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ΜΗΧΑΝΙΚΗ... **Characterization of polymeric materials by modulated differential scanning calorimetry**, by correspondig member of the academy *J. C. Seferis, I. M. Salin*, University of Washington, *P. S. Gill*, TA-Instruments, and *M. Reading*, Imperial Chemical Industries*.

ABSTRACT

Modulated Differential Scanning Calorimetry (MDSC) is a novel DSC technique that applies a sinusoidal small amplitude temperature oscillation with fixed period and amplitude on top of a constant heating rate ramp or isothermal temperature. The measured oscillating heat flow can be deconvoluted into conventional DSC curve, and separated into its reversing and non-reversing components by applying Discrete Fourier Transform. Separation of the alternating heat flow facilitates determination of heat capacity from a single MDSC run instead of multiple conventional DSC runs. For polymers, glass transition is the main reversing transition. Consequently, the most obvious applications of MDSC include determination of heat capacity and separation of glass transition from overlapping non-reversing transitions such as enthalpic relaxation or additional cure, and separation of glass transition from poor baseline. In this study, the MDSC (TA Instruments DSC 2910 with the MDSC capability) was used to evaluate different heterogeneous polymer systems: carbon fiber reinforced bismaleimide (BMI), a thermosetting polyimide, polyethylene terephthalate/polycarbonate blend, and carbon fiber

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reinforced polyethylene terephthalate. In addition, heat capacity was determined for polystyrene sample after calibrating the instrument with standard sapphire sample. Collectively, the results indicated that the MDSC provides many advantages in the analysis of polymeric systems, especially when viewed as intrinsically heterogeneous, anisotropic, and viscoelastic systems. The results generated have far reaching implications not only in material characterization but in scale-up issues dealing with manufacturing, design, and performance concepts.

INTRODUCTION

Differential Scanning Calorimetry (DSC) is a well established technique that gives information about the temperature and heat flow associated with thermal transitions in the sample material. Modulated DSC (MDSC™) is a novel DSC technique, which can separate thermal transitions that are reversing or non-reversing with respect to a small amplitude temperature oscillation [1]. This is accomplished by imposing a sinusoidal temperature modulation on top of a constant underlying heating rate or constant temperature. When the temperature is oscillated around a constant underlying heating rate or temperature, the response of the sample consists of an oscillating heat flow, which has both reversing and non-reversing components. A Discrete Fourier Transform is then used to deconvolute the signal into conventional DSC curve and to separate the reversing and non-reversing components. Also, the separation of the heat flow into its components facilitates determination of heat capacity from a single MDSC experiment as opposed to multiple conventional DSC experiments. Originally conceived by M. Reading, it was reduced to practice by T. A. Instruments with the development of their MDSC™ keeping in focus the wide implications that such a technique may have in both small and large scale utilization. The development of MDSC is an example of a project in which instrument development and evaluation of the fundamental basis has been done in co-operation between Industry and Academia, as illustrated in Figures 1 and 2 [2, 3].

For polymers and their composites, glass transition temperature is the most important reversing event that can be extracted from MDSC data. Non-reversing events include enthalpic relaxation associated with glass transition, additional crystallization, volatile evolution, curing reactions, and degradation. The melting of crystallites usually appears in both reversing and non-

reversing component, since this transition possesses both characteristics depending on the extent of melting and availability of nucleation sites.

In this work, the MDSC™ (TA-Instruments DSC 2910 with the MDSC capability) was used to characterize polyethylene terephthalate/poly carbonate blend, carbon fiber reinforced high temperature bismaleimide, polyimide, and carbon fiber reinforced polyethylene terephthalate prepreg. In addition, the determination of heat capacity was demonstrated using standard sapphire, and polystyrene samples.

BACKGROUND AND OPERATION PRINCIPLES

When a sample is thermally cycled beginning and ending at the same temperature, the integral of the heat flow associated with a reversible phenomena is zero, and the integral of the heat flow associated with an irreversible phenomena is finite. In general, reversible phenomena are thermodynamically controlled, i. e. once the temperature, pressure, etc., are fixed, the state of the system is fixed. Because of the viscoelastic nature of polymeric materials, no thermal event is truly reversible. By applying specific temperature cycles, some events can be reversed and some not. Accordingly, these events can be referred to as being reversing and non-reversing with respect to the specified temperature cycle.

In a conventional DSC experiment, the DSC cell (sample and reference) is either held at constant temperature (isothermal experiment) or heated at a constant heating rate (dynamic experiment). The difference in heat flow required to keep the sample and reference at the programmed temperature is then measured, providing a total differential heat flow curve as a function of time or temperature. Conventional DSC provides no information about the reversing or non-reversing characteristics of transitions since the temperature is not cycled.

In modulated DSC, a sinusoidal temperature oscillation with fixed amplitude (°C) and period (seconds) is imposed on the constant underlying heating rate or isothermal temperature, resulting in a temperature profile oscillating around constant heating rate or isothermal temperature. The oscillating heat flow associated with the sample response then consists of both reversing and non-reversing components. Here, reversing and non-reversing refer to the heat flow components that can or cannot be reversed by oscillating the temperature in a manner described above.

The temperature program of the MDSC can be written as (4)

$$T = T_0 + qt + A \sin(\omega t) \quad (1)$$

where T and T_0 are the temperature and initial temperature, respectively, q is the underlying heating rate, A the temperature amplitude, and ω the frequency of oscillation. The heat flow change in DSC can be expressed as

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T) \quad (2)$$

where Q is the total heat flow, C_p is the heat capacity, dT/dt is the heating rate q , and $f(t, T)$ is a kinetic heat flow component. In principle, the first term on the right in Eqn. (2) is the reversing heat flow component, which is directly related to heat capacity and heating rate. As the temperature is oscillated sinusoidally, the heating rate (derivative of temperature) is a cosine wave. Since the reversing component changes linearly as a function of heating rate, it will oscillate as the temperature is oscillated. The kinetic contribution in Equation (2) can be written as

$$f(t, T) = f'(t, T) + \sin(\omega t) \quad (3)$$

Here, $f'(t, T)$ is the kinetic contribution without the out-of-phase sinusoidal component $\sin(\omega t)$. In addition to the temperature and oscillating heat flow, the instrument will measure the phase lag, i. e. the angle between applied temperature oscillation and measured heat flow oscillation. If this angle is small, the out-of-phase component can be neglected, and Equations (1), (2), and (3) combined as

$$\frac{dQ}{dt} = C_p [q + A\omega \cos(\omega t)] + f'(t, T) \quad (4)$$

The present deconvolution algorithm works according to the principle of Equation (4). Discrete Fourier Transform (DFT) is used to separate the oscillating heat flow component from the underlying signal, which constitutes the conventional DSC curve. Upon comparison of the oscillating component of the heat flow and the first term on the right side of Equation (4), the heat capacity can be determined, since q , A , and ω are measured. The contribution of the heat capacity dependent heat flow component can then be obtained by multiplying C_p by the underlying heating rate. This heat capacity dependent

part is the reversing heat flow component. The non-reversing heat flow component can be obtained by subtracting the reversing contribution from the calculated total heat flow. As a result all the noise will appear in the non-reversing signal.

The heat capacity is a bulk material property, and, therefore, does not depend on orientation. Since polymeric composites are both heterogeneous and anisotropic, analysis based on heat capacity is valid if no anisotropic effects are prevalent. In case of very small samples, no heat transfer effects can be expected. However, because of relatively fast temperature oscillation, anisotropic effects may be observed as sample size is increased since, for example conductivity of carbon fibers is different in longitudinal and axial directions. In this case, an analysis based on anisotropic property, such as thermal conductivity or thermal diffusivity, must be developed. At this point, however, it will be appropriate to examine phenomenologically the information that can be obtained by the MDSC technique.

EXPERIMENTAL

In this study, the TA Instruments DSC 2910 Differential Scanning Calorimeter with the MDSCTM capability was used to study different polymeric material systems that are both heterogeneous and anisotropic. This instrument can be used as a regular DSC or MDSC. The cell used for MDSC experiments is the same as for the DSC, but a different temperature ramp is applied to the sample and the reference. In all experiments, Liquid Nitrogen Cooling Accessory (LNCA) was used to facilitate accurate temperature control and to achieve subambient temperatures. Nitrogen purge at 40 ml/min was used in all experiments.

Various experiments were performed using AS4-carbon fiber reinforced polyethylene terephthalate (PET/AS4) prepreg to investigate the effect of heating rate, amplitude, and period, and to compare conventional and modulated DSC data. These experiments are listed in Table 1.

In addition to simple temperature ramps, some cycling experiments were also performed to investigate changes in the enthalpic relaxation associated with glass transition of amorphous PET/AS4.

In addition, the MDSC was used to characterize polymeric systems for which conventional DSC does not yield satisfactory results. For example, the glass transition of thermosetting polyimides, especially carbon fiber rein-

Table 1: Sample weight, heating rate, amplitude, and period in MDSC and DSC experiments performed.

Material	Weight mg	Heating rate °C/min	Amplitude °C	Period seconds
PET/AS4 prepreg	19.0	10	0.3	30
	21.2	10	—	—
	19.5	5	0.5	40
	20.0	5	—	—
	21.4	2	0.3	30
	18.3	2	—	—
	20.5	1	0.1	30
	20.0	1	0.2	70
	19.0	1	—	—
	22.2	0.5	0.2	30
BASF X 5260 /IM7 laminate	18.0	2	0.4	30
	18.0	2	—	—
NR-150	17.1	2	0.3	30
PET/PC bilayer film	10.0	2	0.4	30

forced, is difficult to determine from conventional DSC data since the signal is often too low and the sensitivity of the instrument not high enough to separate the transition from the baseline. Another area where MDSC can be applied is where non-reversing and reversing transitions overlap. To investigate the applicability of MDSC in these cases, experiments were performed on polyethylene terephthalate/polycarbonate film (bilayer) (PET/PC), a high temperature polyimide (NR-150), and IM7-carbon fiber reinforced Bismaleimide laminate (BMI/IM7) (2). The experiments performed on these samples are listed in Table 1. The possible effects of fiber orientation were investigated using BMI/IM7 laminate, for which anisotropic effects in degradation have been investigated [5, 6]. These experiments were performed as follows: Samples were cut from a 26 ply unidirectional laminate, and then placed into the DSC pan so that either fibers or resin were facing the pan bottom. Two

different fiber angles were used with respect to the pan: 0° and 90° . These experiments were performed at $2^\circ\text{C}/\text{min}$, amplitude $0,3^\circ\text{C}$, and period 30 seconds.

Also, the MDSC was used to determine the heat capacity for polystyrene after calibration with a standard sapphire sample.

RESULTS AND DISCUSSION

Figure 3 shows an example of the MDSC temperature ramp at an underlying heating rate of $2^\circ\text{C}/\text{min}$, amplitude $0,3^\circ\text{C}$, and period 30 seconds, and a constant heating rate ramp at $2^\circ\text{C}/\text{min}$. As can be seen, the modulated DSC heat flow is oscillating around the constant heating rate ramp. The heat flow measured during conventional DSC experiment at $2^\circ\text{C}/\text{min}$ is shown in Figure 4, and the oscillating raw data of MDSC obtained at $2^\circ\text{C}/\text{min}$ is shown in Figure 5 for PET/AS4 prepreg. As can be seen, the oscillating heat flow follows the contour of the conventional DSC signal, and the same thermal events can be seen in both. This oscillating heat flow signal is the raw signal of the MDSC, that can be deconvoluted into the traditional DSC curve. The phase lag, i. e. the difference between the phase of the applied temperature oscillation and observed heat flow oscillation is shown in Figure 6. As can be seen, the phase lag deviates slightly from the baseline phase lag whenever there is a thermal transition, but this change is relatively small except during melting. Thus, the assumption that the sinusoidal term in Eqn. (2) is negligible can be taken as valid except for melting. The baseline phase lag is not zero because of instrumental lag caused by sample cell, pan etc.

A typical example of deconvoluted MDSC curve for PET/AS4 prepreg is presented in Figure 7 at $2^\circ\text{C}/\text{min}$, amplitude $0,3^\circ\text{C}$, and period 30 seconds. Three transitions typical for amorphous PET were observed in the total heat flow curve: combination of glass transition and enthalpic relaxation endotherm at $70\text{-}80^\circ\text{C}$, cold crystallization exotherm at 112°C , and melting of the crystallites above 230°C . Enthalpic relaxation is a relaxation of free volume created in the quenching of the PET to produce amorphous polymer (7). The reversing heat flow component gave the glass transition as 77°C , whereas the enthalpic relaxation and cold crystallization were observed in the non-reversing heat flow component. The crystalline melting was seen in both reversing and non-reversing components since this transition possesses both characteristics depending on the extent of melting and availability of

nucleation sites. When the extent of melting increases, the amount of nucleation sites decreases, and melting becomes more non-reversing with respect to the temperature oscillation. Proof of this can be seen in the data as well. The peak maximum in the reversing component in Figure 8 was observed 7°C earlier than the non-reversing peak maximum.

