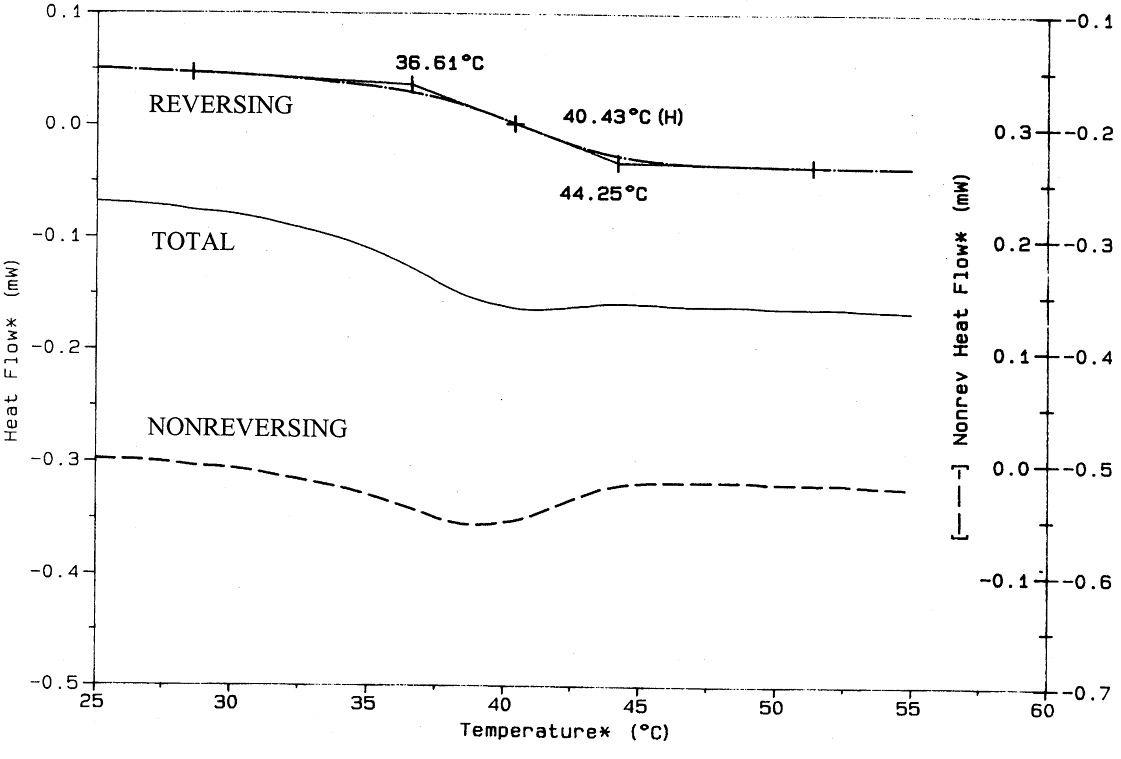

Fig. 4. MDSC heating curves of an aged epoxy resin.

