Mike Reading[1], Duncan M. Price[1] and Hélène Orliac[1]

Measurement of Crystallinity in Polymers Using Modulated Temperature Differential Scanning Calorimetry

---

Abstract: Some time ago a proposal was made [*1*] for an approach to calculating the initial crystallinity for polymers using MTDSC, i.e., the crystallinity of the sample before the start of the experiment. The essence of the technique is that it attempts to estimate the contribution from the vibrational heat capacity to the total enthalpy absorbed by the sample over the temperature range where crystallization, rearrangement and melting occur. This estimate is made from the reversing signal by using interpolation to subtract any contributions to this signal from crystallisation rearrangement or melting processes. The difference between the total enthalpy and the estimate of the vibrational heat capacity contribution must then be a measure of the enthalpy of melting of any initial crystallinity. The thermodynamic basis of this approach is presented in this article together with examples of its application to both simple and complex systems. There are alternatives to this procedure and the advantages and disadvantages of the various possible approaches are discussed.

Keywords: modulated differential scanning calorimetry, crystallinity, ATHAS database

Introduction

In the following discussion we will consider only the case where we assume that a sample is made up of only two phases, crystalline and amorphous.

The thermodynamic basis for measuring crystallinity has been well known for many years. The relevant enthalpy diagram is given in Figure 1. At any temperature the vertical distance between the enthalpy line for a completely amorphous polymer and the enthalpy line for a 100% crystalline polymer gives the enthalpy evolved when transforming from a perfectly amorphous sample to a perfectly crystalline one (supercooling means that this might occur over a range of temperature on cooling from the melt). It can be seen that this enthalpy changes with temperature, thus the enthalpy associated with a given degree of crystallinity, changes as a function of temperature. This is one of the factors that must be taken into account when calculating initial crystallinity.

---

[1] Senior Research Fellow, Research Fellow and Visiting Research Associate respectively, IPTME, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK.
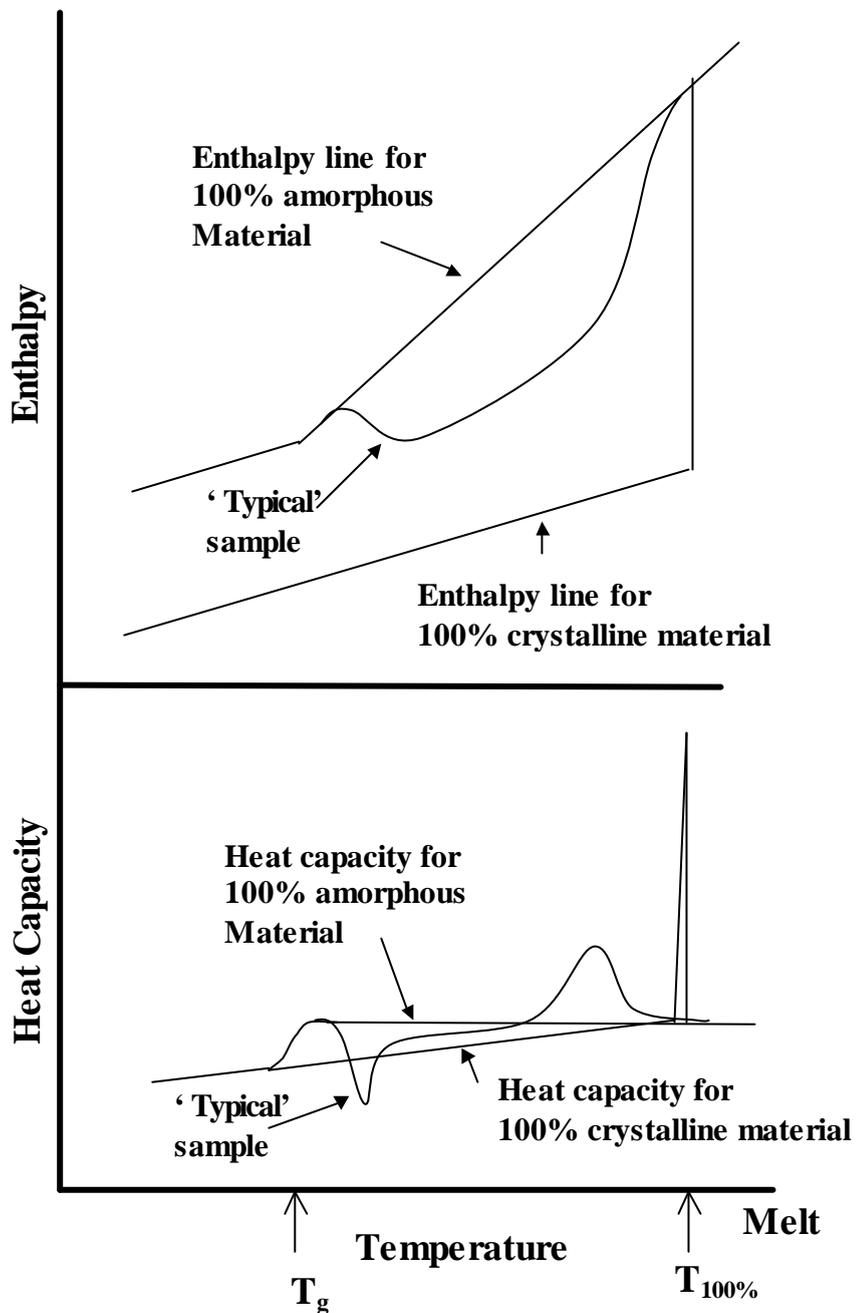
Figure 1- *Schematic of idealized enthalpy diagram for a semicrystalline polymer.*