Figure 8 shows a comparison of MDSC and DSC total heat flow curves for PET/AS4 prepreg at 1°C/min, 2°C/min, and 10°C/min. In addition to the heating rate, the MDSC curves are labelled with the amplitude and period used. In principle, the total heat flow curve obtained by deconvoluting the MDSC signal should be identical to the conventional DSC signal. Consequently, the effect of amplitude and period on the appearance of the total heat flow curve and temperature at which transitions are observed should be negligible compared to the effect of heating rate. If not, the MDSC total heat flow curves created at certain heating rate but different amplitudes and periods could not be superimposable with conventional DSC curve created at the same heating rate. Based on the various experiments performed, this condition seemed to be applicable. At 10°C/min, however, some difference was observed in the shape of the cold crystallization peak*.

The total MDSC heat flow curve between 50°C and 140°C is shown in Figure 9 at heating rates ranging from 1 to 10°C/min. Reversing and non-reversing components between 50°C and 100°C are shown in Figures 10 and 11, respectively. Based on the total heat flow at different heating rates, temperature of both transitions seemed to increase as heating rate was increased. However, when glass transition and enthalpic relaxation were examined separately, the enthalpic relaxation shifted to higher temperatures as heating rate was increased (Figure 10). On the other hand, glass transition temperature appeared to be independent of heating rate in the range of heating rates used. This implies that the heating rate dependence of the combined transition can mainly be attributed to enthalpic relaxation. To further investigate the heating rate dependence of various transitions, the temperatures at which they were observed were determined from different experiments using the standard analysis software capable of handling MDSC data. These results are shown in Table 2.

* In general, a certain number of temperature cycles during a thermal event are required in order for the separation to work ideally. Thus, 10°C/min is too high a heating rate to be used.

Table 2. Temperatures of thermal transitions for PET/AS4 prepreg as determined from conventional and modulated DSC experiments at various heating rates.

Experiment	sample weight, mg	Tg, °C rev. ¹	Tg, °C total ²	Enth. non-rev. ³	Relax. total	Add. non-rev.	Cryst. total	Melting total
0.5°C/min, 0.05°C, 30s	21.9	77.5	N/A	N/A	N/A	104.7	104.9	258.7
1°C/min, 0.1°C, 30s	20.5	77.5	72.5	74.5	74.4	109.0	109.0	258.4
1°C/min, 0.2°C, 70s	20.0	78.1	72.7	74.1	74.6	108.8	109.0	258.3
1°C/min	19.0	N/A	72.0	N/A	73.3	N/A	108.6	258.0
2°C/min, 0.3°C, 30s	21.4	77.0	74.2	75.0	76.4	111.9	111.9	257.0
2°C/min	18.4	N/A	74.2	N/A	76.6	N/A	112.3	257.1
5°C/min, 0.5°C, 40s	19.5	78.8	75.9	77.8	77.9	117.3	117.0	255.9
10°C/min, 0.3°C, 30s	19.0	76.8	77.8	83.0	81.4	123.3	123.1	255.1
10°C/min	21.2	N/A	77.8	N/A	81.1	N/A	122.6	255.3

¹, ², ³ rev. (reversing), non-rev. (non-reversing), and total refer to the heat flow signal from which the value was determined.

Glass transition temperature was determined from MDSC total signal as well as reversing heat flow curve. T_g values (72,0-77,8°C) determined from total heat flow of both MDSC and DSC increased as heating rate was increased, and values obtained from conventional and modulated DSC experiments at the same heating rate corresponded well with one other. However, the T_g determined from MDSC reversing component ranged from 76,8°C to 78,8°C without any apparent heating rate dependence. On the contrary, the enthalpic relaxation temperature determined as a peak temperature from the relaxation endotherm increased as heating rate increased. Temperatures determined from MDSC total and non-reversing heat flow as well as conventional DSC at same heating rates were again in excellent agreement with each other. The T_g and enthalpic relaxation temperatures determined from different heat flow curves further confirmed that the heating rate dependence of T_g in conventional DSC for PET was caused by the overlapping enthalpic relaxation. This implies that over the heating rate range used (0.5°C/min to 10°C/min), the relaxation of molecules during glass transition is relatively fast, and therefore, T_g is observed at constant temperature regardless of the heating rate. In this case, utilization of MDSC provided information about the relaxation time associated with the glass transition and enthalpic relaxation that could not have been obtained by conventional DSC. Comparison of the heating rate dependence of T_g and enthalpic relaxation implied that the relaxation of molecules associated with glass transition was faster than that associated with enthalpic relaxation. Since enthalpic relaxation may be associated with internal stresses created in the material during processing [7], this technique may offer new possibilities in processing studies as glass transition and enthalpic relaxation can be examined separately.

As the heating rate was increased, the cold crystallization peak temperature increased and the melt peak temperature decreased slightly. Peak temperatures from conventional DSC and MDSC performed at the same heating rate corresponded well to each other. Figure 6 shows the calculated phase lag (phase angle, in radians) as a function of temperature for PET/AS4 MDSC experiment at 2°C/min, amplitude 0.3°C, and period 30 seconds. The phase lag and out-of-phase component were negligible for the entire experiment except melting. This implies that the separation of melt endotherm into reversing and non-reversing components cannot provide accurate quantitative information, but should be viewed qualitatively.

The enthalpic relaxation and glass transition temperature were further examined by cycling the temperature around this region. The total heat flow curves during this cycling are shown in Figure 12. $2^{\circ}\text{C}/\text{min}$ with amplitude of 0.3°C and period 30 seconds were used in both heating and cooling cycles. The sample was first heated to 83°C , then cooled to 40°C , and heated again to 104°C . During the first heating, the dip of enthalpic relaxation was observed at 77°C . During the second and the third cycle, it was observed at 80°C . Based on the reversing heat flow component, the glass transition temperature was not affected by cycling. The non-reversing component showing the enthalpic relaxation is shown in Figure 13 during the same temperature cycle. As observed in Figure 12, the enthalpic relaxation moved to higher temperature after the first heating, and did not change during subsequent cycles. This observation was confirmed by conventional DSC. A similar cycling experiment was performed at $2^{\circ}\text{C}/\text{min}$ between 25°C and 90°C . The sample was cycled through four cycles. The resulting heat flow curves are shown in Figure 14. Again, the dip of relaxation endotherm was observed at 75°C . After the first cycle, it moved to 77°C , and did not change during subsequent cycles.

In MDSC, the enthalpic relaxation appeared in the non-reversing component, indicating that it was non-reversing with respect to the applied temperature oscillation. However, upon cooling and reheating, the transition temperature increased by $2\text{-}3^{\circ}\text{C}$, but the transition itself did not disappear, as one would expect from a truly non-reversing phenomena. This implied that this relaxation was non-reversing with respect to the MDSC temperature oscillation, but reversed upon the application of cooling profile at $2^{\circ}\text{C}/\text{min}$.

In addition to PET/AS4 prepreg, the MDSC was used to investigate materials for which conventional DSC is not applicable. In a bilayer film of polycarbonate and polyethylene terephthalate, the polycarbonate glass transition and PET crystallization were observed as overlapping transitions in the total heat flow curve. However, as shown in Figure 15, the T_g of PC and crystallization of PET are clearly separated in the reversing and non-reversing components, respectively.

Another application where conventional DSC failed, but MDSC gave good results was determination of T_g for NR-150, which is a high temperature thermosetting polyimide (8). Total heat flow as well as the reversing and non-reversing components are shown in Figure 16. T_g was determined from the

reversing component as 358°C. For comparison, T_g was determined by DMA at 5°C/min as 362°C, which is in excellent agreement with the MDSC result.

Finally, the MDSC was used to determine the T_g of carbon fiber reinforced BMI/IM7. The MDSC total heat flow and its reversing and non-reversing components are shown in Figure 17. The glass transition temperature of BMI/IM7 could not be accurately determined from the total heat flow curve, since additional cure exotherm was observed immediately following the glass transition. Upon separation of the signal into its components, cure was observed in the non-reversing signal whereas T_g was easily determined from the reversing component as 241°C as illustrated in Figure 17. For comparison, T_g was also determined by Dynamic Mechanical Analysis (DMA, TA Instruments DMA 983) using resonant frequency mode at 5°C/min. T_g was observed as 248°C from the maximum of the loss modulus (E'') peak.

The MDSC experiment shown in Figure 17 was performed using a sample placed in the pan so that the resin rich tool surface of the composite was facing the pan. Figure 20 shows a comparison of the reversing component of this experiments with two experiments done with fibers facing the pan. The sample size for all these experiments was 18 mg, and samples were cut so that the overall dimensions with respect to the pan were constant from sample to sample. These two precautions eliminated the possible sample size and bulk heat transfer differences between the samples. The glass transition temperature as well as the sharpness of the transition seemed to change as different surfaces faced the pan. Since the longitudinal thermal conductivity of carbon fibers is higher than axial, the lowest T_g was observed when fibers were in 90° angle with respect to the pan bottom. Clearly, the anisotropic effects were pronounced for these samples, and should be taken into account in future developments of the MDSC technique.

Determination of heat capacity was investigated by determining the heat capacity for a polystyrene sample, for which reference values were available [1]. First, the MDSC was calibrated for the heat capacity determination using a standard sapphire sample. Sapphire sample was scanned at one heating rate, and a heat capacity coefficient was determined so that the obtained heat capacities as a function of temperature matched reported literature values. Then, the sample was scanned at other heating rates, and the obtained heat capacity values were multiplied by the heat capacity coefficient. This multiplication was performed by available software. Once the heat capacity

coefficient was determined, it is automatically used to adjust heat capacity values. The comparison of the values obtained in this manner is shown in Figure 19. The single curve represents three different scans performed at different heating rates, and crosses represent conventional DSC results. Next, the MDSC was used to determine the heat capacity of polystyrene between 50°C and 230°C. Results at two different heating rates are shown in Figure 20. The crosses, again, represent conventional DSC results. The T_g of polystyrene was observed as a step change in the MDSC heat capacity curves at around 100°C.

In general, the reversing and non-reversing heat flow components correspond to thermal events that are reversible and non-reversible, respectively, with respect to the applied temperature oscillation. Truly reversible phenomena are thermodynamically controlled, and the temperature at which they are observed should not depend on heating rate, but only on the thermodynamic state of the material. Because of the viscoelastic nature of polymeric materials, no thermal event is truly reversible. During glass transition, polymer chains require certain time to relax, and some heating rate dependence can be expected. Depending on the relaxation time, there may be a heating rate range during which no heating rate dependence is observed, since relaxation may be fast compared to the rate of temperature change. After a limiting heating rate is exceeded, heating rate starts to increase the measured T_g , since relaxation is slow compared to heating rate.

For a truly irreversible phenomena, the integral of heat flow over a temperature cycle is always finite. This means that once the event has taken place, it cannot be reversed. Curing reactions of polymers are an example of irreversible phenomena. In MDSC experiments, in addition to cure reactions, cold crystallization of amorphous polymers, enthalpic relaxation, degradation, and part of the melt endotherm appear in the non-reversing component. However, not all these phenomena are non-reversing under all temperature cycles, since the integral of the heat flow over a temperature cycle starting and ending at the same temperature can be zero or finite. For example, consider an experiment with a semicrystalline polymer having a maximum degree of crystallinity. Upon heating to temperature above the melting temperature, the crystallites will melt. If polymer is then slowly cooled down to the starting point of the experiment, it will recrystallize and return to its original macroscopic state. The integral of the heat flow over this cycle is

zero. However, by increasing the cooling rate, it is possible to produce a polymer with less crystallinity, which means that the integral of heat flow would be finite. Thus, the value of the integral of the heat flow associated with non-reversing phenomena can be affected by the temperature cycle, and therefore, the event is kinetically controlled. For reversing phenomena such as glass transition, the temperature cycle does not affect the value of the integral as long as the polymer is not changed as a result of reaction, degradation etc.

As seen in Eqns. (2) and (4), the reversing contribution is the part of the signal that is directly dependent on the heat capacity. Therefore, it can be argued that the MDSC, in essence, separates transitions during which the heat flow change is directly related to heat capacity and heating rate from transitions during which heat flow changes are related to time and temperature in a more complicated fashion (reaction kinetics, crystallization kinetics).

The MDSC has a certain analogy to Dynamic Mechanical Analysis (DMA). In DMA, the sample is oscillated mechanically, and the sample response then divided into elastic (storage modulus E') and viscous (loss modulus E'') contributions. In MDSC, the sample experiences thermal oscillation, and response is divided into reversing and non-reversing contributions. Theoretically speaking, the elastic storage modulus should not depend on frequency, but in practise it does depend on frequency. Even though the reversing and non-reversing contributions of MDSC signal did not show any frequency (period of oscillation) dependence in this work, some could be expected based on the viscoelastic nature of polymeric materials.