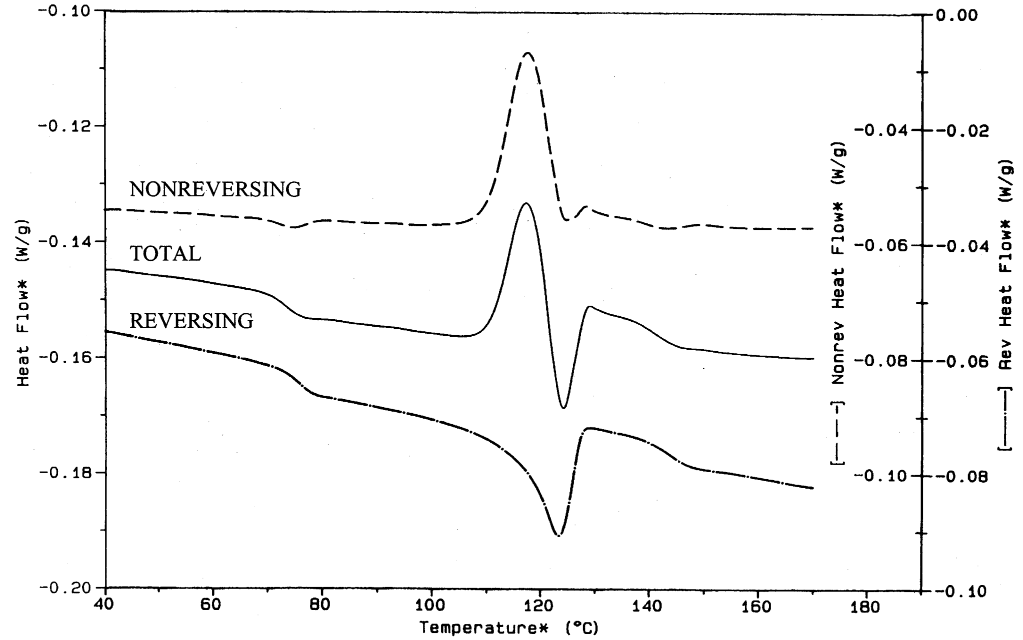

Fig. 5. MDSC heating curves of a HDPE/PC/PET blend.

determined more easily, since the enthalpic relaxation peak is removed. More importantly, the PE melt (in the reversing heat flow) can be distinguished from the PET cold crystallization (in the non-reversing heat flow).

The determination of a weak glass transition with DSC can be substantially hampered by baseline effects and other transitions in the same temperature range. Fig. 6 shows a polymer resin where the presence of moisture in the as-received sample has such severe effects on the baseline that the step change at T_g is difficult to determine definitively in the total heat flow signal. In the MDSC experiment, however, the baseline curvature and/or drift are eliminated from the reversing heat flow because this signal is calculated from the ratio between the modulated heat flow amplitude and modulated heating rate amplitude and not from the absolute value of heat flow which can drift over time. So the T_g can be determined unambiguously in the reversing heat flow, since baseline effects are resolved into the non-reversing heat flow.

With DSC, sensitivity and resolution are both affected by the heating rate but in a converse way. Therefore, choosing the heating rate in conventional DSC is always a compromise. MDSC eliminates this need to compromise by exposing the sample to different heating rates simultaneously. The underlying heating rate can be as low as zero to optimize resolution, while in the same experiment the modulated heating rate can be higher than 20°C/min to maximize sensitivity. The result is both good resolution and sensitivity. Fig. 7 shows an MDSC heating experiment for a blend of PC and polyetherester (PEE). The small glass transition is readily detectable in the reversing heat flow, and its shape changes slightly on each reheating experiment (see the three curves in Fig. 7). A clearer picture is obtained by looking at the derivative signal. The first time that the sample is heated, two overlapping T_g's are visible (curve 1). After cooling and reheating (curves 2 and 3), the fraction of material devitrifying at the higher temperature decreases at the expense of the material devitrifying at the lower temperature. These effects are caused by the variations in the material's thermal history. This example shows how subtle and broad transitions, occurring close in temperature, can still be accurately detected and resolved with MDSC.

