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MODULATED DIFFERENTIAL SCANNING CALORIMETRY

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Modulated DSC™ (MDSC) is a new, patent-pending extension to conventional DSC which provides information about the reversing and nonreversing characteristics of thermal events, as well as the ability to directly measure heat capacity. This additional information aids interpretation and allows unique insights into the structure and behaviour of materials. A number of examples of its use are described.

Keywords: modulated DSC

Introduction

Differential scanning calorimetry (DSC) is a thermal analysis technique which has been used for more than two decades to measure the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. DSC is the most widely used thermal analysis technique with applicability to polymers and organic chemicals, as well as various inorganic materials.

Modulated DSC™ (MDSC) is a new, patent-pending extension to conventional DSC which provides information about the reversing and nonreversing characteristics of thermal events. This additional information aids interpretation and allows unique insights into the structure and behavior of materials.

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Theory

In a typical heat-flux DSC cell, the sample (contained in a metal pan) and reference (an empty pan) sit on raised platforms formed in a thermoelectric (constantan) disk, which serves as the primary means of heat transfer to the sample and reference from a temperature-programmed furnace (heating block). Traditionally, the temperature of the furnace is raised or lowered in a linear fashion, while the resultant differential heat flow to the sample and reference is monitored by plate thermocouples fixed to the underside of the disk platforms. These thermocouples are connected in series and measure the differential heat flow using the thermal equivalent of Ohm's Law:

$$dQ = dT/R$$

where dQ = difference in heat flow between sample and reference, dT = temperature difference measured, and R = thermal resistance of the cell.

In modulated DSC™ (MDSC), the same heat-flux DSC cell arrangement is used, but a different temperature (heating/cooling) profile is applied to the sample and reference via the furnace. Specifically, a sinusoidal ripple (modulation) is overlaid on the standard linear temperature ramp (Fig. 1). As a result, there are three heating-related experimental variables which can be used to im-

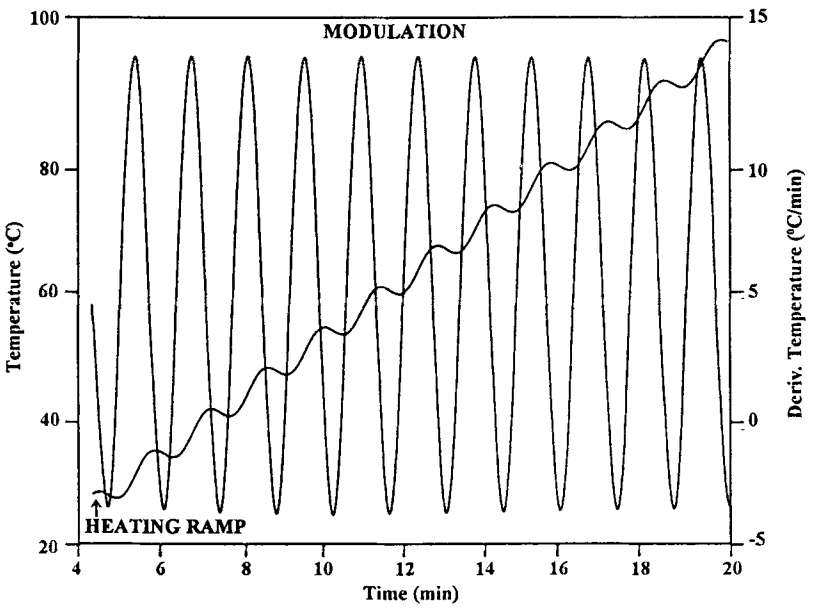

Fig. 1 Modulated DSC™ heating profile

prove DSC results. These variables are heating rate, amplitude of modulation, and frequency of modulation. To appreciate the effects these variables can have, the general equation describing calorimeter response needs to be examined.

One way to represent this heat flow mathematically is:

$$dQ/dt = -\frac{dT}{dt}[C_p + f'(t, T)] + f(t, T)$$

where dQ/dt = heat flow out of the sample, dT/dt = heating rate, C_p = sample heat capacity, t = time, T = temperature, $f'(t, T)$ = thermodynamic heat flow component, and $f(t, T)$ = kinetically-limited heat flow.

This equation shows that total heat flow comprises two contributions, one of which is heating-rate dependent and another which is dependent only on absolute temperature. The relative effect of these two contributions varies depending on the transition being evaluated. Heating-rate dependent transitions tend to be larger when evaluated using faster heating rates and are 'reversing', i.e. the transition can be cycled by alternating heating and cooling. Absolute temperature dependent transitions, on the other hand, once initiated cannot be reversed by cyclic heating/cooling and are considered 'nonreversing'.

