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Using microthermal analysis to characterize the nanoworld

THERMAL METHODS such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) are well-established techniques for characterizing the morphology and composition of polymers. It is often possible to identify and quantify materials by reference to their characteristic transition temperatures and thermal stability. By investigating the changes in the measured property (e.g., enthalpy, weight, length, stiffness, etc.) with temperature, it is also possible to study the effects of processing on, for example, crystallinity or cross-link density. The introduction of Modulated DSC[®] (MDSC[®], **TA Instruments, Inc.**, New Castle, DE), whereby a temperature modulation is superimposed on the conventional linear heating or cooling program, has further increased the resolution and sensitivity of DSC for monitoring, in particular, glass-rubber transitions in polymer blends.¹⁻⁴ The recent application of modulated temperature programming to TGA has also enhanced this technique by providing continuous kinetic information about decomposition processes.⁵

Despite these advances, conventional thermal methods give only a sample-averaged response. A DSC measurement, for example, may indicate the presence of more than one phase (and, with calibration, quantify the amount of each component), but the technique cannot give any information regarding the size or distribution of phases. In order to obtain spatially resolved information about a sample, the investigator must resort to microscopy. Without employing staining or etching techniques, it may be difficult to determine differences in composition across a specimen. Infrared and Raman microspectrometry may be used to investigate chemical composition on a local scale, but often the resolution (spatially and structurally) is poor. Imaging secondary ion mass spectrometry (SIMS) or X-ray photoelectron spectrometry (XPS) can provide similar information



Figure 1 The μ TA 2990 Micro-Thermal Analyzer, with sample ready for loading.

but also suffer the same drawbacks in addition to requiring the sample to be in a high vacuum.

An earlier article⁶ described the initial results of academic research in bringing together the capabilities of thermal methods with microscopy. Part of this work has been commercialized in the μ TATM 2990 Micro-Thermal Analyzer (**TA Instruments, Inc.**). The μ TA 2990 (*Figure 1*) is the result of continuing cooperative technical developments with Dr. Mike Reading of Loughborough University (Loughborough, U.K.); Dr. Hubert Pollock and Dr. Azzedine Hammiche of Lancaster University (Lancaster, U.K.); **TopoMetrix Corp.** (Santa Clara, CA); and **Linkam Scientific Instruments, Ltd.** (Tadworth, Surrey, U.K.). The instrument combines the visualization power of atomic force microscopy (AFM) with the characterization ability of thermal methods by replacing the standard probe in an AFM with a thermal probe (*Figure 2*). The system is capable of providing four images or views of the surface of a sample: topography, thermal conductivity, modulated temperature (amplitude), and modulated tem-

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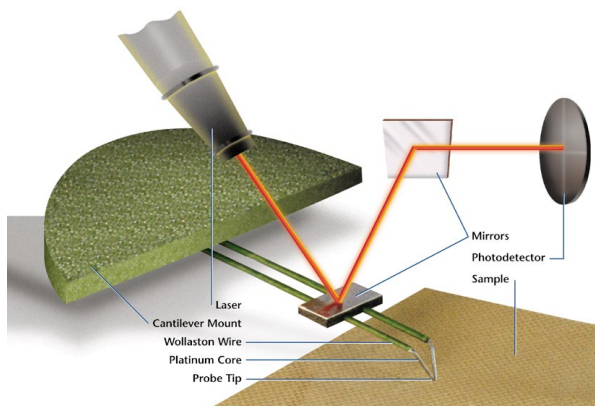


Figure 2 Thermal probe schematic.

perature (phase). After these images have been acquired, any specific location on the sample can be analyzed by Local Thermal Analysis (LTA) using two new thermal techniques: Micro-Thermomechanical Analysis (μ TMATM) and Micro-Modulated Differential Thermal Analysis (μ MDTATM) (both by **TA Instruments**). The results from these “micro” techniques are comparable with their “macro” counterparts.

