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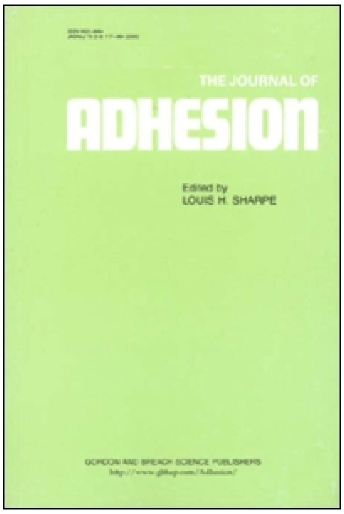

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Interfaces in Polymeric Systems as Studied by C.A.S.M. – A New Combination of Localised Calorimetric Analysis with Scanning Microscopy*

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Unlike almost all other variants of scanning probe microscopy, scanning thermal microscopy allows sub-surface imaging of polymers and other solids to be performed. Although on its own it provides no information that could help with chemical fingerprinting or analysis, when combined with a microscopic version of modulated-temperature differential scanning calorimetry (M-T DSC), the resulting simultaneous measurements of thermal data and spatial detail allow us to obtain useful data on the structure of polymer blends, phase separation, and the formation of diffuse interfaces. So far, for a number of polymers, we have performed localised calorimetric analysis to record events such as glass transitions, meltings, recrystallisations and thermal decomposition within volumes of material estimated at a few tens of cubic microns.

Here we review our own work only, in order to introduce the CASM technique together with the results of preliminary studies. As introduction we include also some examples of relevant published work on polymer interfaces performed by means of the parent "bulk" thermal analysis technique (M-T DSC): the topics covered include miscibility, shifts in glass transition temperature as a diffuse interface is formed, and determination of weight fraction and thickness of the interface.

Keywords: Polymer interfaces; calorimetry; scanning thermal microscopy; phase separation; interface development; glass transition; CASM

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**Corresponding author.

INTRODUCTION

One of the last understood aspects of the physics and chemistry of polymers is what processes take place at buried interfaces. In response to this challenge, over the past two years we have developed a technique known as CASM (Calorimetric Analysis with Scanning Microscopy). This has been fully described in earlier publications, as referenced in a later section. Although the work of applying it to the study of topics in polymer science is at a preliminary stage, it seemed appropriate to review the research in progress, but covering our own work only, and leaving till a future date the full details of experimental conditions and interpretation. Accordingly, this paper aims to review how simultaneous measurements of thermal data and spatial detail are beginning to yield useful data on the structure of polymer blends, phase separation, and the formation of diffuse interfaces.

Of the various powerful types of scanning probe microscopy that have been developed in recent years, scanning thermal microscopy (SThM), with its potential for sub-surface imaging, is an attractive option here. However, SThM on its own, like almost all other variants of scanning probe microscopy, provides no information that could help with chemical fingerprinting or analysis. Fortunately, as regards thermal properties, there exist a number of thermal analysis techniques which characterise changes in material properties (heat capacity, thermal conductivity...) with temperature, and before describing the microscopic technique it seemed appropriate to outline the relevant types of calorimetric study that we have performed in parallel:

INTRODUCTORY REMARKS ON THERMAL ANALYSIS

Recently, a new form of Differential Scanning Calorimetry was developed [1], known as Modulated-Temperature DSC or M-T DSC, in which a sinusodial modulation is superimposed on an underlying heating ramp. The corresponding cyclic heat flow signal "sees" only the reversible heat capacity associated with molecular vibrations, whereas the underlying measurement also sees endotherms and exotherms associated with kinetically controlled events. Thus, heat capacity changes due, for example, to glass transitions can be separated from non-reversible processes occuring at the same time (recrystallisations, cure reactions or the loss of volatiles): multiphase materials, interphases, miscibility, relaxation behaviour, premelting transitions, etc., can now be studied in greater detail than before. Some examples follow, taken from work that we have published previously:

Processes that are Controlled by Miscibility and Diffusion

The mutual diffusion of two polymers is involved in phase separation, and also in the formation of *diffuse interfaces*. These are important in adhesion, welding, crack healing and film integration. Many questions arise in connection with the physical processes involved, for example:

a. Integration of core-shell latex films (involving *decreasing* interface thickness): what diffusion mechanism is involved?
b. Phase separation: under what conditions does this occur,
    - either on a micro-scale, by segregation at interfaces so as to give *increasing* interface thickness ("diffuse interface development"),
    - or by nucleation and domain growth (from an initially miscible state?