Transition	Characteristic
Heat Capacity	Reversing
Glass Transition	Frequency Dependent
Melting	Freq. & Amp. Depend.
Cold Crystallization	NonReversing
Relaxation	"
Curing	"
Evaporation	"
Decomposition	"

Fig. 2 DSC measured transitions

Figure 2 summarizes typical material transitions (properties) measured by DSC and indicates whether each is reversing or nonreversing. Note that several transitions, particularly polymer melting, contain both reversing and nonreversing characteristics. MDSC™ facilitates the separation of reversing and nonreversing transitions.

The 'raw' MDSC™ experimental curve for quenched PET is shown in Fig. 3. This experimental curve can be deconvoluted using discrete Fourier transforma-

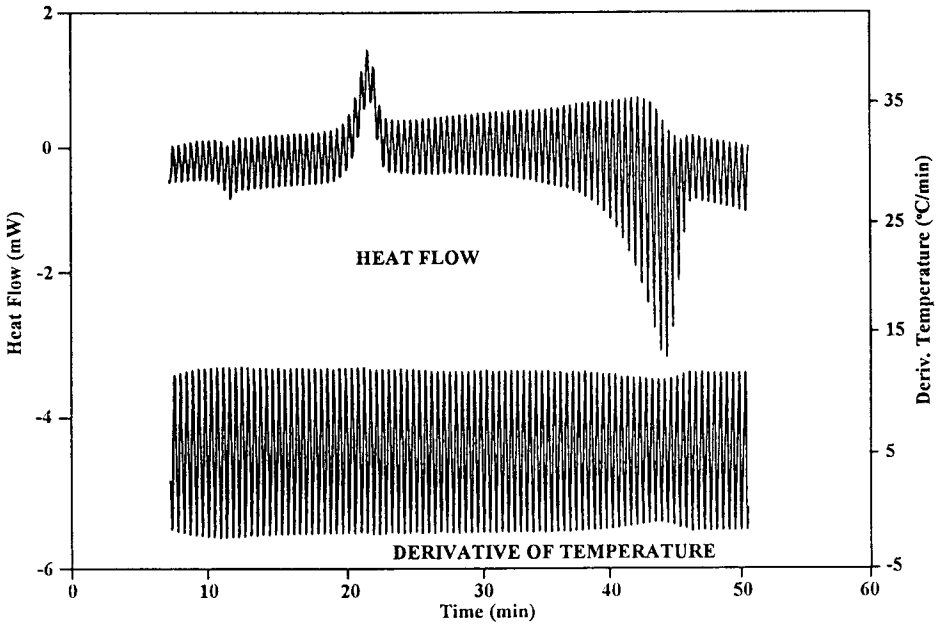

Fig. 3 PET modulated DSC™ curve

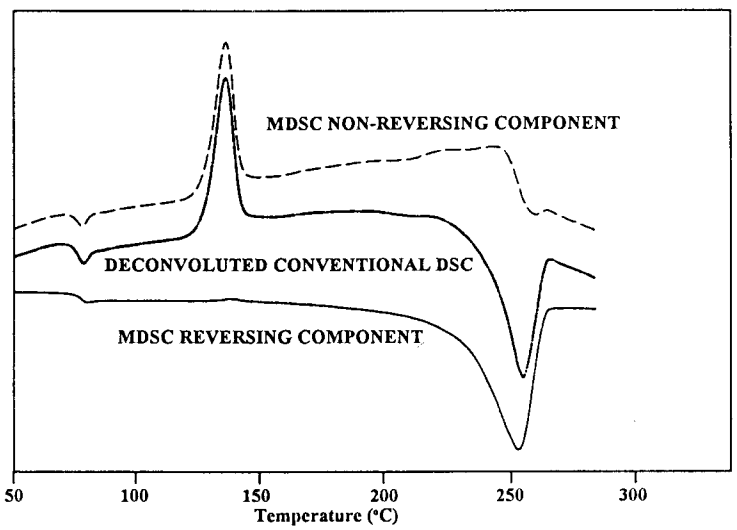

Fig. 4 Deconvoluted modulated DSC™ PET curves

tion software to obtain a conventional DSC curve (solid line) and/or both its reversing and nonreversing components (Fig. 4). Quenched PET exhibits three thermal transitions a glass transition (T_g) with an associated relaxation peak at 85°C, a crystallization exotherm at 135°C, and a melting endotherm at 250°C. Theoretically, the relaxation peak associated with the T_g and the crystallization peak associated with rearrangement of the less stable amorphous internal structure to the more stable crystalline structure should be nonreversing transitions. This is in fact what is observed in the separated MDSC™ results. The T_g on the other hand, is a reversing phenomenon and appears only in the reversing portion of the MDSC™ results. Finally, the crystalline melting peak contains both reversing and nonreversing components. Hence, the melting endotherm observed in conventional DSC is not identical to the MDSC™ reversing curve, particularly in the latter stages of melting where the transition becomes nonreversing. This change in behaviour is easily explained. During the early stages of melting, the presence of many crystallites facilitates melting and recrystallization as heating modulation occurs. Eventually, however, all the crystallites (sites for recrystallization) have melted and recrystallization cannot occur. At that point, melting becomes nonreversing. The relative amounts of reversing and nonreversing melting behaviour depends primarily on the modulation frequency. The results observed provide valuable insight into the kinetics and thermodynamics of semicrystalline polymer melting.