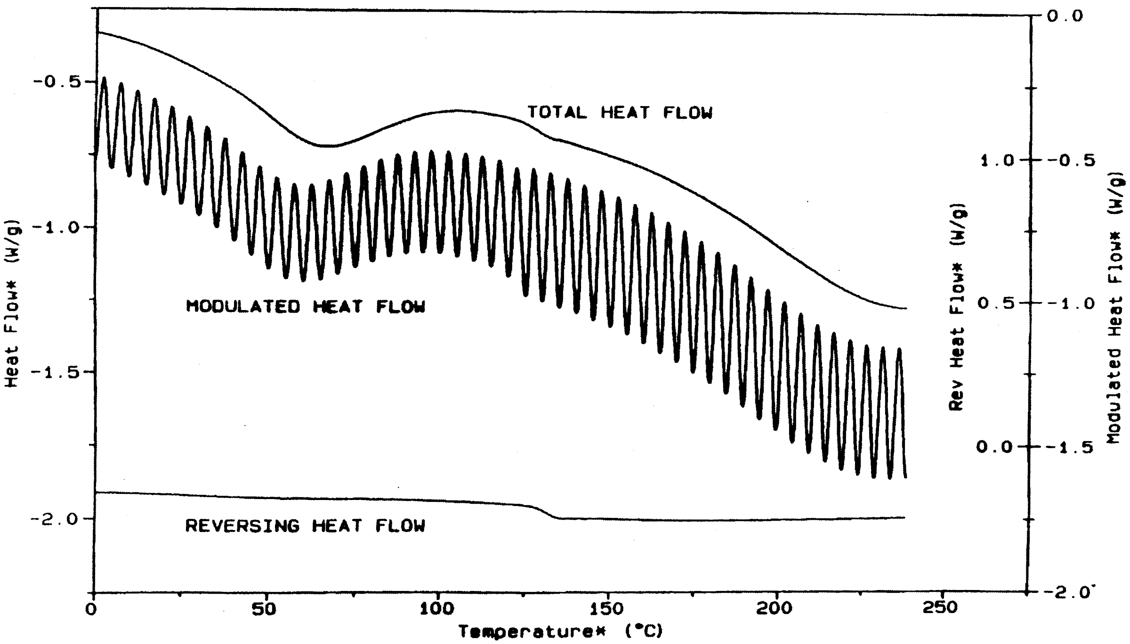

Fig. 6. MDSC heating curves of an as-received polymer resin.

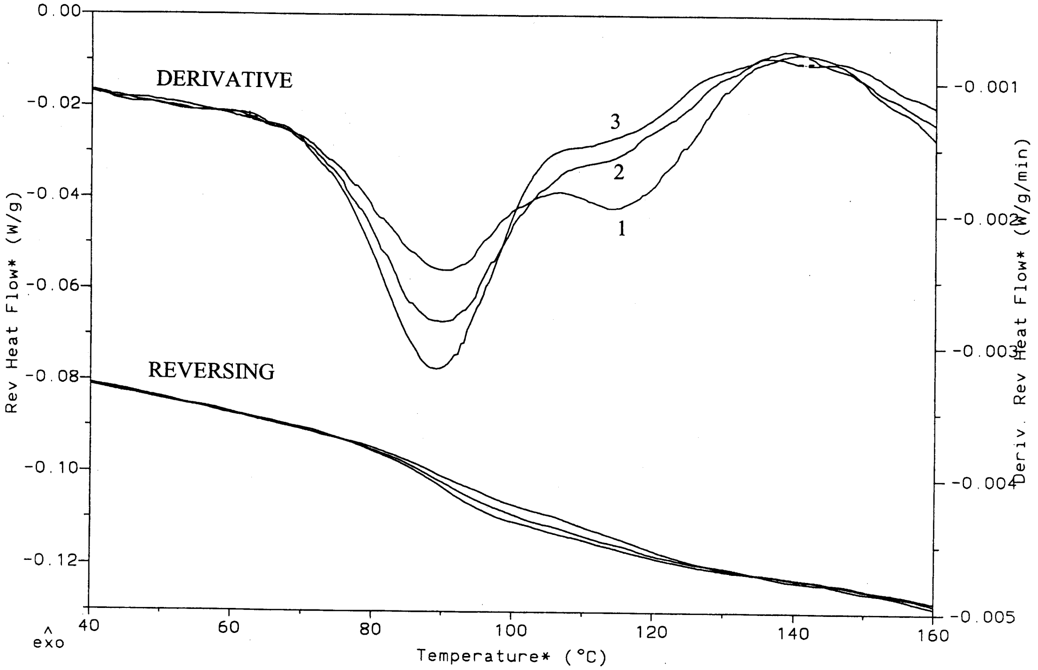

Fig. 7. MDSC heating curves of a PC/PEE blend; curves 1 to 3 represent consecutive heating experiments.