In this connection, we have been able to derive valuable information on miscibility from bulk M-T DSC studies. We have shown [2] that the formation of a diffuse interface may be followed by M-T DSC, through measurements of shifts in the specific heat increment ΔC_p.[1] Moreover, the dC_p/dT signal given by M-T DSC may be used to characterise multi-component polymeric systems [3,4] with high resolution of differences in T_g: even for multi-phase networks, we can determine weight fractions of less than 7%. For a PMMA-SAN18

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[1] It is often not easy to obtain information about the degree of miscibility of pairs of polymers or copolymers when their glass transition temperatures are very similar; also, because thermograms can have a variety of shapes in the T_g region, the conventional T_g extrapolations are often somewhat subjective. It is often the case that the measurement of the increment of heat capacity, ΔC_p, in the glass transition region is also subjective, and it is known that the T_g value depends on many parameters, such as the nature of the polymer, its thermal history, different residual stresses and so on. These effects appear in the total heat flow signal from DSC or from M-T DSC. However, in spite of the great number of influences on the value of T_g, it is possible to use heat capacity output information from M-T DSC experiments to obtain T_g and ΔC_p values accurately and simply for polymers.

[poly(styrene-co-acrylonitrile)] blend, where there is 18 wt.% of acrylonitrile in the SAN copolymer, the difference of T_gs between the two constituent polymers in only about 10°C, but the derivative of heat capacity *versus* temperature data are able to distinguish between the miscible blend and the physical mixture, which shows two separate transition peaks [4].

Interface Thickness, Weight Fraction of Interphase

(Decreasing Interface Thickness) – Film Integration; Diffusion Measurement

Film-forming emulsion polymers are widely used in paper coatings, latex paints, water-based adhesives and other applications: the properties of the film itself depend upon the way in which individual particles are able to integrate. Indeed, mechanisms of film integration from latex particles, and interface development between two compatible polymers, are hot topics in polymer science at present – for example, the properties of the particle – particle interface affects the performance of the resulting coating, in the case of films used in paper coating, latex paints and water-based adhesives.

For film integration of core-shell latices, modulated-temperature differential scanning calorimetry gives quantitative information on the formation of a diffuse interface, and allows the shift in glass transition temperature to be followed. The two competing processes, molecular difffusion at the interface and free volume diffusion, may be distinguished. It is difficult to estimate interfacial thickness and weight fraction of interface for core-shell latex particles from SANS, TEM or DMA measurements.[2] Instead, we have successfully used M-T DSC for this purpose, using PMMA/PVaC [poly(vinyl acetate)] core-shell latex particles (Fig. 1a). The magnitude of the dC_p/dT signal for the pure PMMA and PVaC phases increases during the anneal, i.e., the ΔC_p value increases; the weight fractions of the phases may thus be calculated [5]. We thus find that the initial weight fraction of the interface in the PMMA/PVaC core-shell latex particle is about 45%,

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[2] Small-angle neutron scattering; transmission electron microscopy; dynamic mechanical analysis.