Any degree of crystallinity can be represented by an enthalpy line similar to the one given in Figure 2 for a 50% crystalline sample. These types of lines correspond to samples made up of a given fraction of amorphous material with the remaining fraction being perfectly crystalline. In reality, the crystalline material will always be less than perfect and thus melt at a lower temperature than the equilibrium melting temperature.
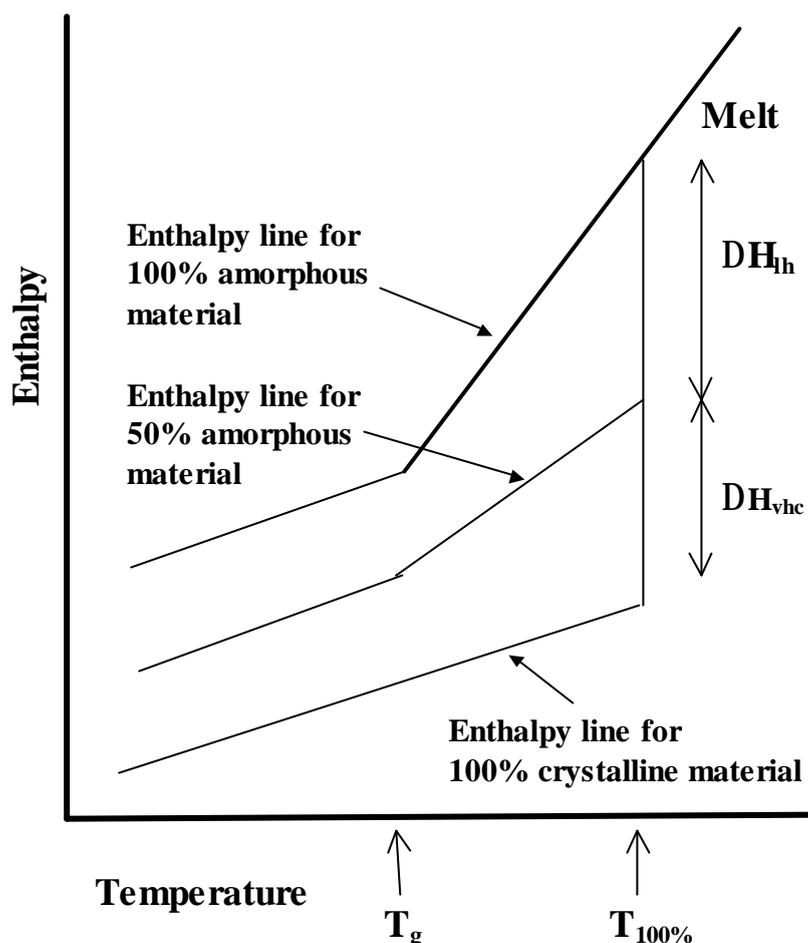
Figure 2 – Schematic of idealized enthalpy plot for 50% crystallinity.

However, when a single figure is used to express crystallinity, it can be said that the sample with the less than perfect crystals is held to be equivalent, in terms of enthalpy, to a sample made of some combination of perfectly amorphous and perfectly crystalline polymer. For each of the lines given in Figure 2 the total enthalpy from just above the glass transition to just after the melt can be divided into a contribution from the vibrational heat capacity ΔH_{vhc} and that from the latent heat of melting, ΔH_{lh}. Now let us consider the case represented by the "typical" sample in Figure 1. In this example, as the sample is heated, it partially crystallizes then increase its crystallinity as it is heated up before, finally, all the crystalline material melts. This kind of behavior is often encountered in practice. The initial crystallinity of this sample can be found by determining the total enthalpy change in moving between the glass transition and the equilibrium melting temperature then subtracting from this figure the enthalpy change for the perfectly amorphous case over the same temperature region. The answer, in this case, can be seen to be zero.

We now turn to real samples, all experiments were carried out using a TA Instruments 2920 heated at 2 °C/min., 60 second period, 1°C amplitude. The total signal from a MTDSC trace for quenched poly(ethylene terephthalate) (PET) is given in Figure 3 (equivalent of conventional DSC). We can see that, after the glass transition,

crystallization occurs then a melting endotherm is clearly seen at higher temperatures. We know from other evidence, to be described later, that in between these two events, rearrangement is occurring although this is not apparent from the DSC alone. The first step in applying the procedure outlined above for determining the initial crystallinity is to express the heat flow in terms of apparent heat capacity.
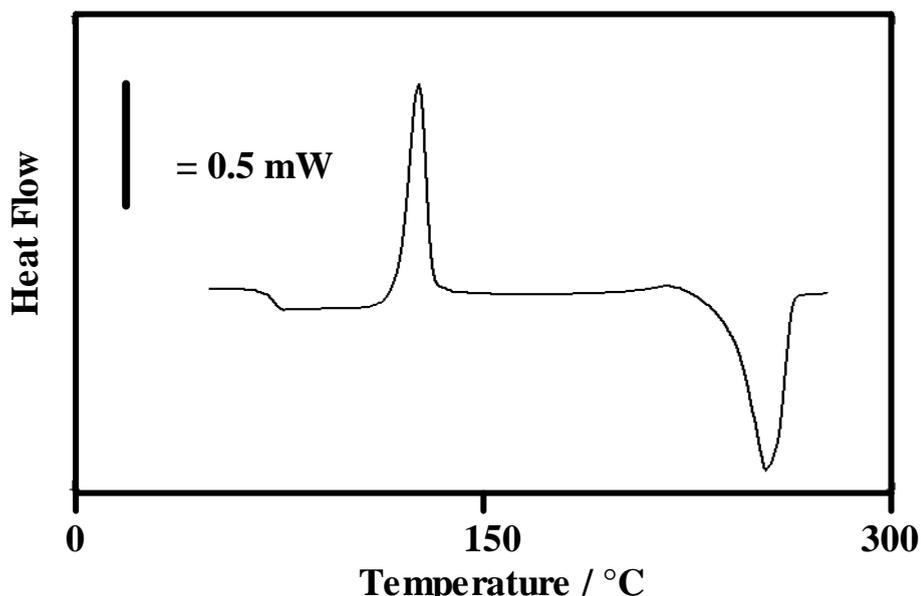
Figure 3 – *Quenched PET.*