Presented here are several new applications of Micro-Thermal Analysis relating to the visualization and characterization of polymeric systems.

Phase miscibility

The characterization of the morphology of polymer blends is of particular interest to the materials scientist. When two polymers are blended, they can exist either as discrete phases, or mix to form a single phase with properties that are a function of the individual phases and composition of the blend.

Figure 3 shows the thermal conductivity images of two blends of polyethylmethacrylate (PMMA) and polycarbonate (PC). One sample shows a two-phase domain structure, while the other clearly shows phase miscibility. Subsequent μ -TMA experiments (Figure 4) give the softening points for the two-phase material and the single-phase material. As one would expect, the softening point for the phase miscible material lies between the softening points of the individual phases in the phase immiscible sample.

Multilayer films

Figure 5 shows the topography and thermal conductivity images for a multilayer packaging film typically used in the packaging of convenience foods. The construction of the film comprises a central gas and flavor barrier layer surrounded by HDPE (high density polyethylene) and LDPE (low density polyethylene) outer surfaces designed to accept printing ink. The ther-

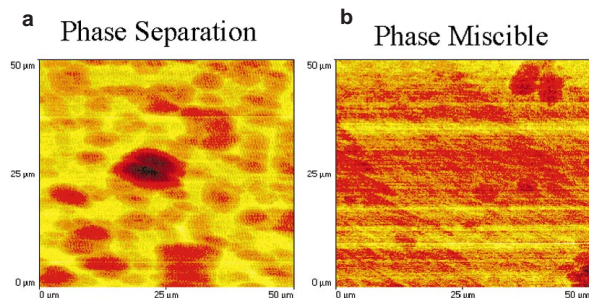


Figure 3 Thermal conductivity images of two samples of polyethylmethacrylate/polycarbonate blends.

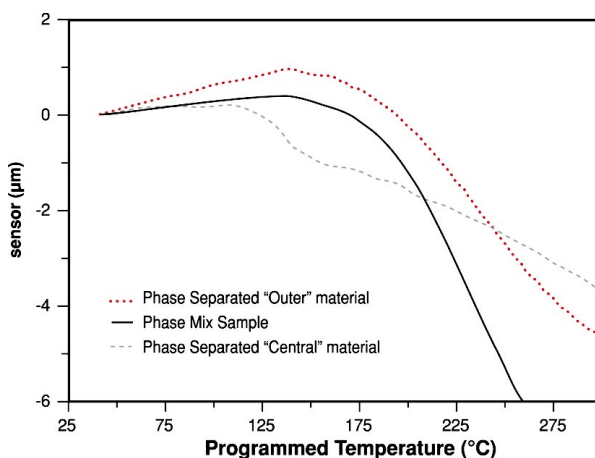


Figure 4 μ TMA data for two polymethylmethacrylate/polycarbonate blends.

mal conductivity image shows that there is a central layer of polymer flanked by two outer layers, with a possible intermediate tie layer. Figure 6 shows the softening temperatures obtained from each layer at a heating rate of 500 °C/min. Such fast heating rates are possible because of the small sample size and low thermal mass of the thermal probe. The softening temperatures are indicative of each polymer present in the film. Curves 1 and 5 are typical of HDPE; curves 3 and 6 correspond to the EVOH (ethylene vinyl alcohol) layer; curve 2 (the tie layer) has a lower softening point than HDPE and is probably MDPE (medium density polyethylene); curve 4 is obtained from the EVOH/tie layer interface; and the measured response is a combination of each material’s individual response.