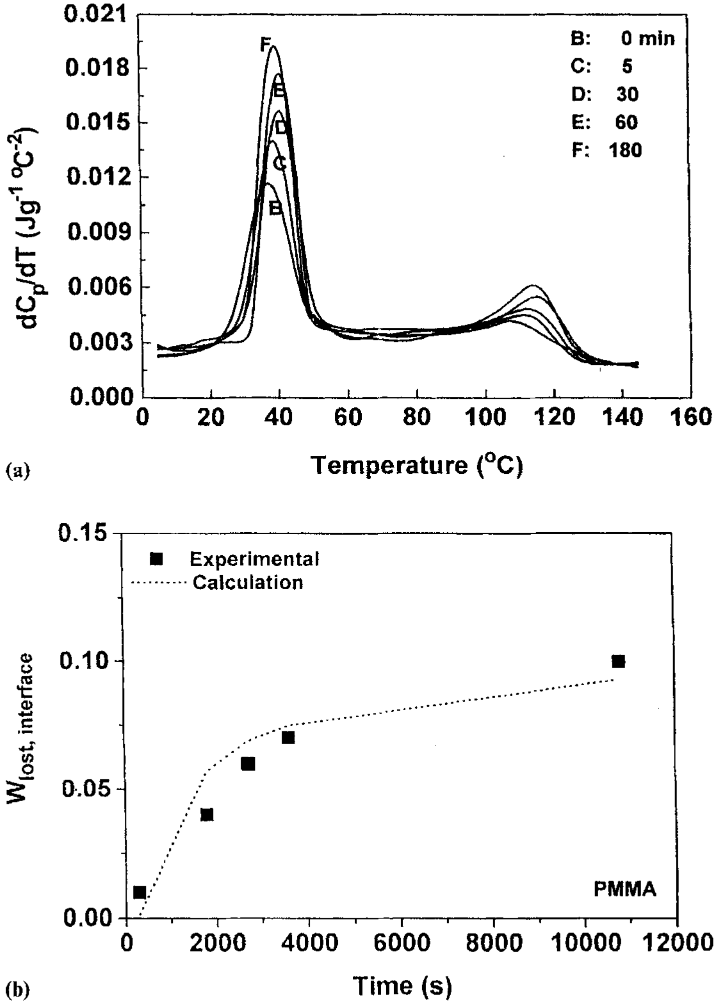


FIGURE 1 Copolymer core-shell latex film (PMMA-co-PVaC): a. Bulk M-T DSC data: dC_p/dT as a function of annealing time (min) at 150°C. b. Lost weight fraction of interface as a function of annealing time. (From Ref. [16]; as detailed there, the dotted line shows the result of a theoretical calculation based on a simple diffusion analysis).

with a thickness of *ca.* 28 nm. This large value of weight fraction is not surprising given that the system is at least partially miscible, although in prinicple it is possible that there could be enhanced free volume along the interface, and in this case a small correction to the above values would be needed. With increasing annealing time the interface thickness decreases, and we find that the lost weight fraction varies as the square root of annealing time (Fig. 1b). This relation is consistent with reptation behaviour ("worm-like motion" [5]), suggesting that the mechanisms of macromolecular diffusion in phase separation, and of interdiffusion between two compatible polymer films, may be the same.

(Increasing Interface Development) – Micro-Scale Phase Separation by Segregation at the Interface

A thermal method with the potential to determine the weight fraction and the thickenss of the interface in multi-phase polymer materials has been described [2]. The extent of mutual diffusion, and hence the development of an interface between two miscible polymers, PECH (polyepichlorohydrin) and PVaC with annealing time, has been studied by means of M-T DSC. By measurement of the change of increment of heat capacity in the glass transition region, the total interface content can be determined. With increasing diffusion time, the thickness of the interface increase, as shown in Ref. [2].

The formation of interpenetrating polymer networks (IPNs) is an example of micro-scale phase separation. So far, however, the spatial resolution of scanning thermal microscopy has allowed us to follow coarser phase separation process only, as described later.

LOCALISED THERMAL ANALYSIS: THE DEVELOPMENT OF CASM

This background work in thermal analysis serves to emphasize the potential advantages of being able to resolve spatial detail at the same time as calorimetric analysis is being performed. The Lancaster/Loughborough collaboration aims to develop a scanning probe version of M-T DSC in three stages:

(i) The application of scanning thermal microscopy (SThM) to the study of polymer blends, using thermal waves to allow sub-surface imaging [6, 7];

(ii) The development of *localised* M-T DSC in which data that provide chemical fingerprinting are obtained from regions of a few cubic μm in volume [7, 8];

(iii) Our next aim is to be able to use any particular M-T DSC peak or feature, chosen according to the particular component of the specimen that is of interest, to determine the image contrast.

As before, most of the following material reviews work that we have already published, with the exception of the phase separation study.

Most SThM studies have employed a thermocouple probe [9,10] where samples are generally probed at a constant amplitude of either surface temperature or heat flow. Rather than heating an entire specimen, we raise precisely defined regions of the sample through the temperature range of interest, the heat being supplied by the probe itself – a tiny resistance thermometer (the TopoMetrix "SThM probe") having a very small thermal time constant [11]. We use temperature feedback as well as force feedback, either to hold the temperature constant, or to generate evanescent temperature waves within the sample. The sub-surface detail detected corresponds to variations in heat capacity or thermal conductivity. By suitably choosing the temperature modulation frequency, and hence the penetration depth of the wave, we control the depth of material below the sample surface that is contributing to the image.

Computer predictions that a 1 μm-radius probe in air will give a lateral resolution of *ca.* 200 nm, with a depth detection of a few μm have been compared [6] with observations of model samples of high thermal conductivity buried beneath the surface of a low-conductivity matrix (metal particles in a polymer). At present the lateral resolution is of the order of a micron, and the probed region is a few μm^3 in volume.