CONCLUSIONS

MDSCTM is a novel DSC technique that utilizes a sinusoidal small amplitude temperature oscillation to separate thermal events that are reversing and non-reversing with respect to this temperature oscillation. A Discrete Fourier Transform is used to deconvolute the measured oscillating heat flow into conventional DSC curve and its reversing and non-reversing components. For polymers, the main event appearing in the reversing heat flow curve is glass transition, whereas enthalpic relaxation, additional crystallization, reaction, and degradation appear in the non-reversing curve. Melting will appear in both components since it has both characteristics with respect to the applied oscillation.

A model carbon fiber reinforced thermoplastic system, PET/AS4 prepreg, was used to study the effect of heating rate on different transitions and to compare the MDSC results to conventional DSC results in more detail. The transition temperatures obtained from conventional and modulated DSC total heat flow curves were practically equal. An interesting observation was made when comparing the heating rate dependence of glass transition and overlapping enthalpic relaxation. When T_g was determined from total heat flow curve, it was clearly a function of heating rate. However, when T_g was determined from reversing heat flow curve, it had no detectable heating rate dependence when heating rate was between 0.5°C/min and 10°C/min. The enthalpic relaxation temperature, however, determined from the non-reversing component, increased with increasing heating rate. This indicated that the heating rate dependence of T_g determined from total heat flow curve was created by the shifting of the overlapping enthalpic relaxation to higher temperatures as heating rate was increased. This information could not have been obtained by conventional DSC, and may provide information about the relaxation behavior of the polymer, and associated relaxation times.

Also, the MDSC was used to determine the T_g of some model systems for which conventional DSC does not yield satisfactory results. The T_g of NR-150 polyimide is relatively high, and could not be seen in the total heat flow curve. However, it was easily obtained from the reversing heat flow component. The MDSC was also used to separate the glass transition of PC from crystallization of PET in a bilayer PET/PC film. The glass transition temperature of a BMI/IM7 laminate could not be determined from conventional DSC because of poor baseline and additional reaction starting after T_g . However, the T_g was easily determined from the MDSC reversing component. In addition, anisotropic effects were identified.

Finally, the heat capacity of polystyrene was obtained from a single MDSC run as opposed to multiple DSC experiments. The MDSC was calibrated using a standard sapphire sample, and heat capacity was then determined. Results obtained using MDSC were in excellent agreement with conventional DSC results.

Collectively, the MDSC is a tool that can provide information that cannot be obtained by other thermal analysis methods. Its ability to separate reversing and non-reversing events is of both practical and theoretical inte-

rest, and carefully planned experiments can yield fundamental information about the behavior and utilization of polymeric materials.

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Π Ε Ρ Ι Λ Η Ψ Η

Διαμορφωμένη διαφορική θερμιδομετρία σαρώσεως διά τόν χαρακτηρισμόν συγχρόνων ύλικών.

Ἡ διαμορφωμένη διαφορική θερμιδομετρία σαρώσεως (MDSC) ἀποτελεῖ νεοφανῆ τεχνικὴν διαφορικῆς θερμιδομετρίας ἢ ὅποια ἐφαρμόζει μικρὰν ἡμιτονοειδῆ ταλάντωσιν τῆς θερμοκρασίας μὲ ὀρισμένην περίοδον καὶ εὖρος, ἐπιπροσθέτως πρὸς τὴν σταθερὰν αὐξήσιν τῆς θερμάνσεως τοῦ δοκιμίου ἢ τὴν ἰσόθερμον θερμοκρασίαν. Ἡ μετρούμενη ταλαντούμενη ροὴ τῆς θερμότητος, ἀποσυντίθεται εἰς μίαν συμβατικὴν (DSC) καμπύλην καὶ ἀποχωρίζεται εἰς τὰ ἀντιστρεπτά καὶ μὴ ἀντιστρεπτά στοιχεῖα δι' ἐφαρμογῆς τοῦ διακεκριμένου μετασχηματισμοῦ Fourier. Διαχωρισμὸς τῆς ἐναλλασσομένης ροῆς θερμότητος διευκολύνει τὸν προσδιορισμὸν τῆς θερμοχωρητικότητος ἀπὸ τὴν ἀπλήν (MDSC) καμπύλην ἀντὶ τῶν ἀναγκαίων πολλαπλῶν συμβατικῶν καμπυλῶν DSC. Διὰ τὰ πολυμερῆ ἢ μεταβατικὴ θερμοκρασία ὑαλώδους καταστάσεως ἀποτελεῖ τὴν κυρίαν ἀναστροφικὴν ἀλλαγὴν. Συνεπῶς αἱ πλέον προφανεῖς ἐφαρμογαὶ τῆς μεθόδου MDSC περιλαμβάνουν τὸν καθορισμὸν τῆς θερμοχωρητικότητος τοῦ ὑλικοῦ καὶ τὸν διαχωρισμὸν τῆς μεταβατικῆς καταστάσεως τοῦ ὑαλώδους σώματος ἀπὸ τὰς μὴ ἀναστρεψίμους μεταβατικὰς καταστάσεις τὰς εὐρισκόμενας ἐν ἐπαλληλίᾳ μὲ αὐτὴν. Τοιαῦται καταστάσεις εἶναι ἡ ἐνθαλπικὴ χαλάρωσις, ἢ πρόσθετος κατεργασία καὶ ὁ διαχωρισμὸς τῆς ὑαλώδους μεταβάσεως ἐκ τῆς πτωχῆς βασικῆς ἀναφορᾶς.

Εἰς τὴν μελέτην αὐτὴν ἡ μέθοδος MDSC ἐφηρμόσθη διὰ τὸν καθορισμὸν διαφορῶν ἑτερογενῶν πολυμερικῶν συστημάτων, ὅπως τοῦ δισ-μαλεῦμιδικοῦ πολυμεροῦς ἐνισχυμένου μὲ ἱνας ἄνθρακος (BMI) τὸ ὅποῖον εἶναι μίγμα θερμοσκληρυνόμενου πολυϊμιδίου, τερεφθαλικοῦ πολυαιθυλενίου μὲ πολυκαρμπονάτον. Ἴνες ἄνθρακος ἐνισχύουν τὸ τερεφθαλικὸν πολυαιθυλένιον. Ἐπιπροσθέτως, ἡ θερμοχωρητικότης ἐμετρήθη εἰς δοκίμια πολυστερενίου μετὰ ἀπὸ βαθμονόμησιν τοῦ μηχανήματος μὲ τυποποιημένα δοκίμια ἀπὸ σάπφειρον. Συνολικῶς τὰ ἀποτελέσματα ἐδειξαν ὅτι ἡ μέθοδος MDSC παρέχει πολλὰ πλεονεκτήματα διὰ τὴν ἀνάλυσιν πολυμερικῶν συστημάτων, ἰδιαιτέρως ὅταν αὐτὰ ἀντιμετωπίζονται ὡς ἐσωτερικῶς ἑτερογενῆ ἀνισότροπα καὶ βισκοελαστικὰ συστήματα. Τὰ προκύπτοντα ἀποτελέσματα ἔχουν σημαντικὰς ἐπιπτώσεις ὅχι μόνον διὰ τὸν χαρακτηρισμὸν τῶν ὑλικῶν, ἀλλὰ καὶ εἰς τὰς ἀρχὰς τῶν ἐφαρμογῶν τὰς σχετιζόμενας μὲ τὴν βιομηχανίαν, τὴν παραγωγὴν, σχεδίασιν καὶ συμπεριφορὰν τῶν ὑλικῶν.

POLYMERIC COMPOSITES CONCEPT INTEGRATION

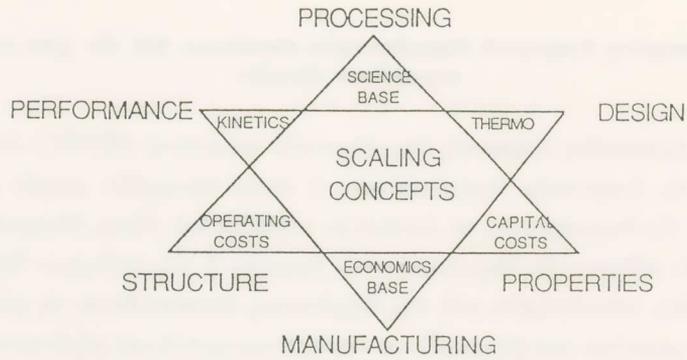


Fig. 1. Polymeric composites concept integration, the Double Trinity Methodology.

MDSC DEVELOPMENT

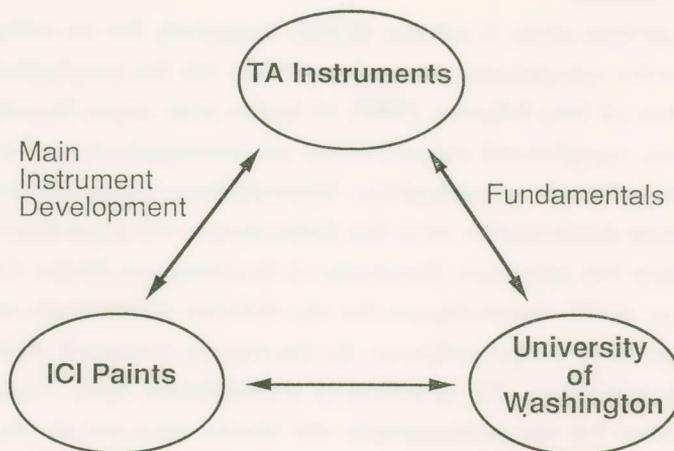


Fig. 2. Development of the MDSC.

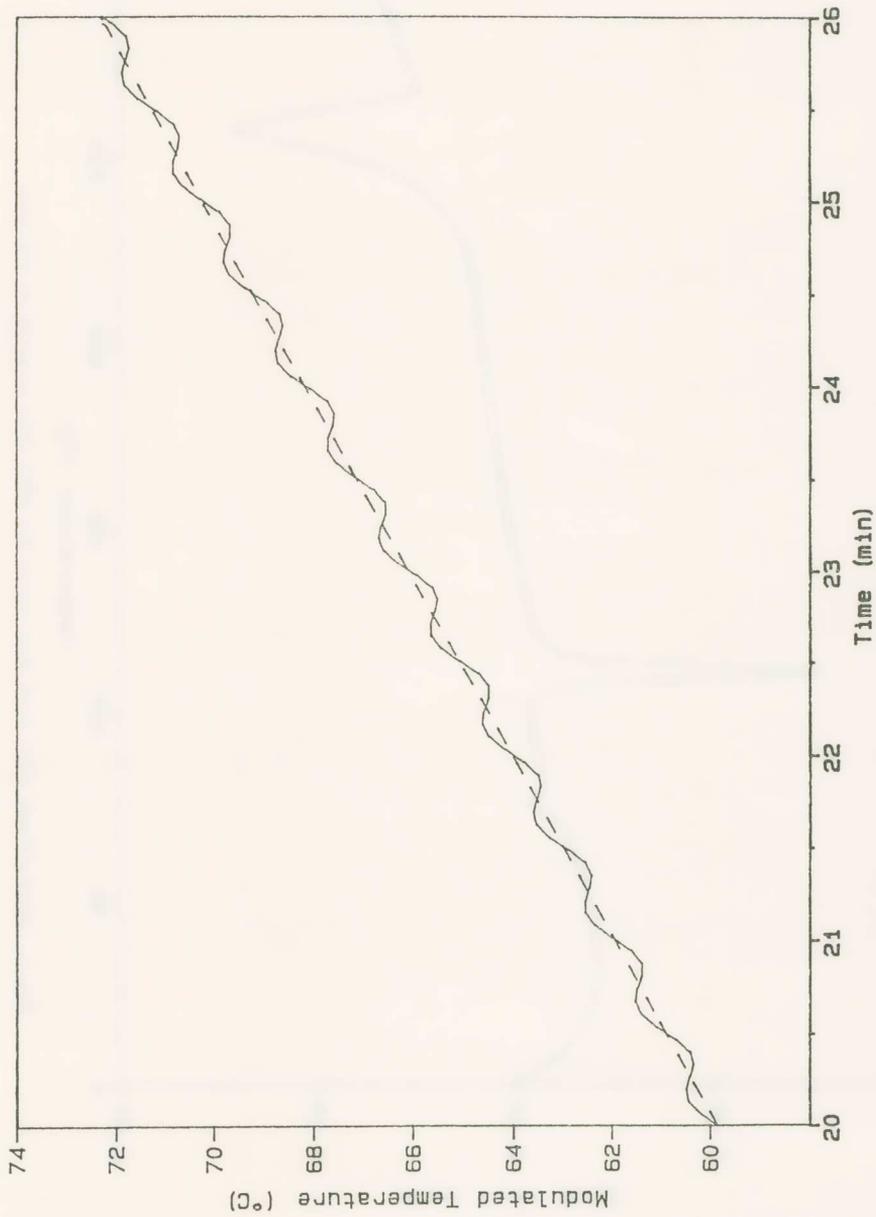


Fig. 3. Comparison of oscillating MDSC temperature profile and constant heating rate ramp.
Heating rate 2°C/min, amplitude 0.3°C, and period 30 seconds.