The simplest method of doing this is: 1) make a baseline correction by subtracting the heat flow from an experiment carried out under the same conditions using an empty pan of equivalent weight and 2) divide the resulting heat flow by the heating rate and sample mass. The results of doing this are shown in Figure 4. Also given in Figure 4 are the theoretical values for the vibrational heat capacity of PET from the ATHAS database compiled by Wunderlich and available over the internet (http://web.utk.edu/~athas/). There are some discrepancies below the glass transition and above the melt that can only be ascribed to experimental error. Here we have applied a simple linear baseline correction to the experimental results to bring them into agreement as shown in Figure 5 (see [2]). From this we have constructed the complete enthalpy diagram given in Figure 6. To do this we have measured the area under the heat capacity curves from the equilibrium melting temperature (also obtained from the ATHAS database) downwards. To the crystalline heat capacity we add the enthalpy of melting of the 100% crystalline sample (taken as 140 J/g again from the ATHAS database). The result is that, to within experimental error, the initial crystallinity is zero (there is always scope for altering the values obtained by changing the integration limits, errors of a few % are typical).
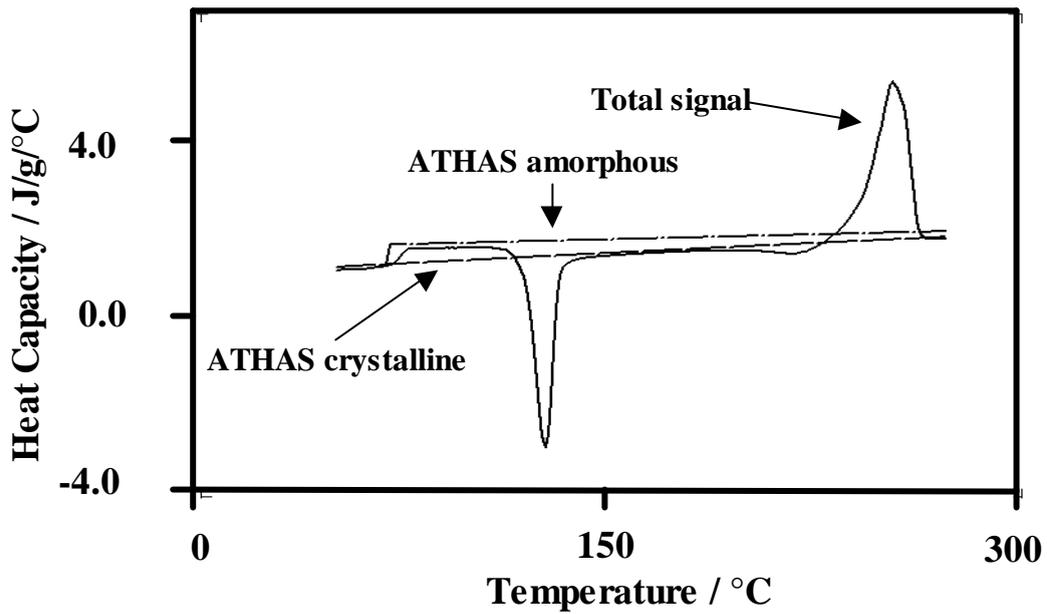
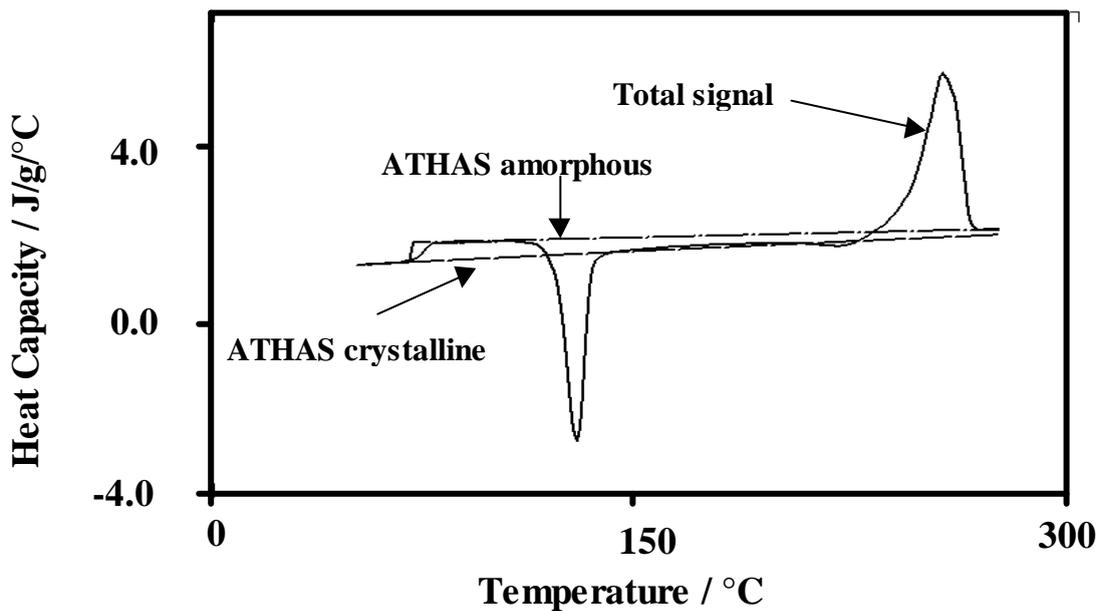Figure 4 – *Quenched PET with ATHAS values for vibrational heat capacity.*

Figure 5 – *Same as Figure 4 with linear baseline shift to force agreement with the ATAHS values below the glass transition and above the melt.*

Alternative Methods for Determining Initial Crystallinity for Simple Systems

An alternative is based on the empirical observation that the heat capacities of amorphous polymers are approximately linear. This being the case, we can extrapolate

from the melt region toward the glass transition as shown in Figure 7. This then gives us the same result for the amorphous vibrational heat capacity as the ATHAS database. If we imagine that we do not have the information contained in the ATAHS system or that this sample is unknown, we can still attempt to investigate its crystallinity using this approach.
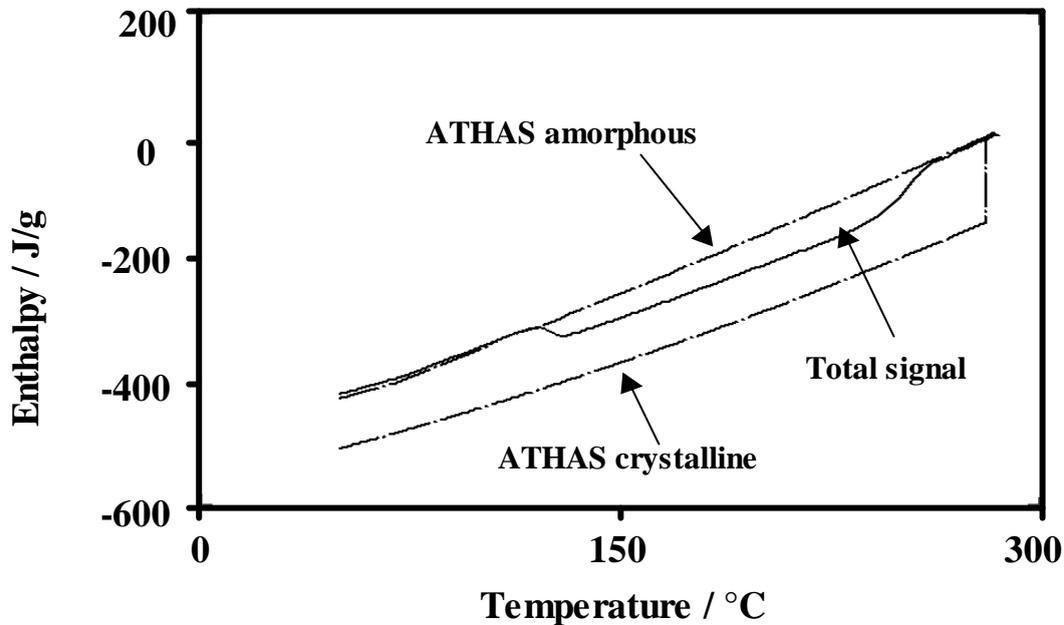

Figure 6 - *Full enthalpy diagram for PET using data from Figure 5.*

Using the extrapolation we could construct part of the enthalpy diagram shown in Figure 6, i.e. the crystalline enthalpy would be omitted. An equivalent approach is to use it as a baseline so that the difference between the extrapolation and the total heat capacity is integrated. The result is, necessarily, again zero.