PHASE SEPARATION OF MISCIBLE BLENDS, BY BINODAL NUCLEATION AND DOMAIN GROWTH

Miscible polymer blends usually form metastable systems: when mutual diffusion is possible, then with the help of controlled phase separation, a range of performance characteristics can be achieved, leading to an even larger number of potentially useful and different products. Since most of the useful polymer blends are immiscible, it is important to be able to study phase separation processes. This has for some time been possible with the help of scattering and solid-state NMR techniques. The former gives information about apparent macromolecular diffusion coefficients, and changes in phase structure with time; the latter reveals qualitative detail on variation of concentration with time, and also on diffusion coefficients when used in combination with optical microscopy. However, it is difficult to obtain information, thereby, on how the distribution of concentration and domain size vary with time, or on the early stages of spinoidal phase separation. Moreover, ternary polymer blends can decompose into more than two phases, in which case the scattering technique loses its usefulness.

We have a special interest in polymer blends that exhibit two-phase behaviour. When an immiscible polymer blend is subjected to a show temperature ramp, we are able to study the behaviour of single polymer domains in real time. Elsewhere [7] we present results for:

- PVC/PB [poly(vinylchloride)/polybutadiene],
- PEO/PB [poly(ethylene oxide)/polybutadiene], and
- PMMA/CPE [poly(methyl methacrylate)/chlorinated polyethylene].

For example, when a film of PMMA/CPE blend, cast from 50/50% solution onto glass, is dried for 24 hours, the two polymers involved segregate, being immiscible: one forms a matrix and the other forms island-like domains (Fig. 2). In this particular system, PMMA, which has a higher thermal conductivity than CPE, segregates into domains (heat "sucked" more rapidly from the probe) in a matrix of CPE.

We have used SThM to carry out some preliminary work on both spinodal and binodal processes in the case of the PVME/PS [poly(vinyl methyl ether)/polstyrene] system. Here we illustrate a case of binodal decomposition. (Fig. 3a) shows a series of constant temperature (35°C) thermal images obtained for a PVME (poly(vinyl methyl ether)/ PS (polystyrene)) (50/50% weight ratio) blend, miscible when initially cast onto a glass slip, but then subjected to an annealing temperature of 105°C for increasing annealing times. A nucleation and growth process is clearly identifiable: PS nuclei are seen to form and grow within the matrix. Intermediate miscibility blends are also observed,