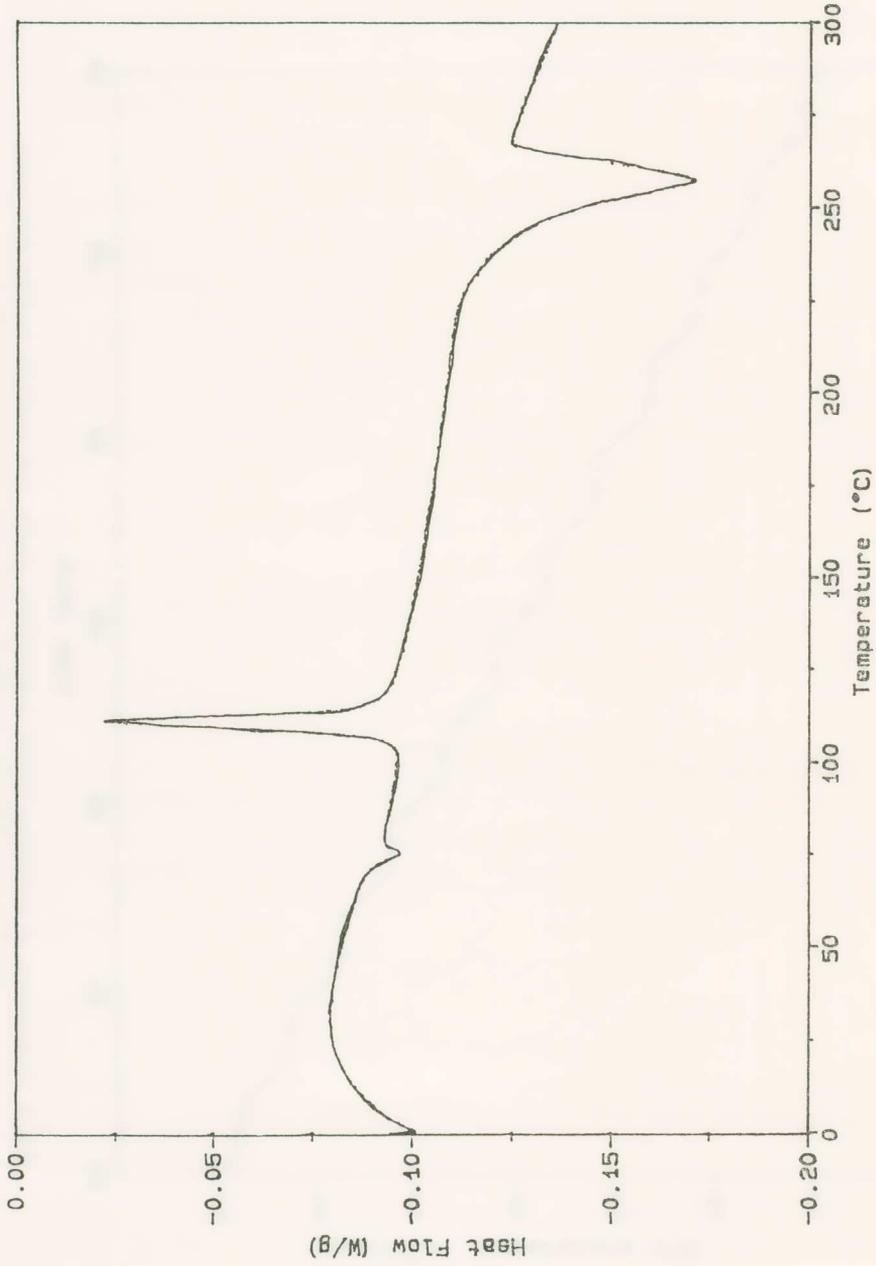


Fig. 4. Conventional DSC heat flow curve for PET/AS4 prepreg at 2°C/min.

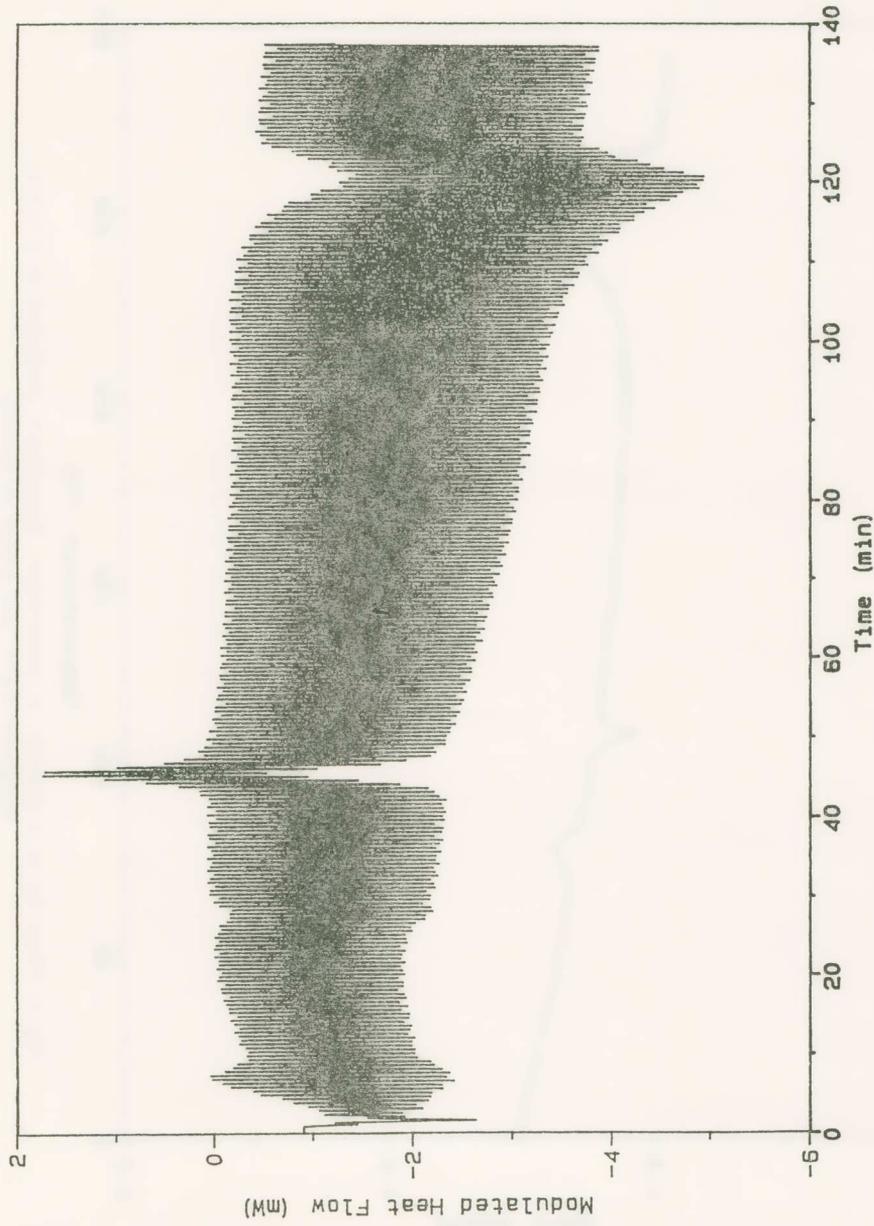


Fig. 5. The raw heat flow signal obtained for PET/AS₄ prepreg at 2°C/min, amplitude 0,3°C, and period 30 seconds.

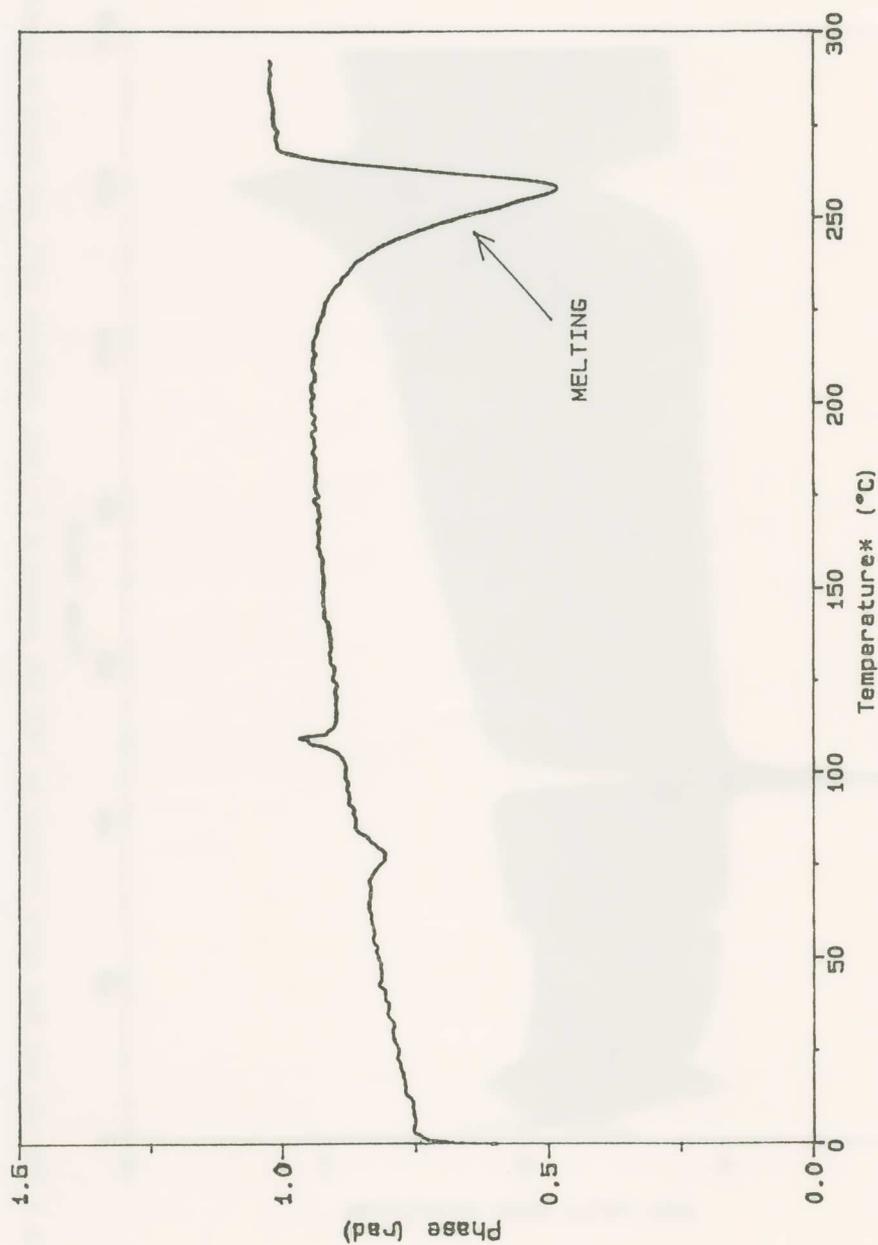


Fig. 6. Phase lag as a function of temperature. Experiment performed at 2°C/min, amplitude 0.3°C, and period 30 seconds.