In Figure 8 the results of an MTDSC experiment on the same sample are shown. We shall omit any use of the phase angle because, as shall be seen, it is not relevant to the analysis that will be demonstrated.

We can consider the complex heat capacity in isolation as shown in Figure 9. A large peak is seen that starts immediately after the cold crystallisation and ends when melting is complete. This is caused by the rearrangement process outlined above. One of the advantages of MTDSC is that the occurrence of this process can be clearly seen whereas conventional DSC gives little or no indication it is happening. Knowing that this peak is not due to vibrational heat capacity, we can attempt to approximate the values of the vibrational heat capacity by interpolation between the beginning and ending of this peak to obtain an approximation to the vibrational heat capacity. This baseline must also be used to eliminate changes due to the cold crystallization. This is because we are attempting to approximate the contribution to the total enthalpy from the vibrational heat capacity as if the sample were composed from a completely amorphous component and a completely crystalline one that does not melt until reaching the equilibrium melting
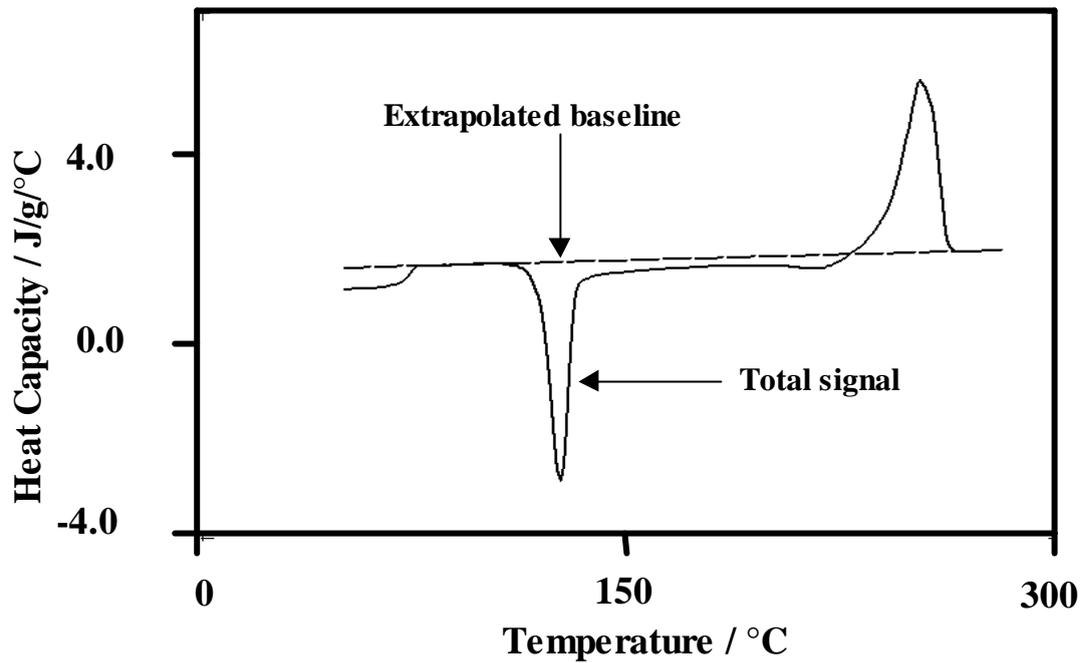
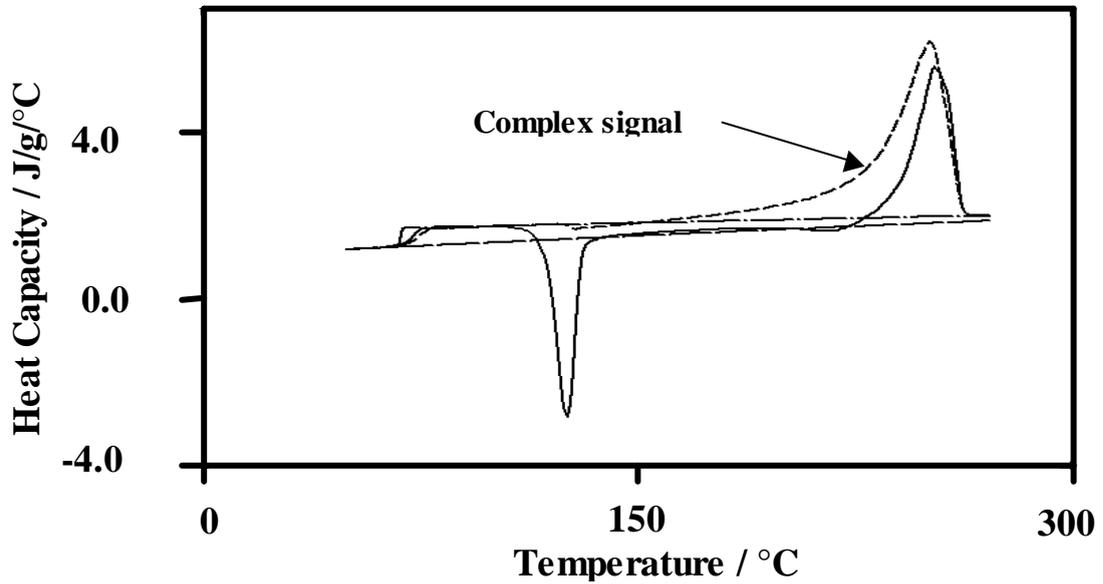**Figure 7** – *Quenched PET with baseline extrapolated from the melt.*