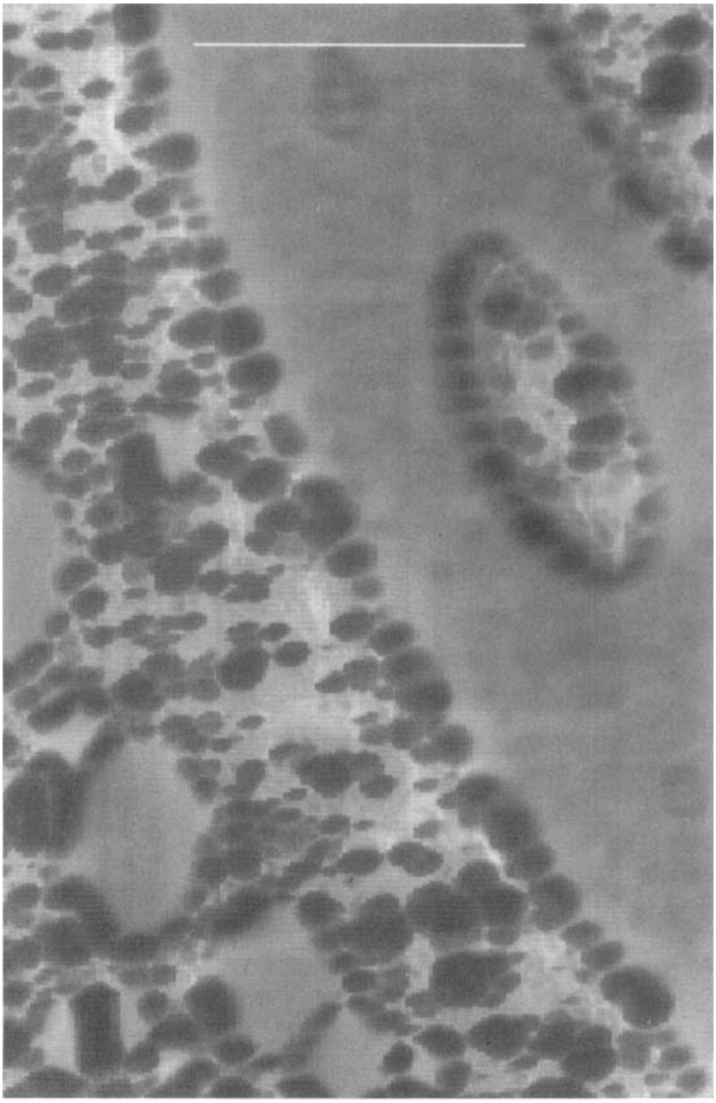


FIGURE 2 Thermal image of an immiscible blend of poly(methyl methacrylate) [PMMA]/chlorinated polyethylene [CPE], formed by segregation from a film that had been dried for 24 h. (Scale mark: 100 microns). In this particular system, PMMA, which has a higher thermal conductivity than CPE (0.193 against 0.144 $J \cdot s^{-1} \cdot m^{-1} \cdot K^{-1}$), segregates into island-like domains (heat "sucked" more rapidly from the probe) in a matrix of CPE. (See Color Plate I).

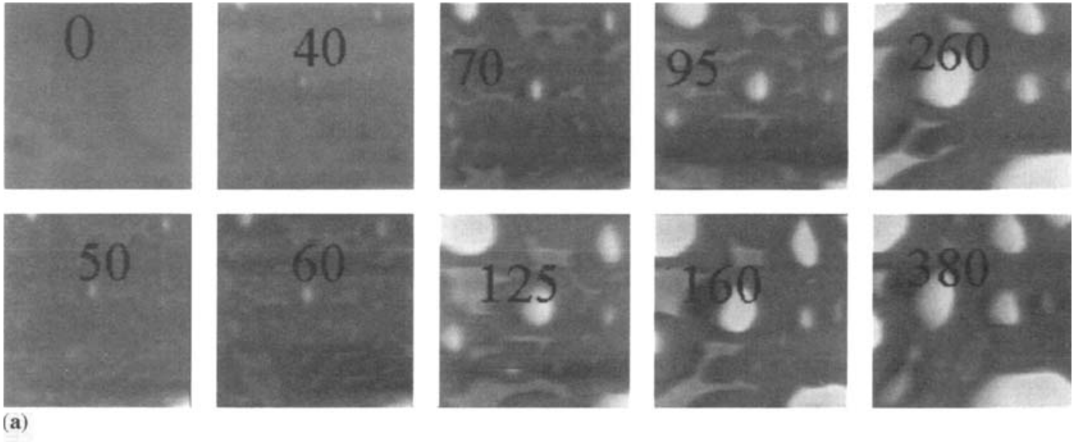


FIGURE 3 Phase separation process of a PVME [poly(vinyl methyl ether)]/PS (polystyrene) (40/60%) blend at 105°C: a. Succession of thermal images over a period of 6 hours, showing the phase separation process to be binodal rather than spinoidal. Area of each image: 120 × 120 μm; times shown are in minutes. b. Mean domain dimension as a function of time. (See Color Plate II).

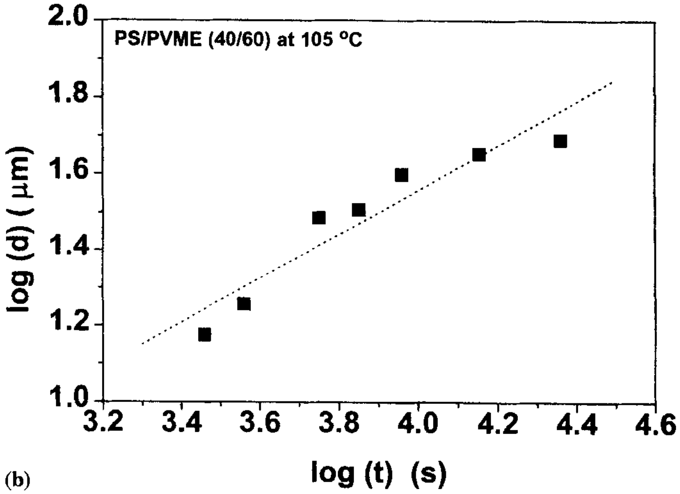


FIGURE 3 (Continued).

but they disappear as decomposition leads towards complete separation of the phases.

We see clearly that the segregated regions (mean dimension *d*) grow with time, *t* (see for example (Fig. 3b)). According to the analysis of Siggia [12], during the "early diffusion" stage, domain growth is controlled by a flow process in addition to diffusion, and the relation

$$d \propto t^{1/3} \tag{1}$$

is followed, whereas during the "diffusion and flow" stage, *d* varies linearly with *t*. We aim to complete a quantitative investigation of the early stage of phase separation as soon as the spatial resolution of the technique has been sufficiently improved.