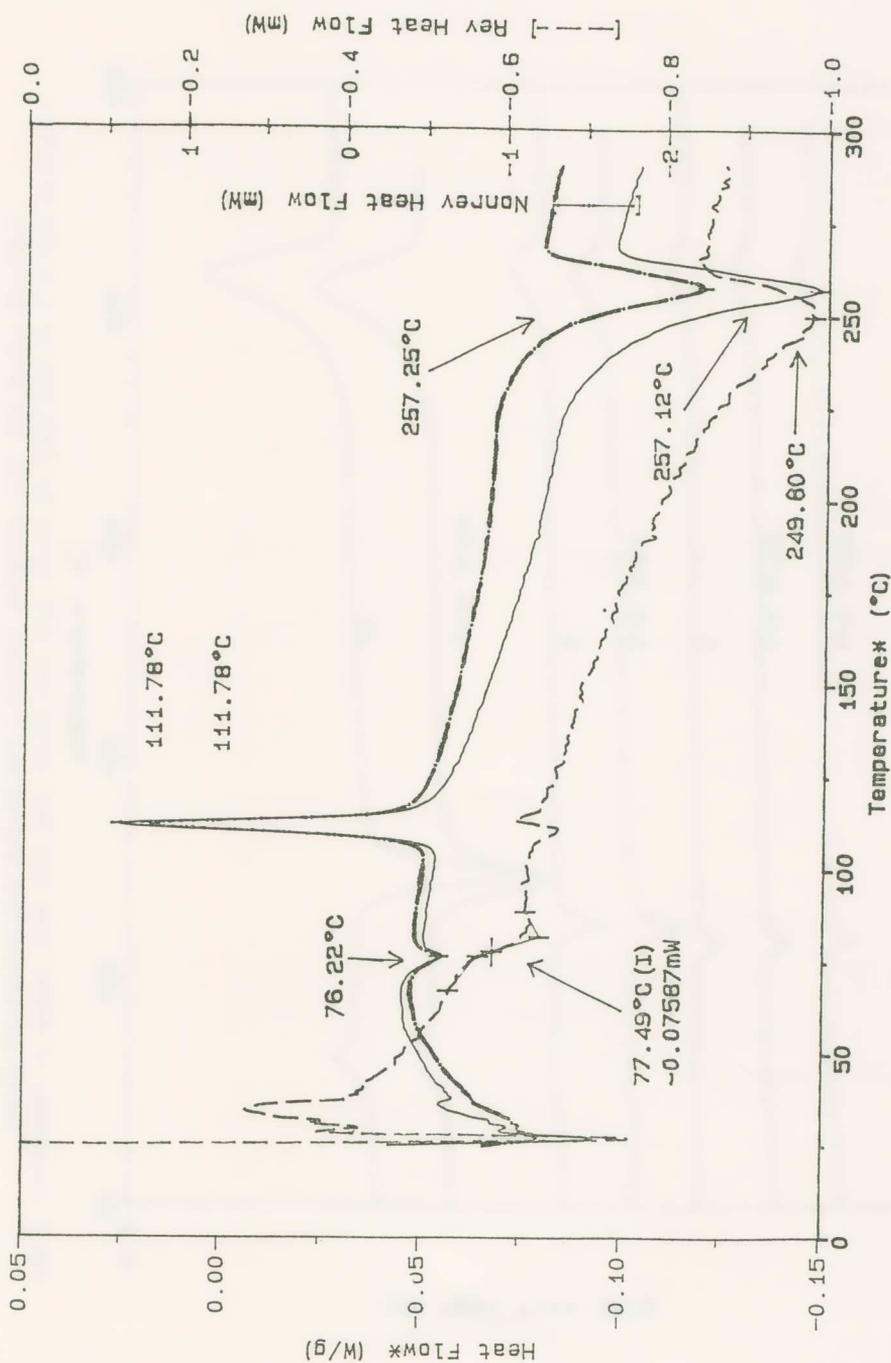


Fig. 7. Total, reversing, and non-reversing heat flow for PET/AS4 at 2°C/min, 0,3°C, and 30 seconds.

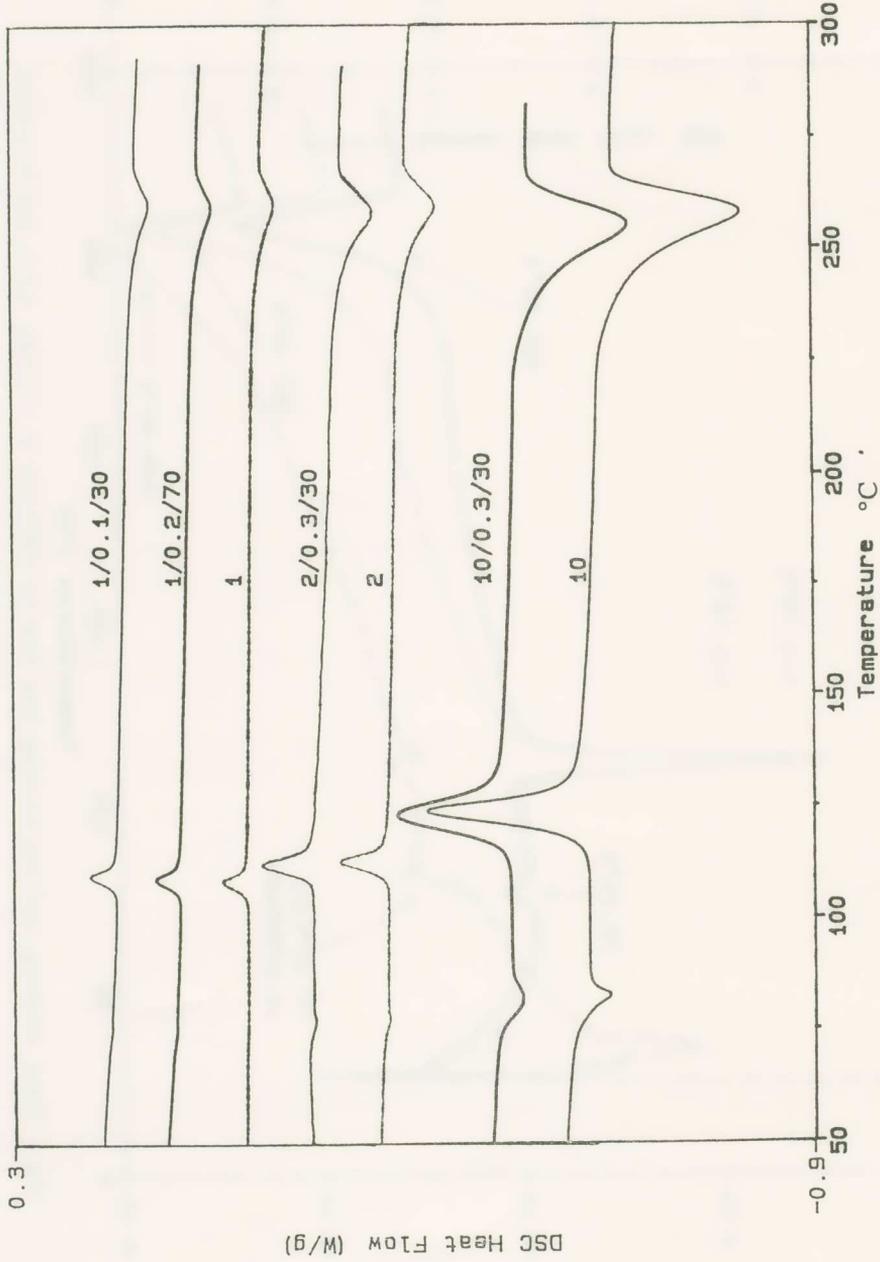


Fig. 8. Comparison of MDSC total heat flow curves and DSC curves for PET/AS4 at 1, 2, and 10°C/min. Curves are labelled with heating rate (°C/min), amplitude (°C), and period (seconds).

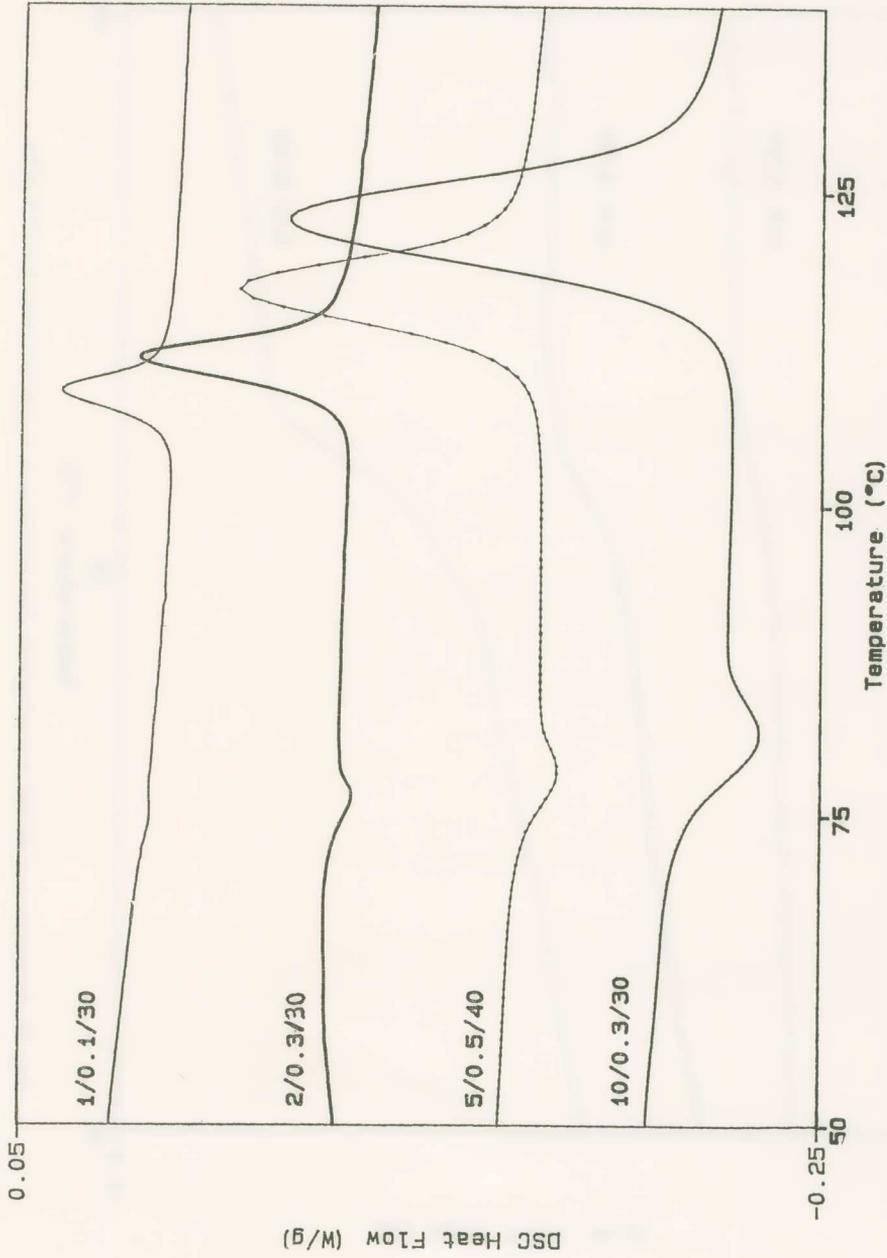


Fig. 9. Comparison of MDSC total heat flow curves at 1, 2, 5, and 10°C/min for PET/AS4.

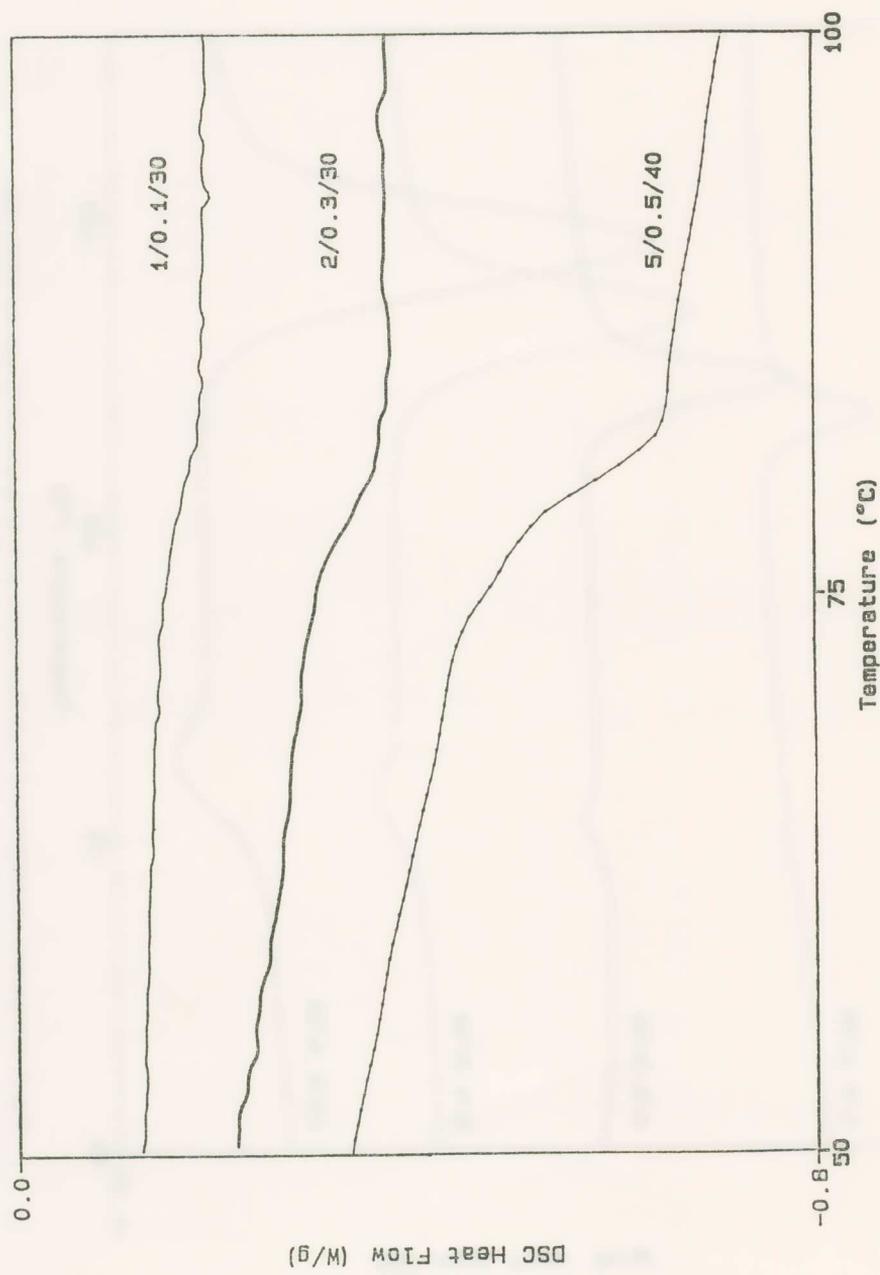


Fig. 10. Comparison of MDSC reversing heat flow curves at 1, 2, and 5°C/min for PET/AS4.