Figure 8 – *MTDSC experiment on PET, same as Figure 5 with complex signal added.*
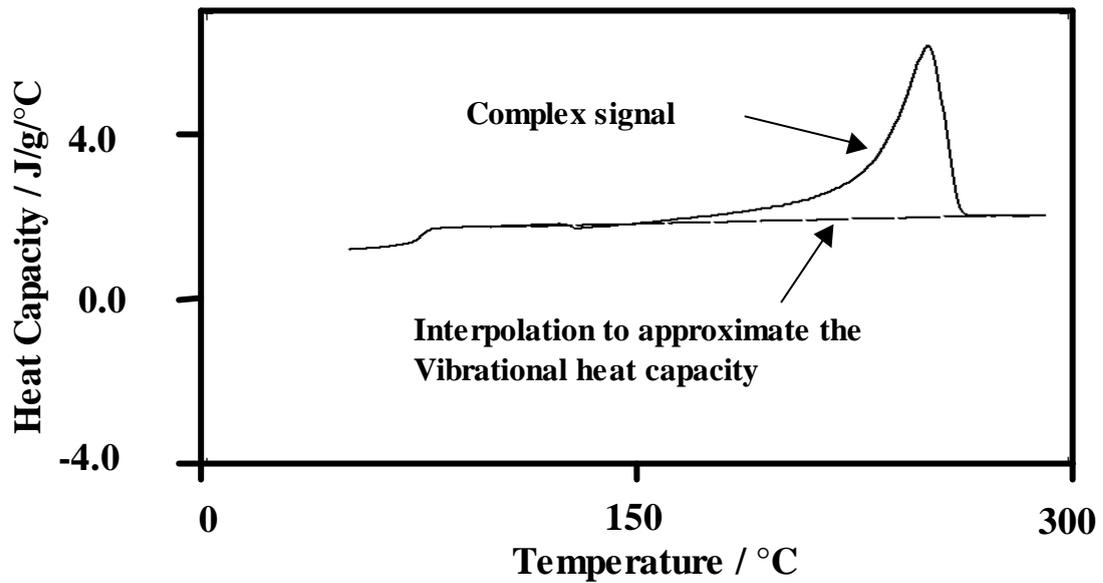
Figure 9 – *Complex heat capacity shown with interpolation.*

temperature. This being the case, we need to eliminate changes that occur as a consequence of crystallization as well as rearrangement and melting.

This is shown in Figure 10 together with the original total apparent heat capacity. This approximation to vibrational heat capacity can then be subtracted from the total to obtain the difference signal which then should contain that part of enthalpy that is due to the crystallisation, rearrangement and melting. The integral of this is then, once again, zero to within experimental error. Note that the peak in the complex heat capacity is subtracted so any change in its height resulting from the use of the phase lag correction would make no difference to the end result. Similarly, changing the frequency of the modulation would change the height of this peak. Again this does not alter the calculation.

The only difference between the method illustrated in Figure 7 and that shown in Figure 10 is that, in the first case, the baseline that is used for the integration is extrapolated from the melt, in the second case, it is derived by interpolating within the complex heat capacity to eliminate effects due to the heats of crystallization, rearrangement and melting. In the case of pure amorphous PET, the extrapolation and interpolation methods are equivalent. However, in other cases they will give quite different answers.
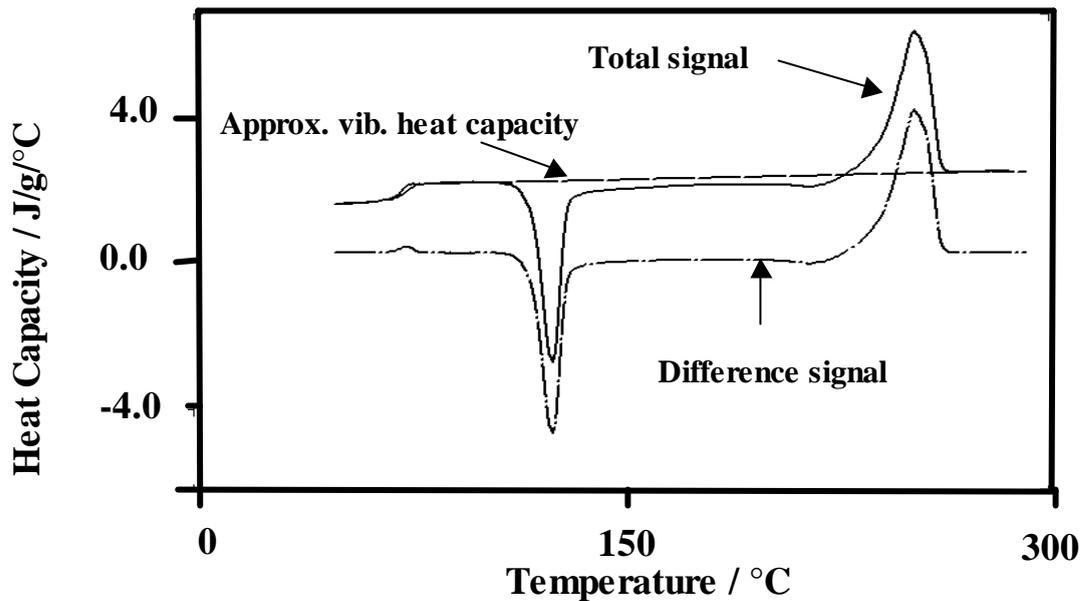
Figure 10 – *MTDSC results for PET after "correcting" the complex signal.*

Determining the Crystallinity of Complex Systems

In Figure 11 the results for and MTDSC experiment on a PET-PC 50-50 mixture (PC = polycarbonate) are given. A baseline correction has been applied and the total and complex heat capacities have been forced to be the same as each other and the ATHAS vibrational heat capacity values just below the first glass transition and just after the melt by use of a linear baseline adjustment. This is a model sample prepared by simply placing some PC in the same sample pan as PET before the combined sample is heated above 280°C then quenched. The glass transition of the PC is obscured by the cold crystallization of the PET in the total signal (which is equivalent to a conventional DSC experiment) but it is clearly visible in the complex heat capacity. Following the procedure outlined above, the peak that can be seen in the complex Cp that is due to the rearrangement process is removed by interpolation to provide the "corrected" heat capacity signal (intended to approximate the vibrational heat capacity). This is shown in Figure 12 together with the difference or "corrected" non-reversing curve. The integration of this signal gives an enthalpy for the crystallinity of 1.8 J/g (= 2.5% calculated using the known fraction of PET), close to the real value of zero. Figure 10 also shows the extrapolated baseline following the method illustrated in Figure 7. The extrapolation method, which fails to take account of the presence of the amorphous PC, gives an apparent enthalpy associated with crystallinity of 116 J/g.