Future plans include:

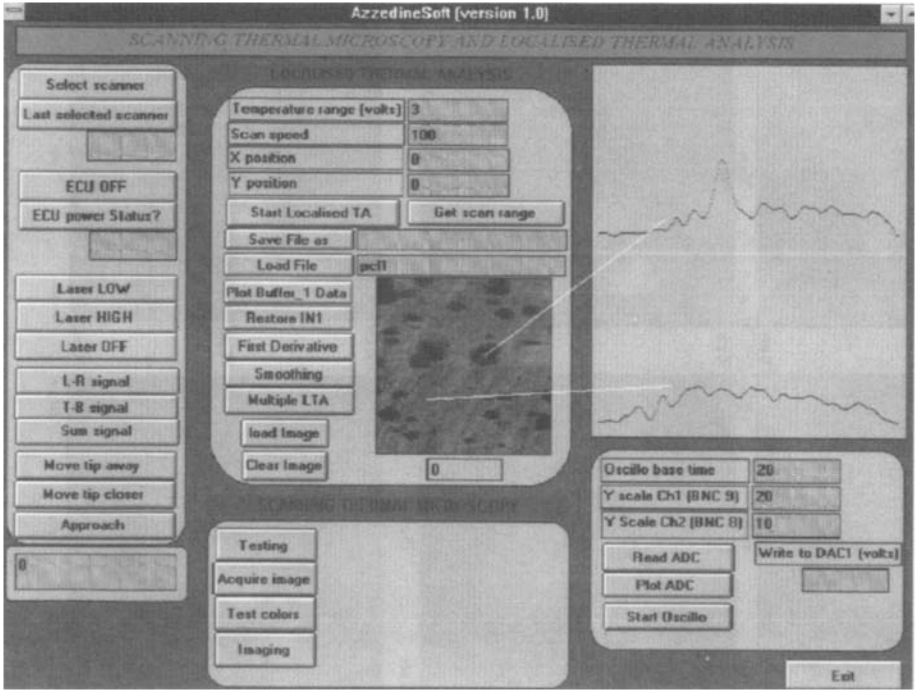
1. Study of growth laws for phase separation in PVME [poly(vinyl methyl ether)]/PS, PMMA/SAN, and PMMA/PVaC;
2. Study of domain distribution during phase separation, in ternary as well as binary blends;
3. Establishing whether the third component forms an individual phase, or alternatively, segregates at the interface between the two principal phases;

4. Studying the role of blend symmetry or asymmetry in the phase separation process;
5. Change in concentration with phase separation time in domains;
6. Use of localised DMA [13] (dynamic mechanical analysis), the mechanical analogue of localised thermal analysis, to examine surface and near-surface mechanical properties of the phase-separated systems, and how these relate to concentration distributions in domains;
7. Computer simulation of the relevant dynamic processes.

LOCALISED CALORIMETRIC ANALYSIS

Our *spatially localised calorimetry* technique is based on M-T DSC and the third harmonic detection principle. In this so-called 3-omega method, a metallic film is deposited on the surfaced of a bulk sample, so as to form a planar resistance. An ac current is passed through it inducing ac heating of the sample. The resistive film is also used as a temperature detector. Calorimetric information is then obtained by subjecting the sample to an underlying temperature rise. As shown by Moon *et al.* [14], the amplitude and phase of the temperature oscillation may be derived directly from those of the third harmonic. The information obtained by M-T DSC and by the 3-omega technique is macroscopic and averaged over most of the volume of the sample (a few mm^3). In our technique, the probe is precisely positioned at a desired location on the surface of the specimen to the investigated (Fig. 4 illustrates the mode of operation), and both the ac and the underlying heat treatment (temperature ramp) are provided locally by the probe which also acts as the sensing resistance. Localised thermal analysis is thus acheived yielding information from a much smaller volume of material.

So far, for a number of polymers, we have performed localised calorimetric analysis to record events such as glass transitions, meltings, recrystallisations and thermal decomposition within volumes of material estimated at a few tens of cubic microns. The estimate is based on complementary experiments in which the probe is used to produce pits or dimples which are left on the sample surface (Fig. 5). The CASM data obtained are compared with those obtained from



Temperature range (volts) 3
Scan speed 100
X position 0
Y position 0
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Y scale Ch1 (BNC 9) 20
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FIGURE 4 Screen menu for CASM. A previously-obtained thermal image is re-displayed, and thermal scans obtained giving data that relate to individual areas chosen from that image. (See Color Plate III).