Gel formation

Figure 7 shows four μ TMA and μ MDTA scans taken from across a section of a polyethylene film containing an imperfection. The middle two runs show the response of the imperfection and the outer two runs show the data for the bulk material. The imperfection itself is only 300 μ m across. It can be seen that the imperfection

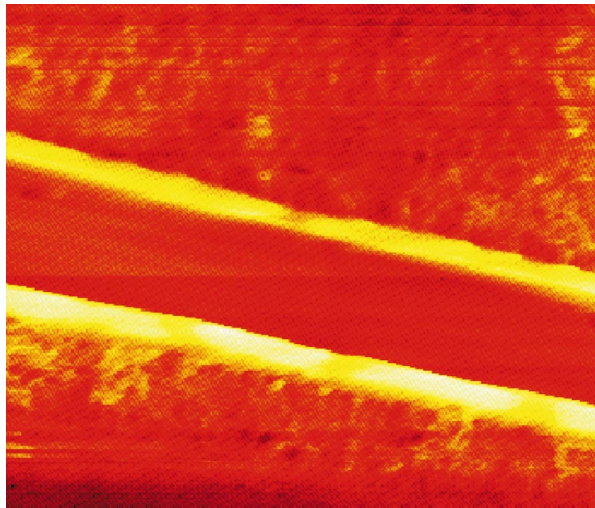


Figure 5 Thermal conductivity image of a multilayer packaging material.

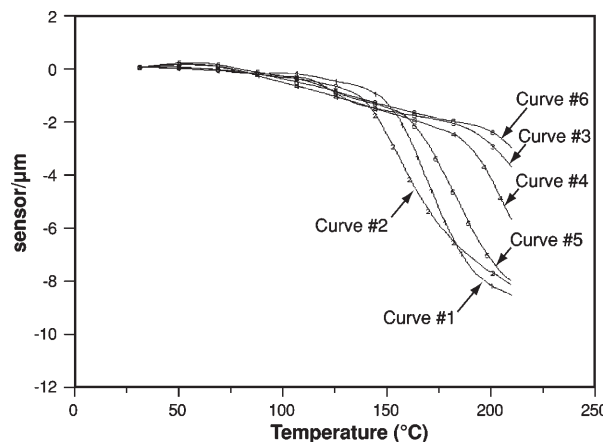


Figure 6 μ TMA results from each layer of a multilayer packaging material.

has a lower crystallinity and higher melting point. As the indentation of the probe is lower (above the melting point), it can be seen that the imperfection has a higher molecular weight. All of these results can be interpreted to indicate that the imperfection is due to unwanted cross-linking of the polyethylene film during production.

Printing and coatings

Figure 8 shows the topography image of an overhead transparency made by photocopying a page from a book. The image area is $100 \times 100 \mu\text{m}$ and is from the dot of the letter “i” that appears on the page. The top right-hand side of the image is that of the plastic film, whereas the remainder of the image is largely toner from the copying process. Figures 9a and b show the

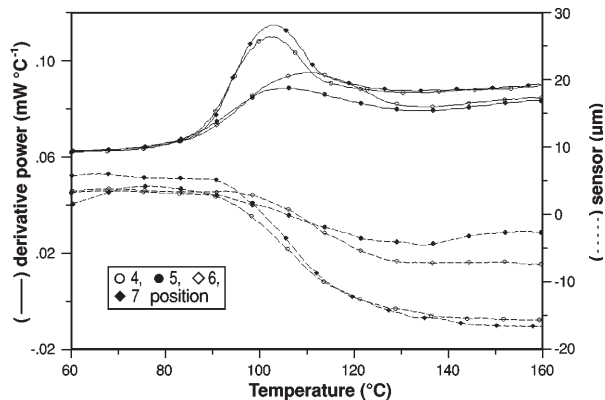


Figure 7 μ TMA and μ MDTA results obtained at several locations, across the surface of an imperfection within a polyethylene film.