One source of error in the interpolation method in this case is the contribution from the difference between the total and complex heat capacities at the glass transition of the PC due to their different effective frequencies and any possible annealing [*3*]. This can be estimated by looking at pure PC as shown in Figure 13. This suggests that, in the mixture, an error of could be expected of 1.2 J/g. If this is taken into account, then the figure for the mixture becomes 0.6 J/g which is 1% crystallinity.

An extreme example of a PET-PC blend is presented in Figure 14. This sample contains only 15% PET. Using the "corrected" complex signal as the baseline, a value of 4.5 J/g is obtained for the enthalpy due to crystallinity. Applying the correction for frequency difference at the PC glass transition gives a value of 2.5 J/g. This does, in this sample, correspond to an apparent crystallinity of 12%. However, given that this is a very challenging system, we consider this to be a reasonable result that encourages confidence in the interpolation method.
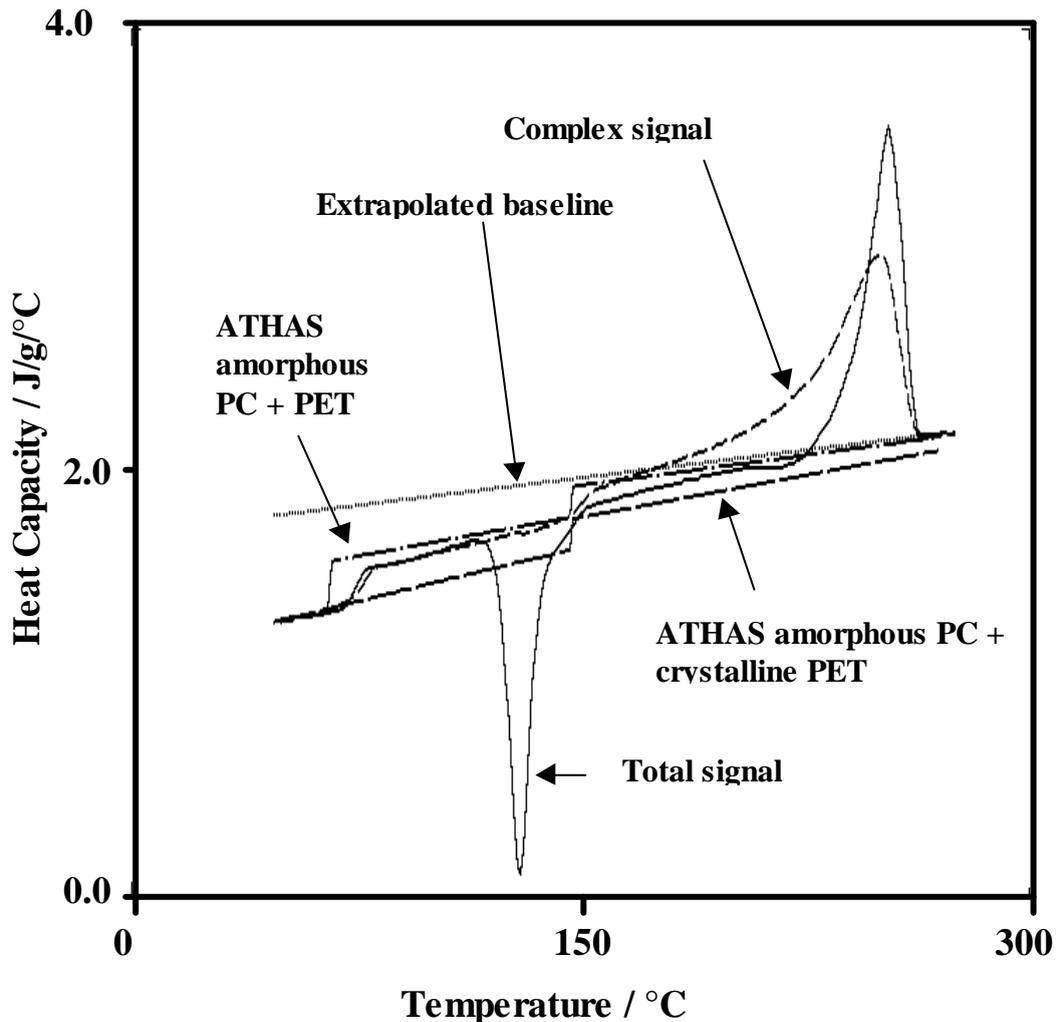
Figure 11 – *MTDSC results for a quenched PC-PET mixture.*

Sources of Error in the Interpolation Method

In addition to the error discussed above that can arise if a glass transition is present in the temperature interval between the onset of crystallization/rearrangement and the end of melting, there are two main sources of error in the interpolation method.

1) In samples that are not almost completely amorphous the linear interpolation may not be accurate because the crystalline vibrational heat capacity is generally not linear with temperature.

2) The higher temperature point selected for the interpolation always has a heat capacity value that is, in effect, taken to be equal to that of the 100% amorphous sample. This will clearly not be correct for crystalline samples.
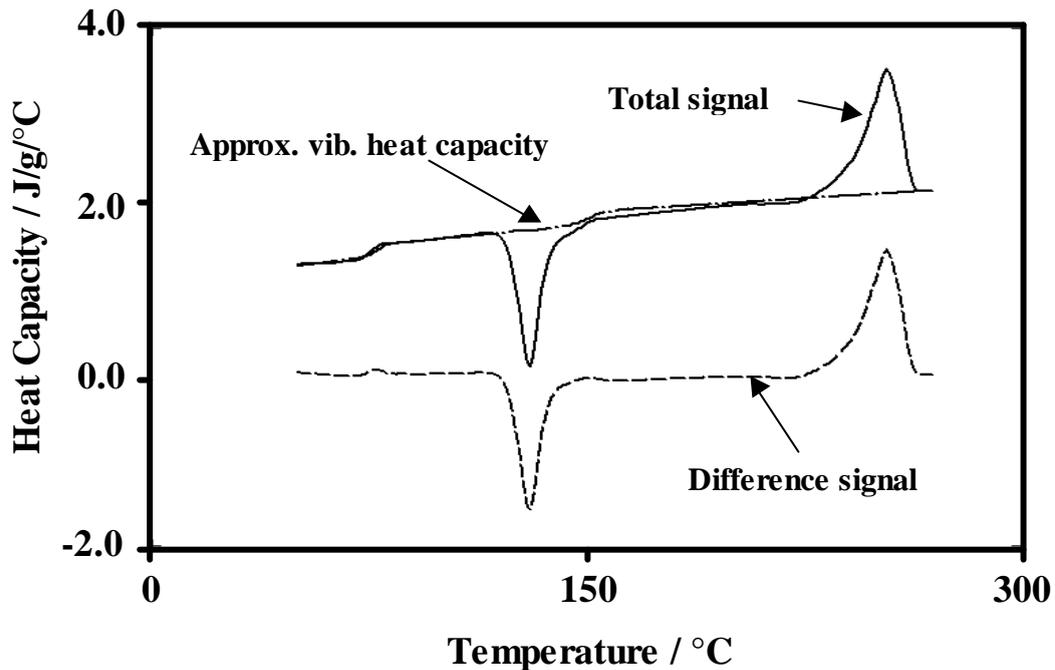
Figure 12 – *Quenched PET-PC mixture after "correcting" the complex signal.*