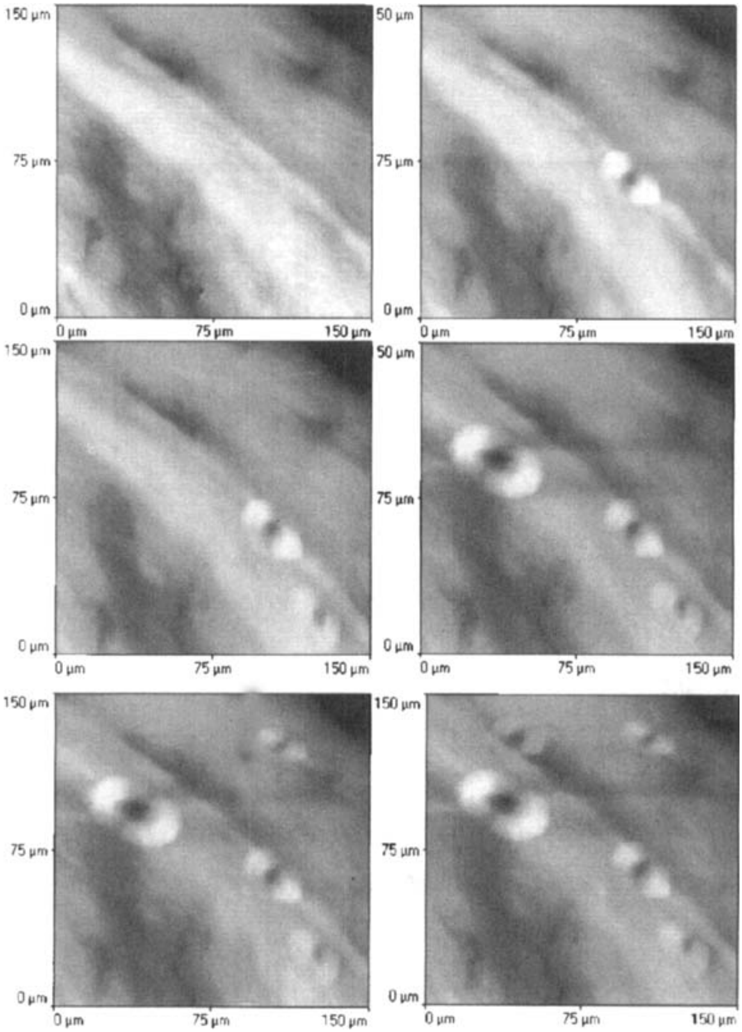


FIGURE 5 A series of pits or depressions produced on the surface of a polymer sample (POM/LPDE) [poly(oxymethylene)/low-density poly(ethylene)]. Each pit was formed when a current pulse was passed through the thermal probe (the procedure differed from that employed in CASM, in that here, the probe was held a few tens of nanometres above the surface). The same magnitude and duration of pulse was used in all cases, but with different probe/surface separations, so that pits of different size were formed. These low-resolution topographic images were obtained with the thermal probe itself, but using force feedback rather than thermal feedback (area of each image: 150×150 µm). (See Color Plate IV).

conventional bulk M-T DSC, and the events registered in both cases are found to match [7, 8]. Meltings are identified by a sharp change in the slope of the phase signal as the temperature is increased, and these changes correspond to the known melting points of the materials. Transition to a rubbery state is identified by a change in the slope of the phase signal taking place at a temperature similar to that obtained by conventional calorimetry. The CASM scans shown in Figure 6 provide evidence of striking variations, from one region to another, in the crystallinity of a sample of polyethylene cooled from the melt. Figure 7 gives quantitative confirmation that the crystallinity of samples of different branched polyethylenes correlates well with the amplitude of the derivative of the CASM phase signal.

Results such as these lead us to predict that the study of interfacial processes in polymers will be helped considerably by the ability to measure *local* variation in the parameters discussed at the start of this review (glass transition temperature, interface thickness, miscibility, weight fractions...).