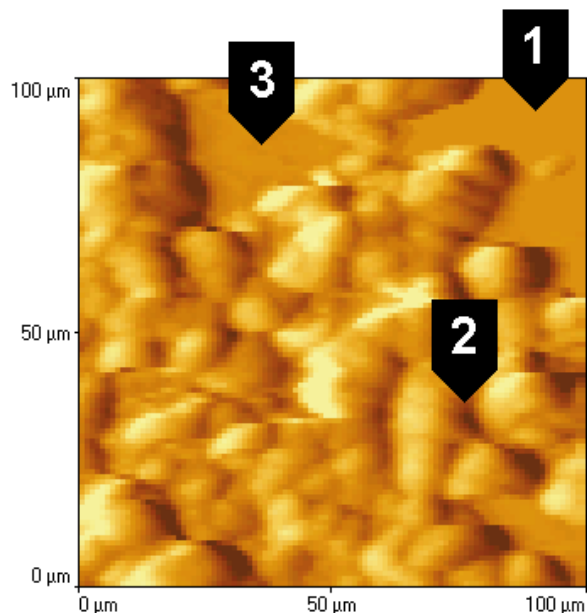


Figure 8 Topography image of an overhead transparency, showing toner particles on a polymer substrate.

μ TMA and μ MDTA data from the overhead transparency. Three local thermal analysis experiments were made, two of the plastic film, and a third on an area of toner. The positions of the scans are labeled in Figure 8. Locations 1 and 3 for the substrate show an expansion in the μ TMA signal to around 225°C , followed by softening and melting. This is confirmed by the peak in the μ MDTA signal with an onset of around 240°C . For location 2, the toner, there is a softening of the toner commencing at 80°C , followed at higher temperatures by the softening of the polymer substrate. It is interesting to observe a feature in the μ MDTA trace at around 150°C , which corresponds to the fuser temperature of the copier. From these data, it can be concluded

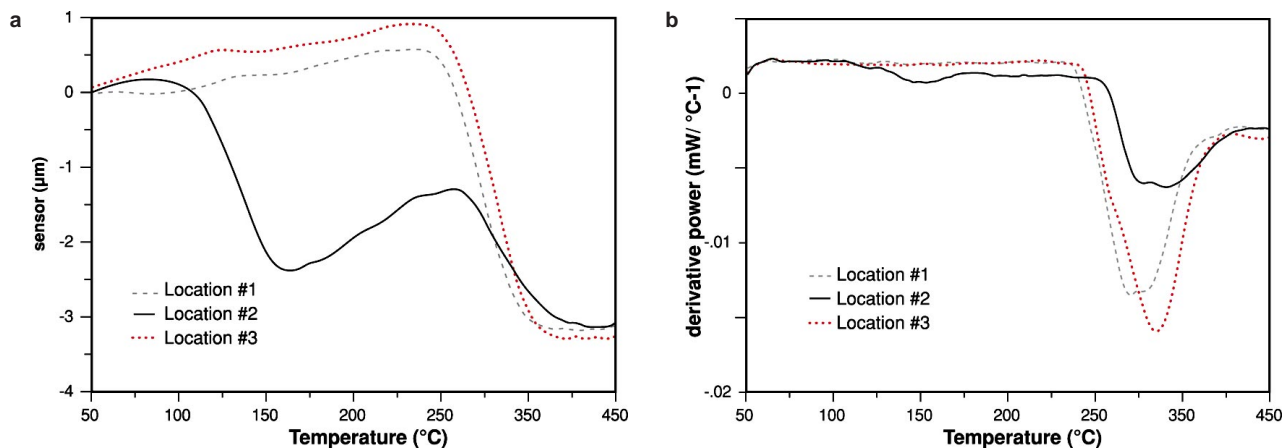


Figure 9 μ TMA and μ MDTA results, taken at three locations upon an overhead transparency.

that the base film is PET (rather than the cellulose acetate alternative) and the toner is likely to be a poly(styrene-co-butyl methacrylate) base.

Summary

Microthermal analysis provides the polymer scientist with a unique blend of thermal analysis and microscopy in a single instrument. New applications are already being developed to solve old problems with this technique.

References

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