At first sight these may seem to be significant problems but in many cases these errors are very small. There are two reasons for this:

1) The first error has a self-compensating feature. It is zero for a fully amorphous sample and then increase as the sample crystallinity increases. As this happens, the temperature interval over which it becomes necessary to make the interpolation becomes smaller consequently the error become smaller.

2) With regard to the second error; it is small when the sample is close to amorphous. As the crystallinity of the sample increases, the potential error increases. However, in many cases the heat capacities for the amorphous and crystalline phases converge as the temperature increases toward the equilibrium melting temperature. This can be seen in the case of PET in Figure 8 and for the blend in Figure 11. The convergence means the error of assuming that the upper heat capacity used for the interpolation is the amorphous heat capacity, is often very small.
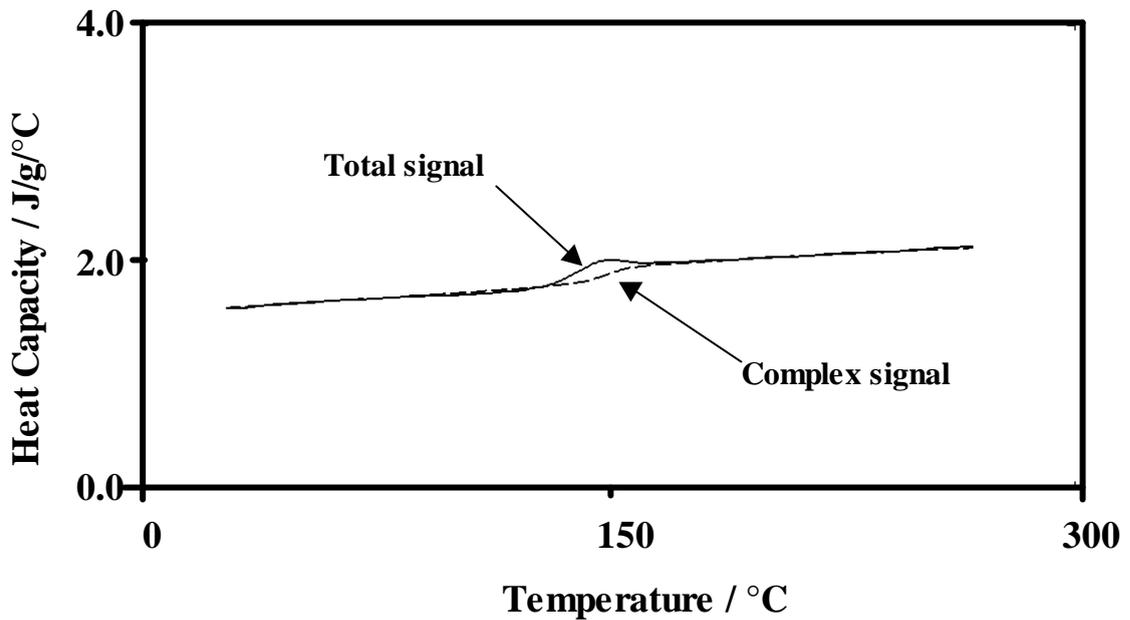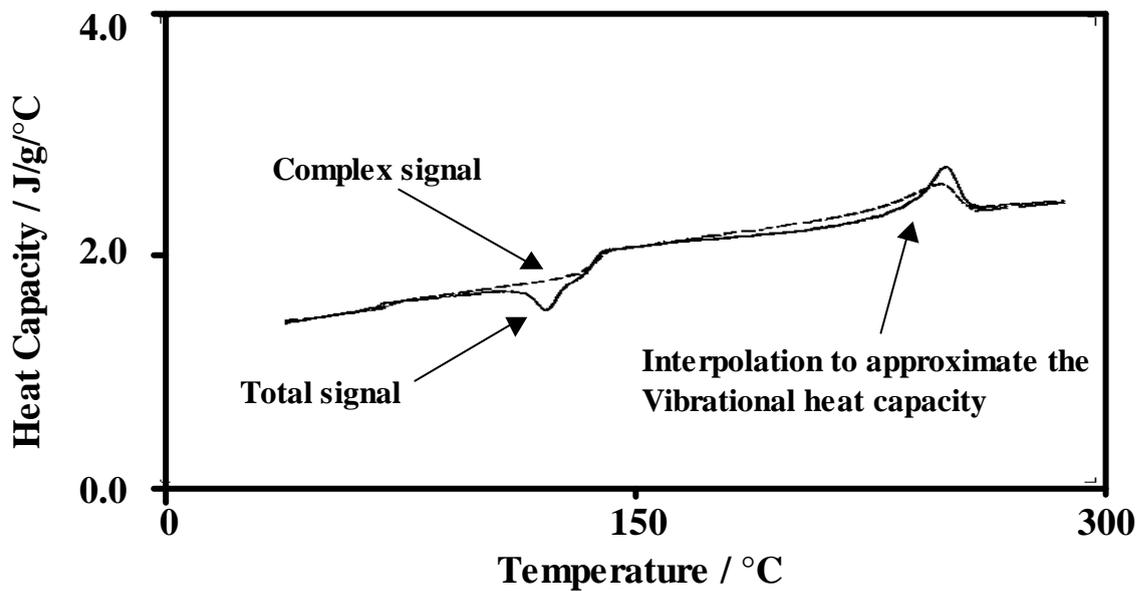
Figure 13 – *MTDSC of quenched PC.*

Figure 14 – *MTDSC of PET-PC blend.*

It is also worth noting that, while both of the above errors increase in terms of enthalpy as the crystallinity increases, as a percentage error they would generally decrease. The second of the above points is illustrated in Figure 15 which gives the MTDSC results for a relatively crystalline sample of PET. The interpolation method gives a crystallinity of 43%. When the theoretical vibrational heat capacity for a 43% crystalline sample is calculated, this and the interpolation are barely distinguishable, as

can be seen in Figure 15. The enthalpy difference between the two methods is less than 1.5%. This then gives us an estimate of a typical error for more crystalline samples from second cause given above. Errors from this source will decrease as the crystallinity decreases.