Applications

The following applications illustrate the types of information which can be obtained from modulated DSC™. These results were obtained using a TA Instruments DSC 2910 differential scanning calorimeter upgraded with the MDSC™ option. Fourier transformation of the modulated heat flow was performed during data collection, yielding separation of reversing and nonreversing phenomena during the experiment.

Separation of overlapping reversing and nonreversing thermal transitions

Figure 5 shows the conventional DSC curve (solid line) for a bilayer film containing polycarbonate (PC) and amorphous PET. The curve exhibits a transition between 130° and 150°C. However, interpretation and quantitation are difficult, because the transition observed represents overlap of the polycarbonate glass transition (T_g) and the PET crystallization exotherm. The MDSC™ results, how-

ever, clearly separate these two phenomena. The polycarbonate T_g is a reversing transition, while recrystallization is a nonreversing phenomenon.

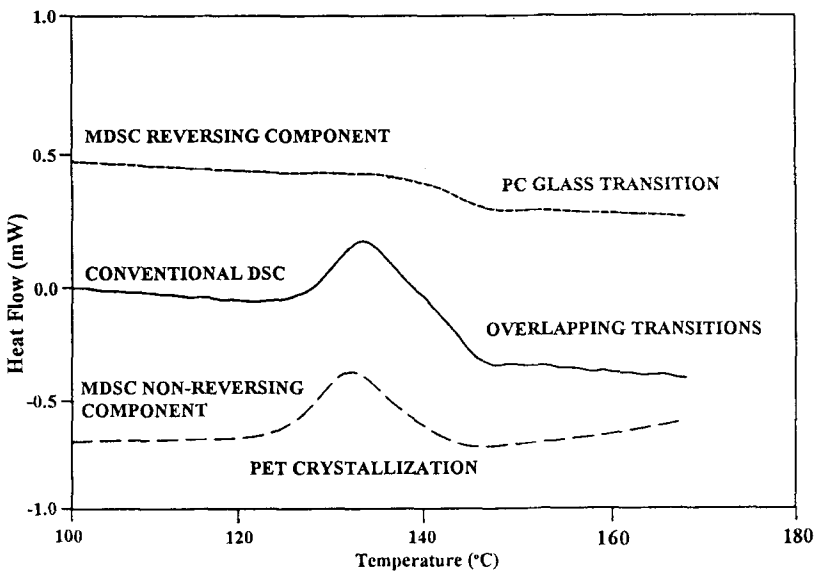

Fig. 5 Modulated DSC™ results for PET/PC bilayer film

Separation of relaxation phenomena from the glass transition

In thermosets and semicrystalline/amorphous thermoplastics, processing can result in internal molecular stresses (thermal history effects) which are relieved on reheating. The release of these stresses appears as a small endothermic relaxation event after the glass transition. The close proximity of the endotherm to the glass transition can make interpretation difficult as shown for a B-stage epoxy in Fig. 6 (solid line). MDSC™ on the other hand, separates the glass transition (reversing) from the endothermic relaxation (nonreversing), thereby improving interpretation. Thermal history effects such as the endothermic relaxation peak can also be eliminated by 'pretreating' the material (heating above the T_g and then slowly cooling) before evaluation. However, in thermosets, this type of pretreatment could advance-cure and alter the results.

Direct measurement of heat capacity

Heat capacity measurement by conventional DSC is a tedious process requiring multiple experiments and considerable operator expertise to obtain results

with reasonable accuracy and precision. Modulated DSC™ provides the ability to measure heat capacity directly in a single experiment, and to measure it even at very slow underlying heating rates. Figure 7 shows the results from three separate MDSC™ evaluations on sapphire, a well-characterized standard material. The crosses indicate reported literature C_p values at several temperatures for com-