With MDSC the heat capacity is measured together with the total heat flow, in one single experiment. This can provide valuable information in the study of certain reactions; e.g. vitrifica-

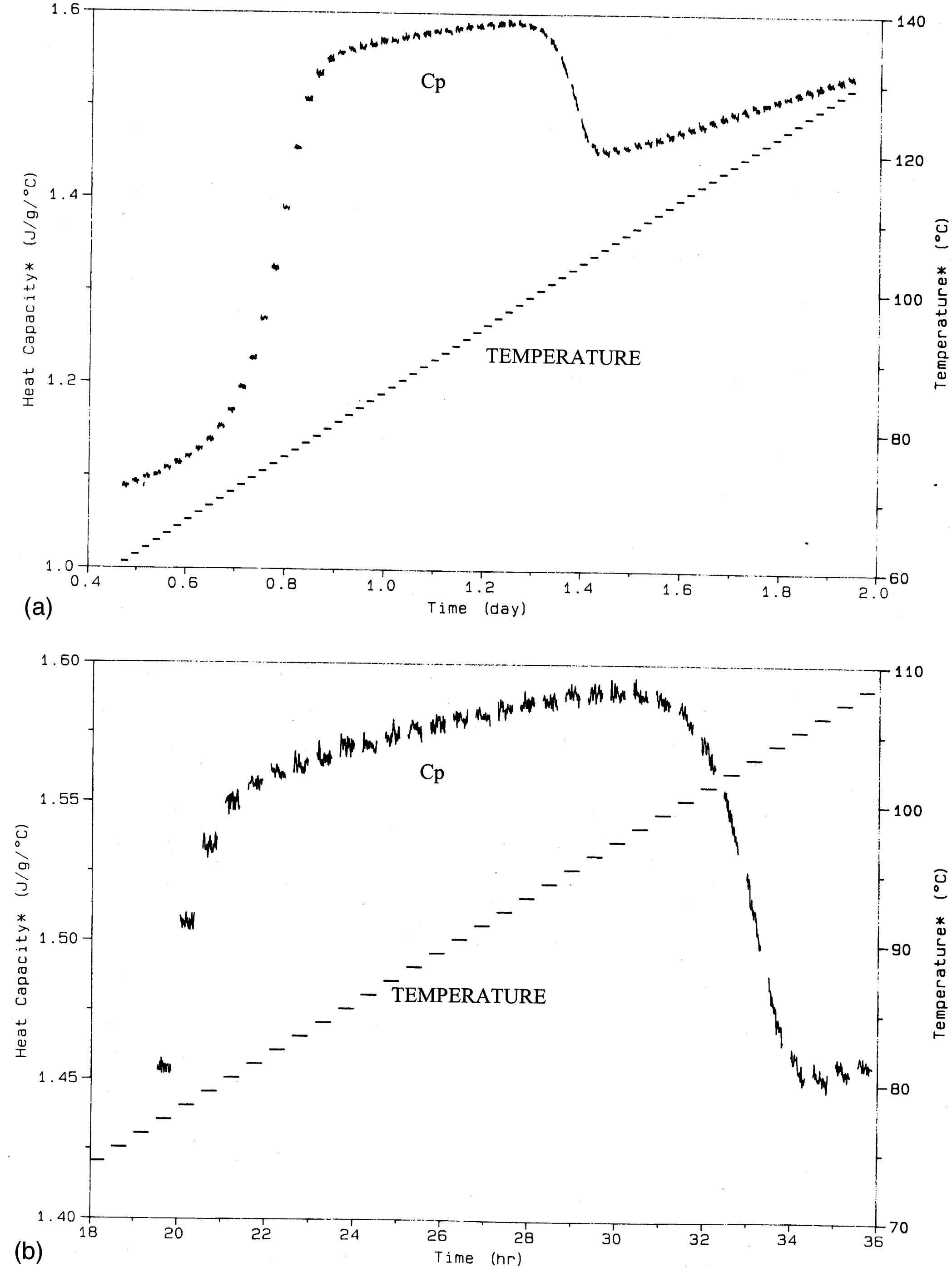

Fig. 8. (a) Stepwise quasi-isothermal MDSC experiment of quenched PET. (b) Magnification of (a).