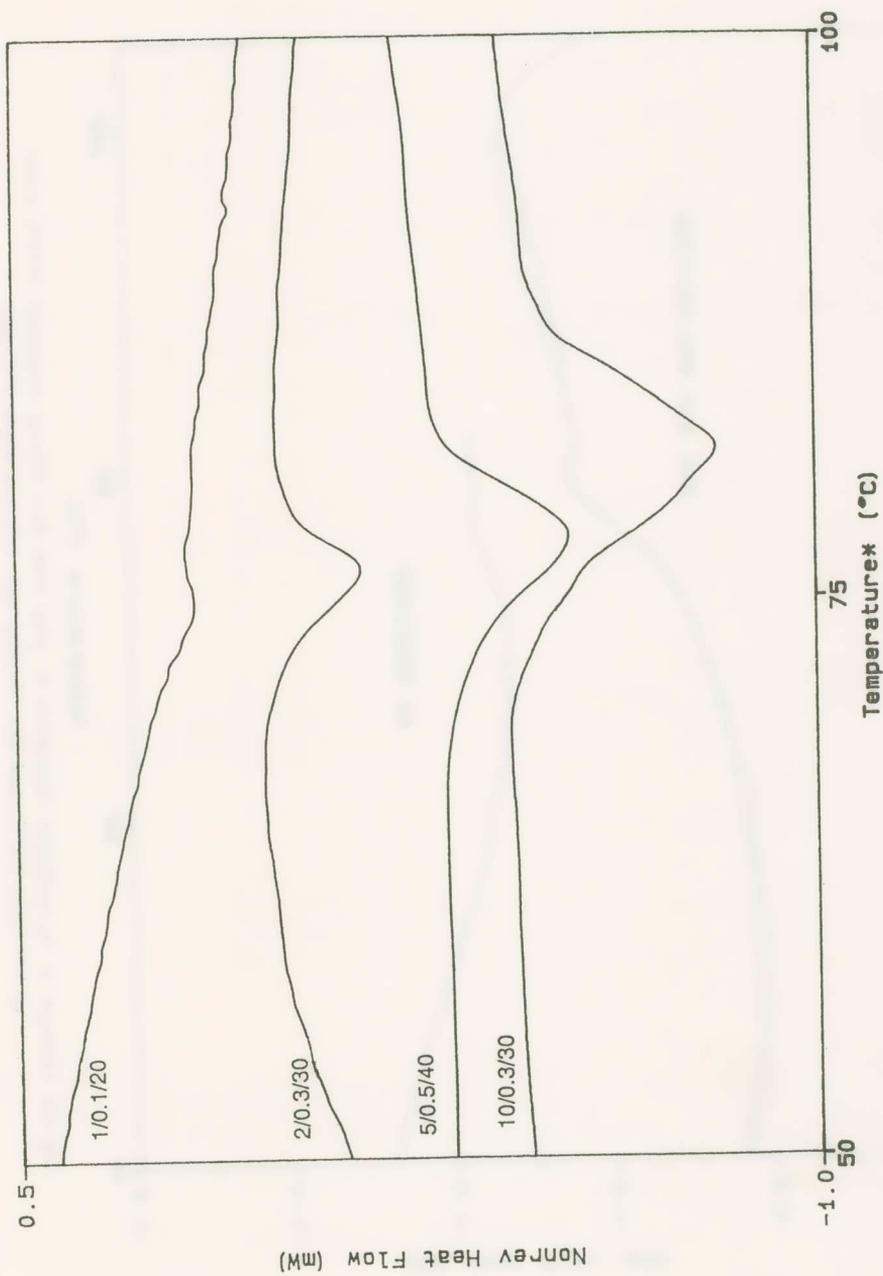


Fig. 11. Comparison of MDSC non-reversing heat flow curves at 1, 2, 5, and 10°C/min for PET/AS4.

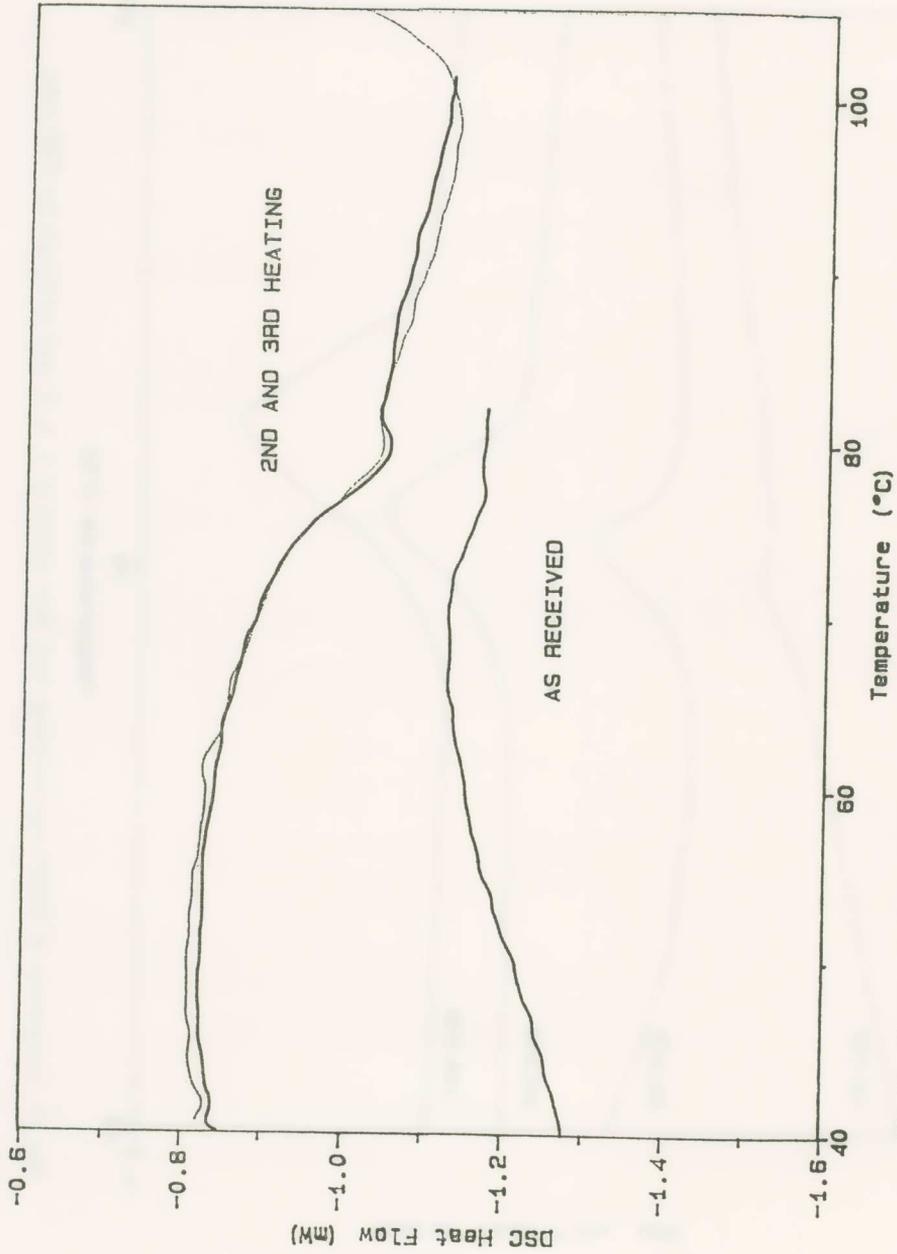


Fig. 12. Changes in T_g /enthalpic relaxation in total heat flow during successive MDSC scans at $2^\circ\text{C}/\text{min}$, 0.3°C , and 30s . Cooling rate between scans $2^\circ\text{C}/\text{min}$.

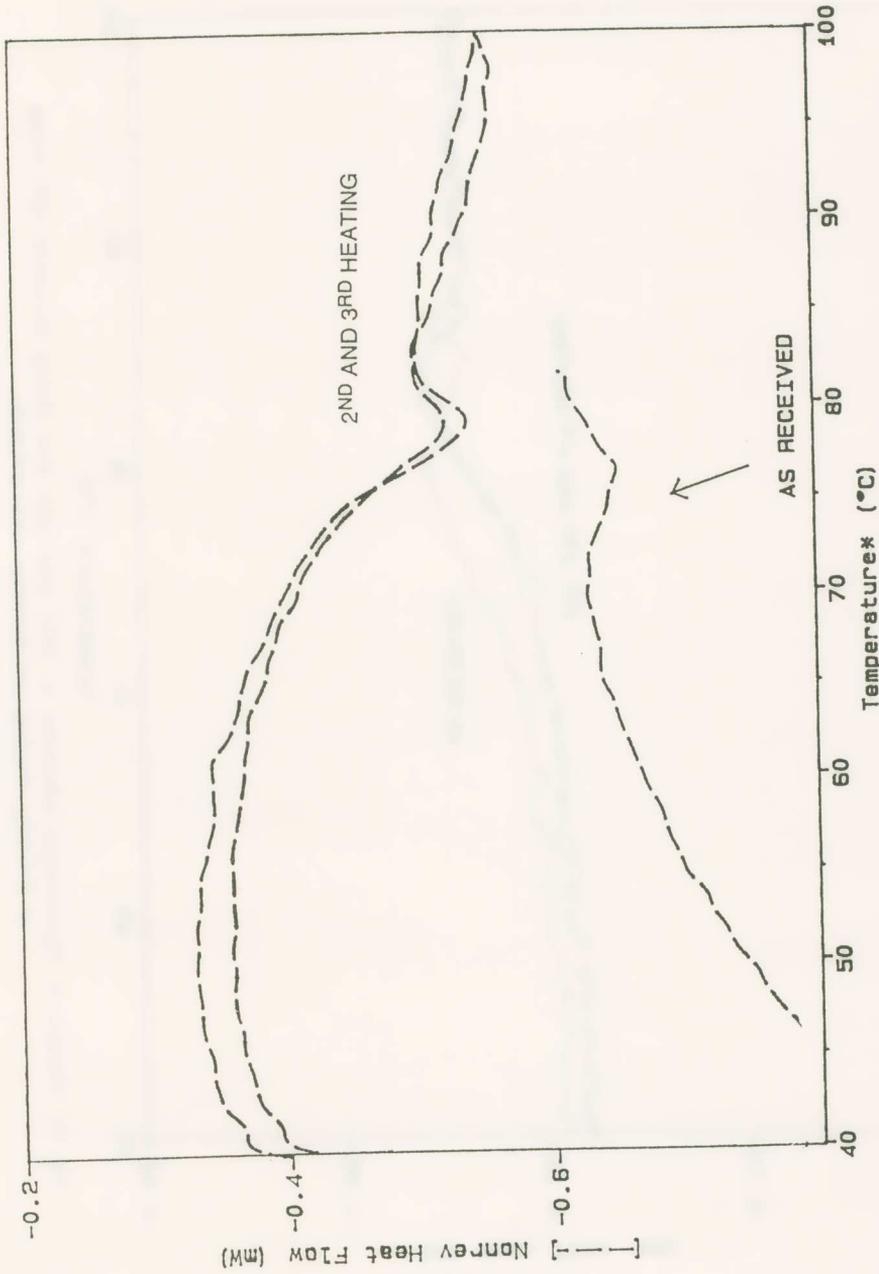


Fig. 13. Changes in enthalpic relaxation in non-reversing heat flow during successive MDSC scans at 2°C/min, 0,3°C, and 30s. Cooling rate between scans 2°C/min.