When considering the question of measuring crystallinity by any of the methods discussed in this article, it should be remembered that in the case of PET, and many other polymers, a rigid amorphous phase is formed which will compromise any calculation of crystallinity based on a simple two phase model. It is important not to push any of the methods outlined here beyond any realistic expectation of their true accuracy.
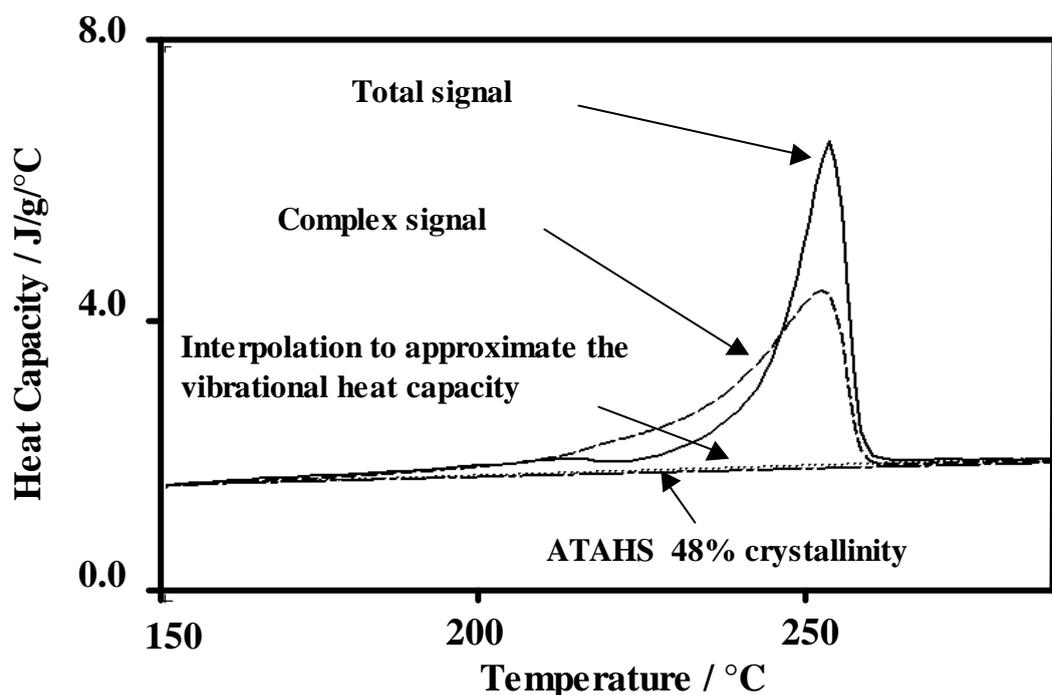

Figure 15 – *MTDSC of crystalline PET.*

Another source of error in the interpolation method arises from the fact that the enthalpy calculated from the difference signal is a measure of the enthalpy associated with crystallinity at the temperature at the end of the melting peak and not the equilibrium melting temperature. However, in this and most other cases, this error will be small enough to be neglected.

Conclusions

In general, for a pure polymer the best method of measuring crystallinity is to construct the complete enthalpy diagram and compare it with reliable theoretical values such as can be obtained from the ATHAS database. However, most real world samples are not pure polymers. They will be plasticised, or blended or contain fillers and other additives. This makes the enthalpy diagram approach unrealistic in many cases.

The extrapolation method has the advantages that it can deal with samples without reference to a database and it does not require that heat capacities be calculated (although heat capacity has been used here, it is just as applicable to the heat flow curve). However it has the disadvantage that the heat capacity or heat flow values beyond the melt have to be known with very high precision in order for the extrapolation be reliable. Any decomposition, loss of volatiles or chemical reactions will make this impossible. Furthermore, the linear extrapolation is only valid when the sample is a pure or nearly pure polymer. Fillers, a second amorphous polymer (as illustrated above) or other additives might not have a linear relationship between heat capacity and temperature. Given the large temperature interval over which the extrapolation must be made, this could lead to large errors.

The interpolation method based on MTDSC does have possible sources of error. However, in practice these errors will often be small and it has the advantage that it can cope with the kinds of problems outlined above with regard to real world samples. It also has the advantage that it does not require that full heat capacities are calculated or that a database is used. It simply requires that, using the linear baseline shift method, the total complex heat capacities (or total and reversing heat flows) are set to be the same below the glass transition and above the melt. The examples of the application of this method to the mixture and blend given above are, admittedly, somewhat extreme. However, the basic point is that, if this method is robust enough to give reasonable values even when dealing with such difficult samples, it should be able to give reliable results on simpler samples. Probably the main source of error is the second one given above. Inspection of the ATHAS database suggests that there are many polymers that follow PET in having closely converging heat capacities for the amorphous and crystalline phases. However, there will undoubtedly be cases where the difference in heat capacity between the crystalline and amorphous phases close to the melt temperature are sufficient to make the use of the interpolation method inadvisable. Whether to apply this method or one of the alternatives must, in the end, a decision made by the experimenter in the light of the possible sources of error when set against the advantages.

Finally, it should be noted that the interpolation method described above is exactly equivalent to adding the reversing and non-reversing signals in MTDSC. In this paper we remove the peak in the "reversing" signal (equivalent to the complex signal here) then calculate the "non-reversing" signal (equivalent to the "corrected" difference signal here) before integrating it. This is equivalent to calculating the 'non-reversing signal' integrating it then adding (subtracting due to the opposite sign) the integral of the peak in the "reversing" signal.

Acknowledgements

References

[*1*]   Reading M., Wilson R. and Pollock H. M., "Modulated Differential Scanning Calorimetry: Theory, Practice and Applications" *Proceedings 23rd NATAS,* Toronto, 1994, pp. 2-11.

[*2*]   Reading M., Luget A. and Wilson R., "Modulated Differential Scanning Calorimetry", *Thermochimica Acta*, 1994, Vol. 238, pp. 295-307.

[*3*]   Jones K. J., Kinshott I., Reading M., Lacey A. A., Nikolopoulos C. and Pollock H. M., "The Origin and Interpretation of the Signals of MTDSC", *Thermochimica Acta,* 1997, Vol. 305, pp. 187-199.