tion during cure of a thermoset can be detected. Moreover, the heat capacity can be measured under quasi-isothermal conditions. This is possible since C_p is measured from the change in heat flow amplitude that results from the change in the heating rate. In a quasi-isothermal MDSC experiment, the underlying temperature is held constant, while the sample is heated and cooled (modulated) around a constant average temperature. An example of a stepwise quasi-isothermal experiment on quenched PET is plotted in Fig. 8a. As the sample is heated stepwise from below its glass transition temperature, an increase in C_p is first noticed, corresponding to devitrification of PET at the glass transition temperature. Subsequently, a decrease in C_p is detected when the sample reaches a point where cold crystallization can occur. Taking a closer look at the C_p signal as a function of time for each quasi-isothermal curve (Fig. 8b), it can be seen that for the lower temperatures, the value of C_p as a function of time is stable. However, in the temperature region where cold crystallization takes place, C_p shows a time-dependent decrease at each constant temperature due to the proceeding cold crystallization. This example demonstrates the valuable extra information that can be obtained from the direct measure of C_p in MDSC. These stepwise quasi-isothermal measurements can be particularly useful in the study of very narrow transitions, where it is difficult to obtain enough modulation cycles for reliable deconvolution of the total heat flow.

The thermal conductivity of insulating materials (polymers, pharmaceuticals, ceramics) at different temperatures can be determined with MDSC. The procedure is based on the measurement of the heat capacity of the material on a thin sample (typically several hundreds of μm) and the ‘apparent’ heat capacity of a thick sample (typically a couple of mm) with predetermined geometry. For the thick sample, the measured ‘apparent’ heat capacity will be lower than the actual C_p measured on a thin sample. This is due to thermal gradients in the thick sample, caused by the finite value of the material’s thermal conductivity. From the measured decrease in the apparent heat capacity, and through calibration with a reference material, the thermal conductivity can be quantified with an accuracy in the order of 5%. For more details on this procedure the reader is referred to the appropriate references in the bibliography.

5. Conclusion

From the previous section, it is clear that the MDSC technique is a powerful addition to DSC that often offers valuable extra information in the study of the thermal properties of materials. Overlapping transitions such as melting/recrystallization in semi-crystalline materials, the heat capacity variation and enthalpic relaxation at the glass transition, and transitions from the different components of a blend can be separated. In addition, MDSC can detect subtle transitions more readily and without loss of resolution. Moreover, MDSC allows the measurement of heat capacity in quasi-isothermal conditions and the quantification of the thermal conductivity of insulating materials.

There are also disadvantages to the technique. An MDSC measurement generally takes more time since a lower underlying heating rate is used than for conventional DSC. Moreover, care must be taken in choosing the modulation parameters (period and amplitude) and interpreting their effect on the results, especially for the melting process.

Therefore, MDSC should not be used as a replacement for conventional DSC. It is better to begin with conventional DSC when investigating an unknown sample. Then the operator can decide if MDSC needs to be used. Advantages of MDSC include help with interpretation of the results of complex transitions in homogeneous materials or overlapping phenomena in blends, knowledge of possible recrystallization as the sample is heated, increased sensitivity for weak transitions, combination of good sensitivity and resolution, determination of heat capacity variations during reactions or other transitions, heat capacity measurements in quasi-isothermal conditions and determination of thermal conductivity of insulators.

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