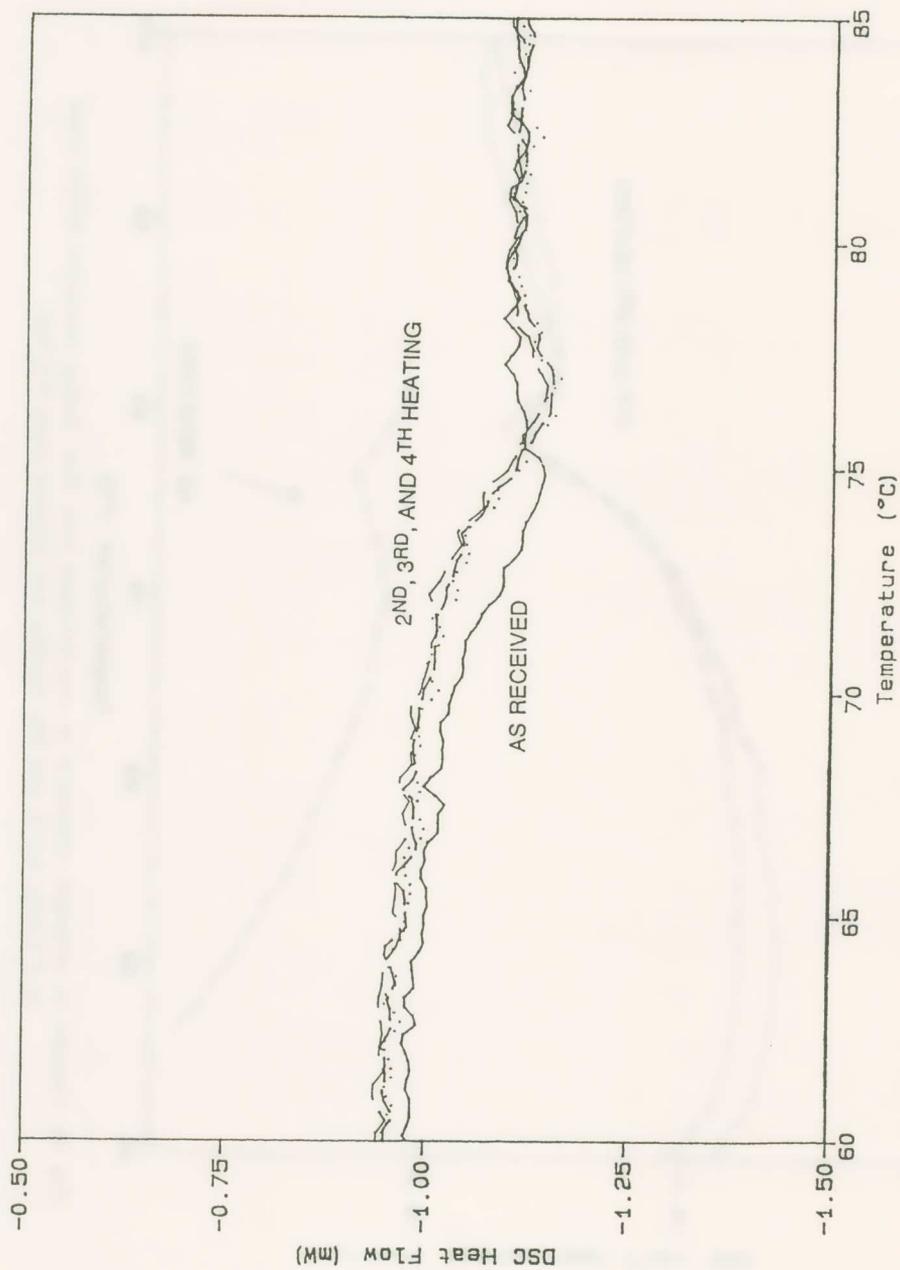


Fig. 14. Changes in Tg/enthalpic relaxation in DSC total heat flow during successive DSC scans at 2°C/min. Cooling rate between scans 2°C/min.

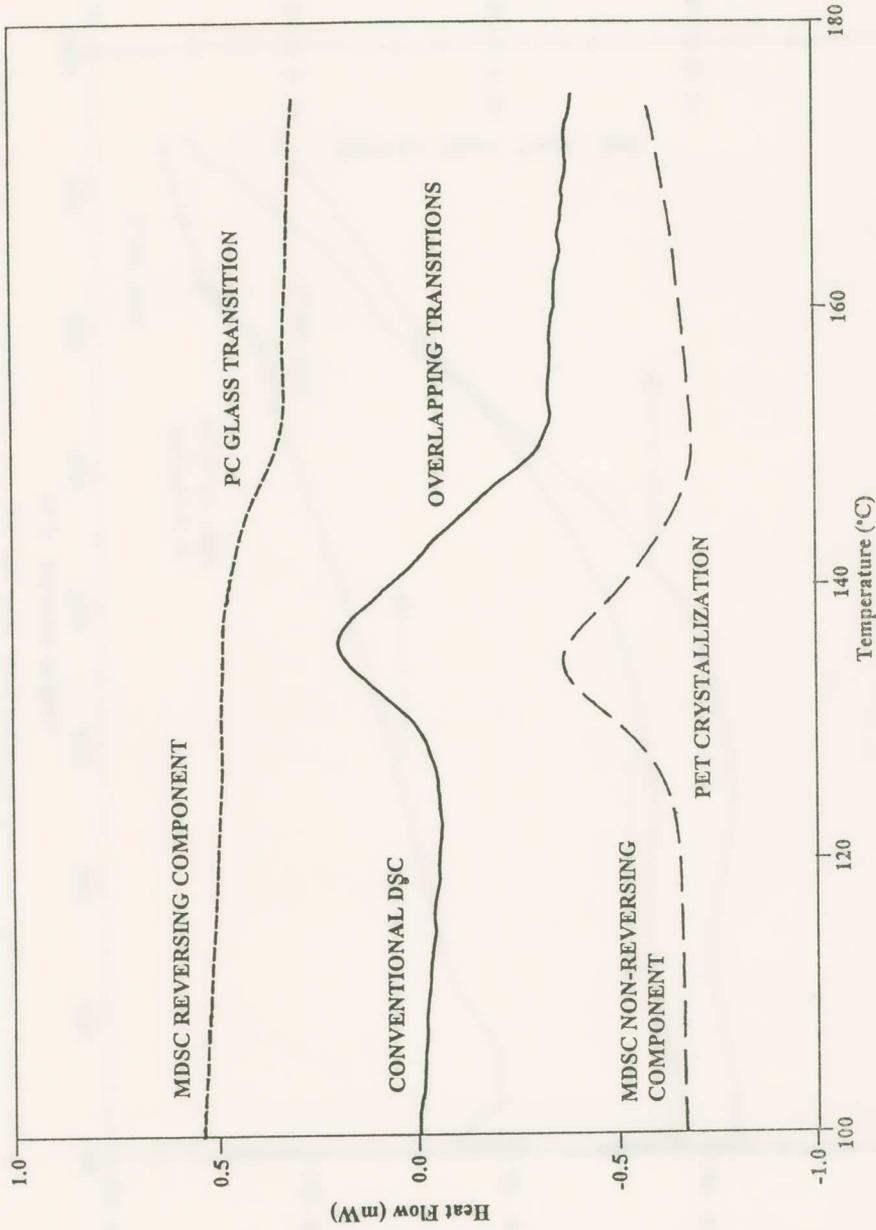


Fig. 15. Total, reversing, and non-reversing heat flow for PET/PC bilayer film.

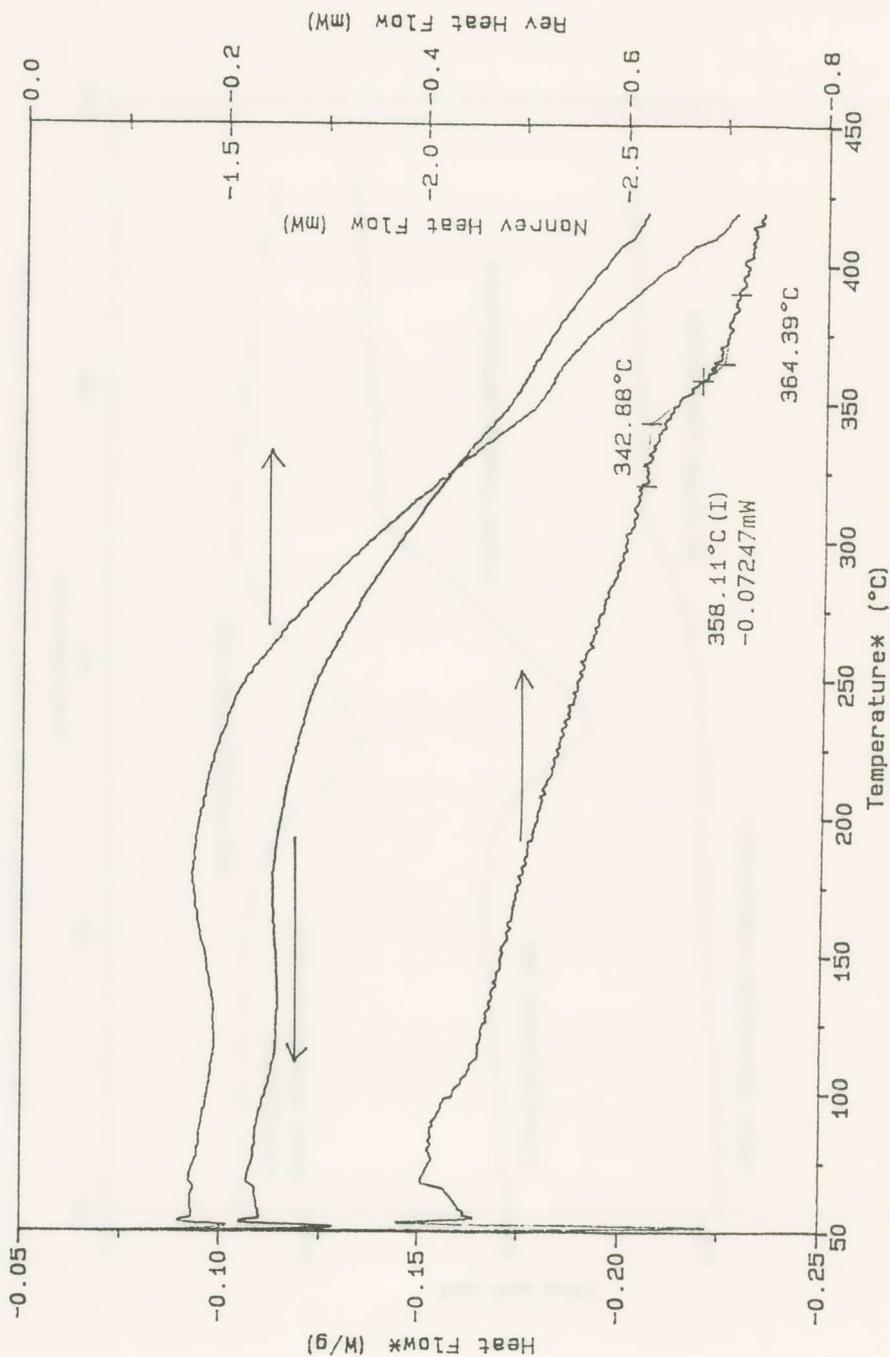


Fig. 16. Total, reversing, and non-reversing heat flow for NR-150 at 2°C/min, 0,3 C, and 30 seconds.