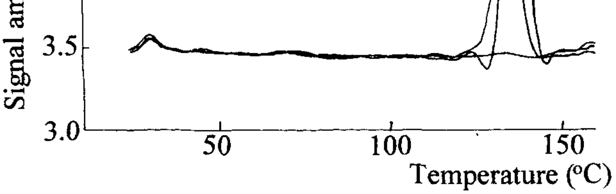
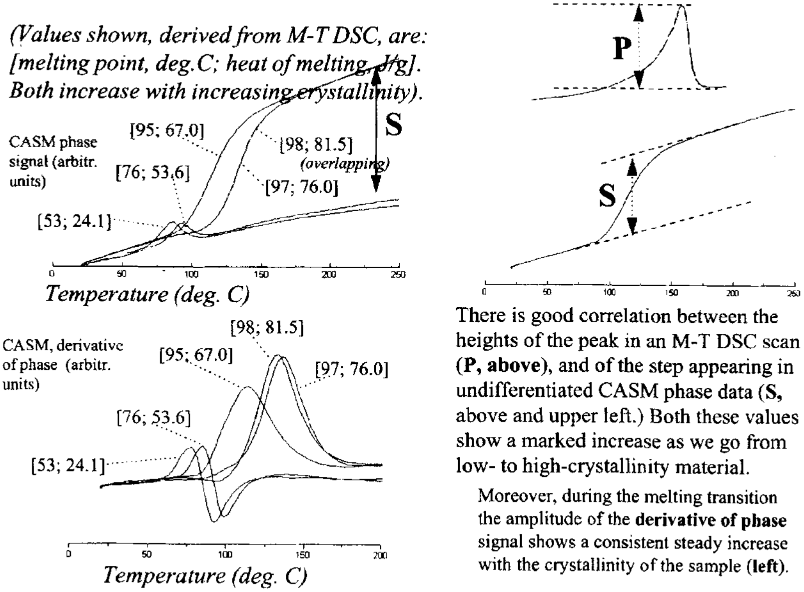


FIGURE 6 Localised calorimetric analysis: polyethylene, cooled from the melt (ca. 130°C) at 5°C/min. to room temperature. Scan rate: 40°C/min., 1 kHz modulation. Signal: 3-ω. Scans obtained at three different sites are shown. At one location, the material appears to be completely amorphous (no melting peak detectable). At the other two, the melting peak is clearly revealed, but the different signal amplitudes indicate different degrees of crystallinity.



(Values shown, derived from M-T DSC, are: [melting point, deg.C; heat of melting, J/g]. Both increase with increasing crystallinity).

There is good correlation between the heights of the peak in an M-T DSC scan (**P, above**), and of the step appearing in undifferentiated CASM phase data (S, above and upper left.) Both these values show a marked increase as we go from low- to high-crystallinity material.

Moreover, during the melting transition the amplitude of the **derivative of phase** signal shows a consistent steady increase with the crystallinity of the sample (**left**).

FIGURE 7 Branched polyethylenes: variation in crystallinity, detected by M-T DSC and CASM. Thermochemical data derived from the M-T DSC traces (heating rate 4 deg./min; modulation amplitude 1 deg, period 60 sec): the samples marked here as having $H_m = 24.1$ and 53.6 are low-density PE, while those having $H_m = 67.0$, 76.0 and 81.5 are high density. Thus, as expected, the crystallinity (defined as the ratio H_m to the value given by fully crystalline material) is seen to be higher for the high-density samples. In all cases, melting peak broadening is seen. CASM details: 3 kHz, 1 to 5 deg. modulation amplitude, ramp rate 300 deg/min. As regards the onset of the melting transition, the agreement with the M-T DSC data is satisfactory.

FUTURE DEVELOPMENTS

In the near future we aim to improve the resolution of these "active SThM probe" techniques, possibly to a value approaching what can be obtained with the fine thermocouple junction described a decade ago by Williams and Wickramasinghe [9]: this gave a spatial resolution of the order of tens of nanometers, with a thermal resolution of about a millidegree. Equally important is the need to develop fully quantitative analysis. To achieve this, a detailed scientific model is needed of the thermal processes involved in the CASM setup itself. Another exciting prospect is that of localised or imaging-DMA [13] (dynamic mechanical analysis), with which "events" such as those mentioned in connection with M-T DSC are revealed in the resulting curves of storage modulus and loss modulus as a function of temperature. Futhermore, for samples being irradiated by tuned infra-red radiation, the SThM probe lends itself to the identification of areas that are selectively heated by energy absorption (localised FTIR spectroscopy at the spatial resolution given by scanning thermal microscopy [15]).

In applying the CASM technique our chief interest is in polymers. In addition, as experience increases it will be possible to judge the prospects for application to a wider range of problems in materials science.

Acknowledgements

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