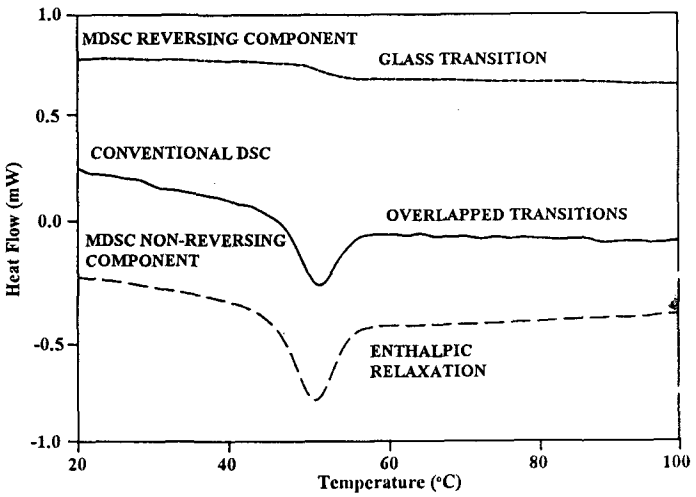

Fig. 6 Epoxy composite T_g by modulated DSC™

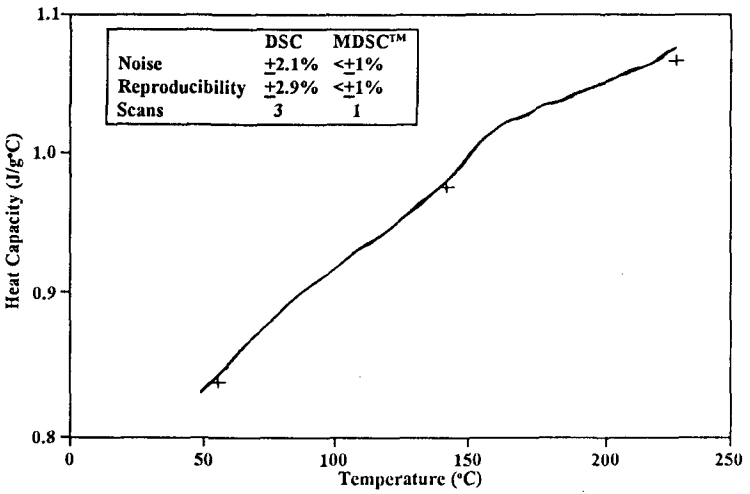

Fig. 7 Sapphire heat capacity measurements by modulated DSC™

parison. The table in the upper left hand corner of the figure compares the typical precision and noise, as well as the number of experiments, associated with heat capacity measurements by conventional DSC (based on ASTM round robin results) and MDSC™. MDSC™ provides better results in less experimental time.

Heat capacity measurement during isothermal curing

The ability to measure a sample's heat capacity change during a near-isothermal experiment is a valuable application of modulated DSC™. Shown in Fig. 8 are the MDSC™ results and DMA of a high-temperature epoxy cured at 90°C. The nonreversing heat flow shows an exotherm due to curing. The DMA modulus increases at exactly the same time as the heat capacity decreases. This implies that the heat capacity decreases during the cross linking portion of the thermoset curing process.

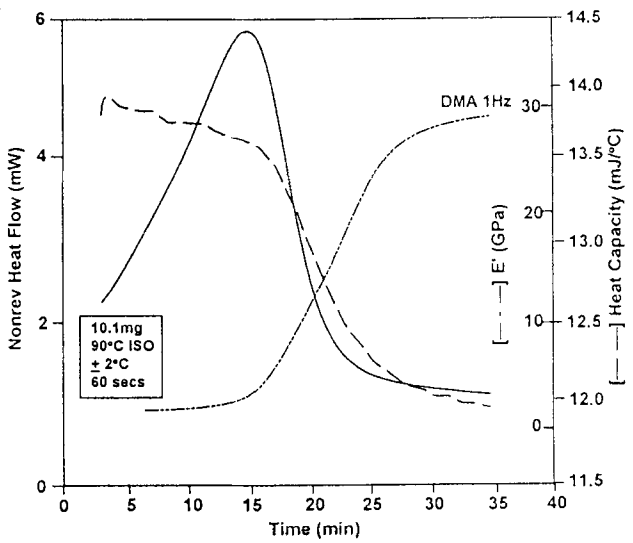

Fig. 8 Isothermal thermoset curing by modulated DSC™

Conclusion

Modulated DSC™ is a new technique that promises to significantly enhance the diversity of information which can be obtained from DSC. The ability to separate reversing and nonreversing transitions, as well as the ability to directly

measure heat capacity, offers thermal analysts another tool for solving difficult materials characterization problems.

Zusammenfassung — Modulierte DSC™ (MDSC) ist eine angemeldete Patenterweiterung herkömmlicher DSC, welche Informationen über reversible und nichtreversible Eigenschaften von thermischen Geschehnissen erstellt und sich zur direkten Messung der Wärmekapazität eignet. Diese zusätzlichen Informationen helfen bei der Interpretation und erlauben ein eindeutiges Verständnis des Verhaltens von Substanzen. Es wird eine Anzahl von Anwendungsbeispielen diskutiert.