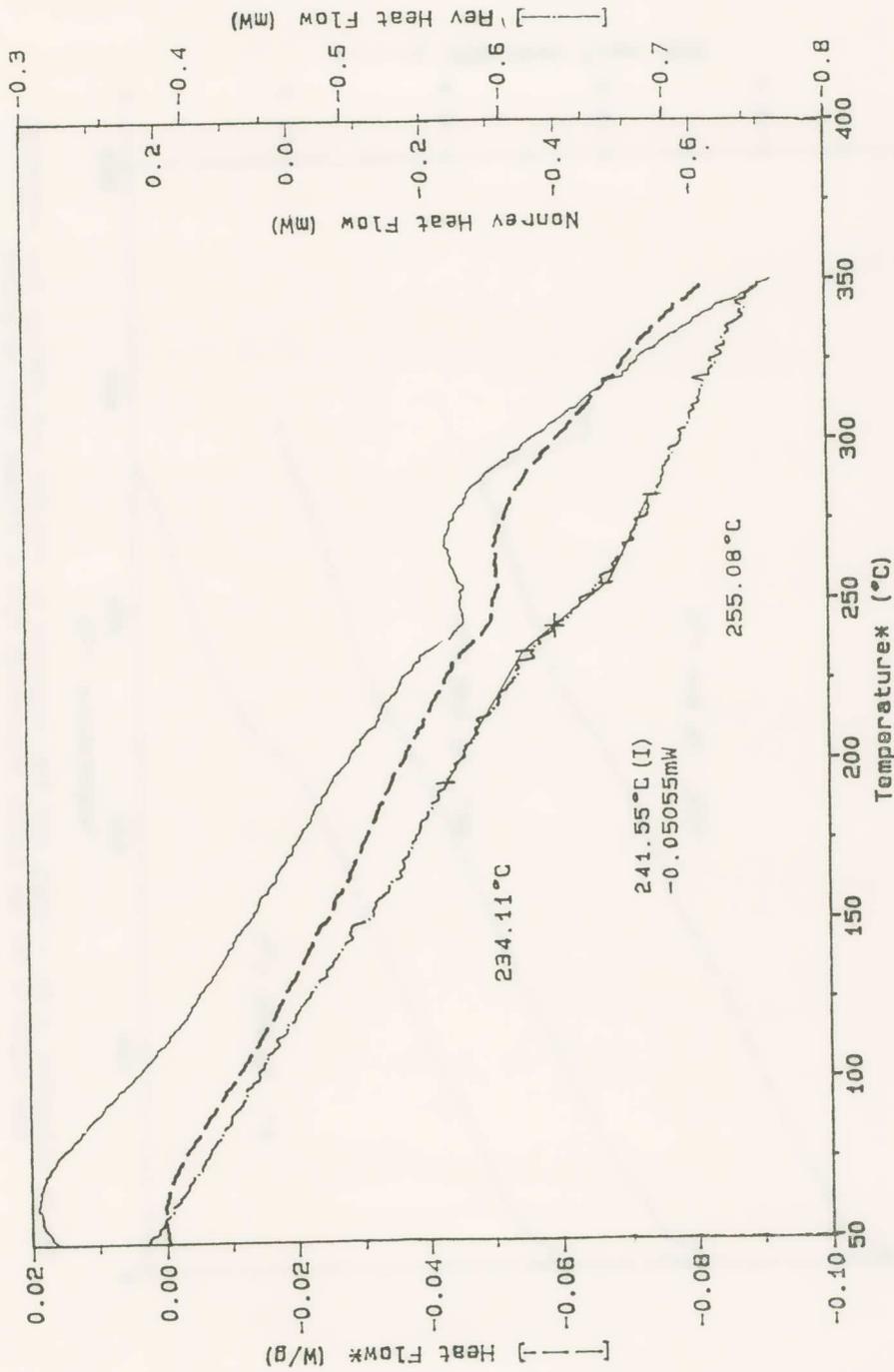


Fig. 17. Total, reversing, and non-reversing heat flow for BMI/IM7 at 2°C/min, 0,4°C, and 30 seconds.

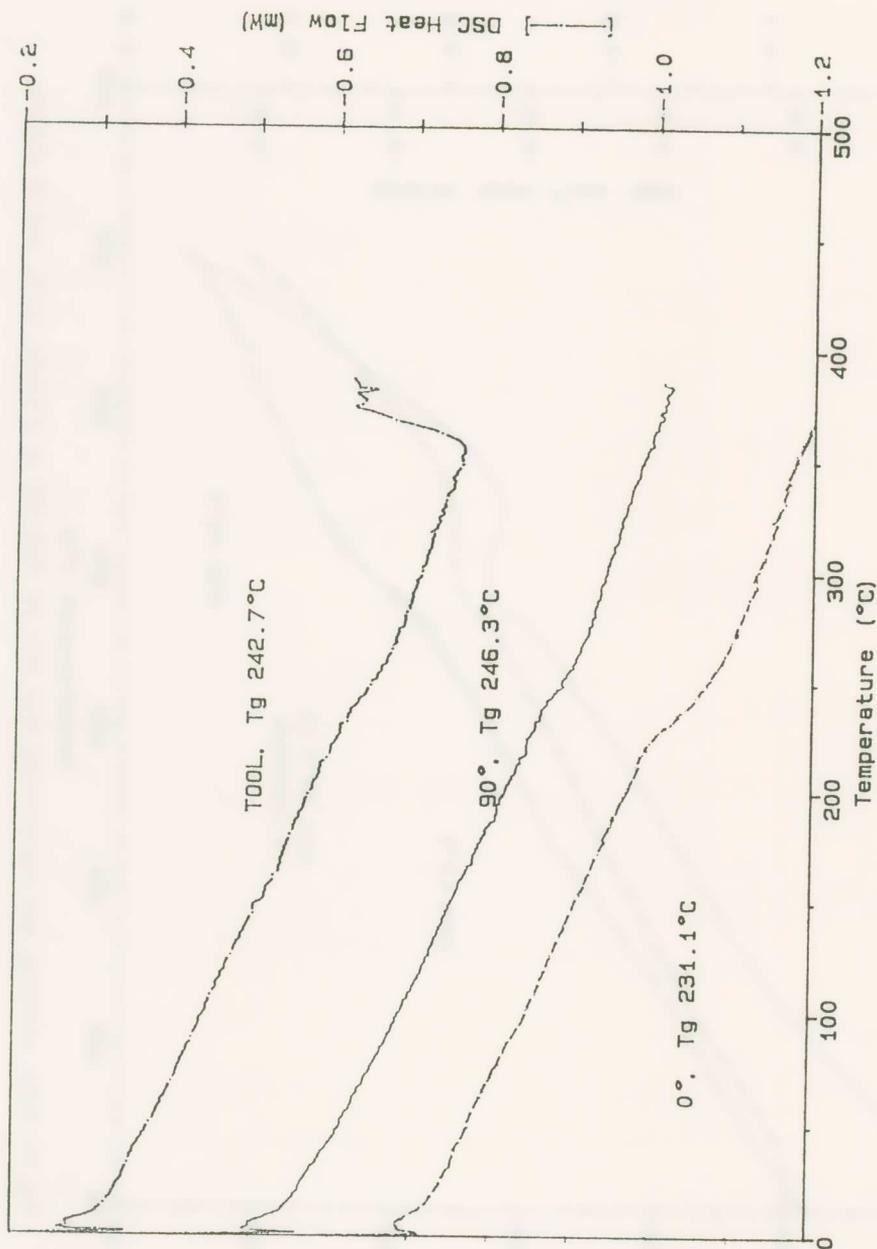


Fig. 18. Comparison of the reversing heat flow component for BMI/IM7 with different fiber orientations with respect to the pan bottom. Experiments done at 2°C/min, 0,3°C, 30 seconds.

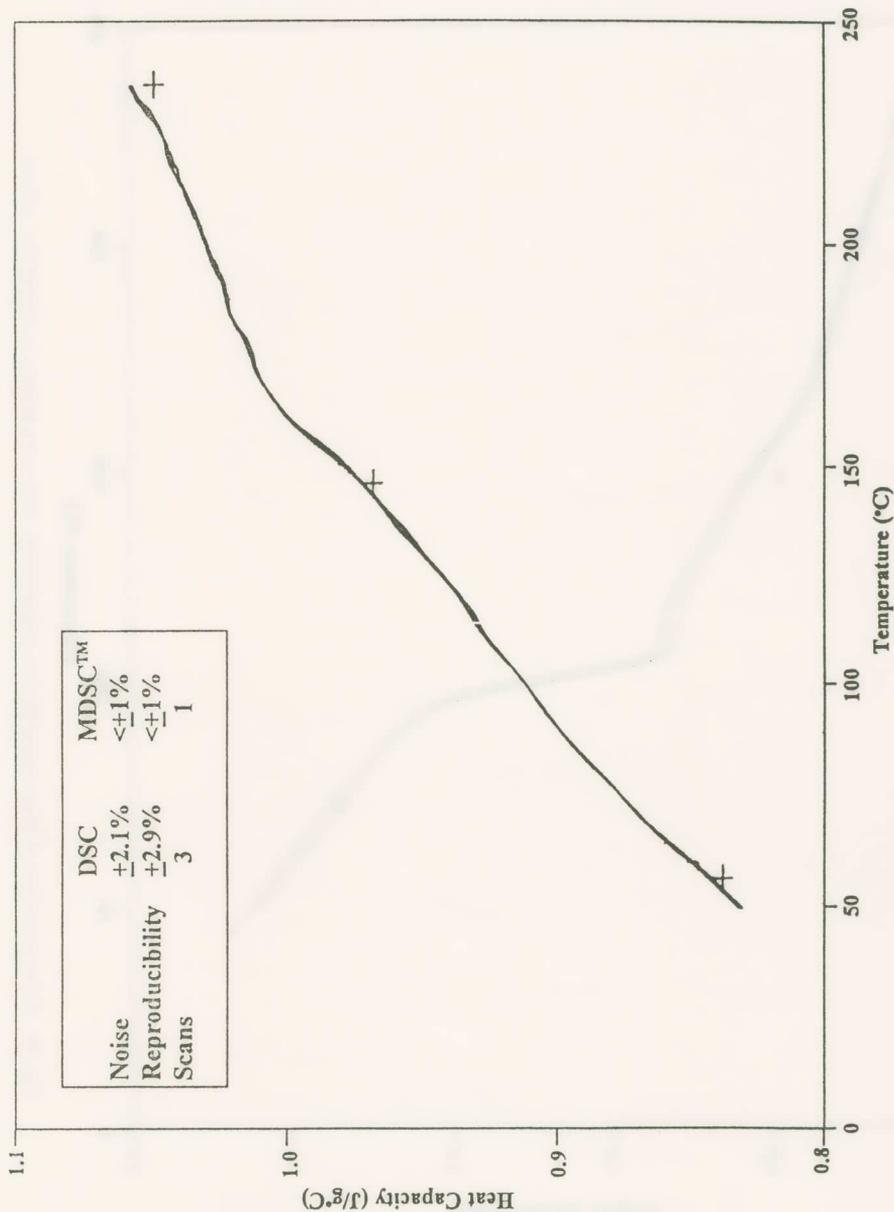


Fig. 19. Determination of heat capacity for sapphire and comparison to literature values.

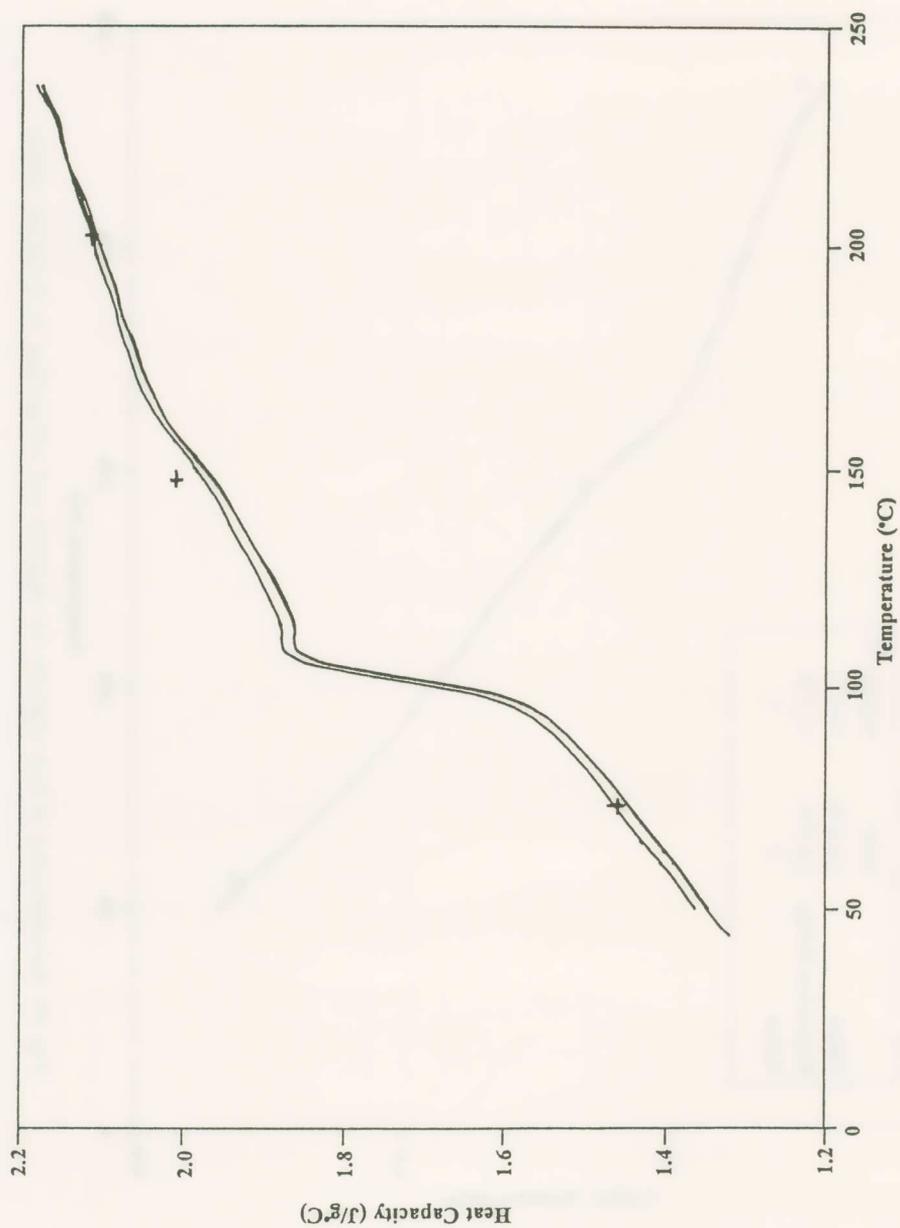


Fig. 20. Determination of heat capacity for polystyrene and comparison to literature values.