Introduction

Thermal methods such as differential scanning calorimetry (DSC) and modulated temperature DSC (MDSC), 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. However, a serious limitation of conventional thermal methods is that they give only a sample-averaged response and cannot provide information on specific features on or within the sample. A DSC measurement, for example, may indicate the presence of more than one phase, but...
the technique cannot generally give any information regarding the size or distribution of phases. This particularly impacts scientists in the field of polymer blends (where the blend morphologies are crucial to determining their material properties), coatings (where imperfections such as gel formations can seriously impact performance), and composites.

To address this problem, Reading et al. developed the Localized Thermal Analysis (LTA) technique [1] using a thermal probe to perform the heating very locally on the sample to obtain the local thermal response instead of heating the whole sample to obtain a sample-averaged response. This technique was restricted to micron scale resolution until a breakthrough in the fabrication of nanoscale thermal probes optimized for atomic force microscopy (AFM) by Prof. William King of the University of Illinois - Urbana [2]. These probes have enabled local thermal analysis to attain sub-100-nm resolution in conjunction with an AFM and led to the nano-TA technique from Anasys Instruments.

nano-TA is a LTA technique which combines the high spatial resolution imaging capabilities of atomic force microscopy with the ability to obtain understanding of the thermal behaviour of materials with a spatial resolution of sub-100nm. The conventional AFM tip is replaced by a special nano-TA probe that has an embedded miniature heater and is controlled by the specially designed nano-TA hardware and software. The AFM enables a surface to be visualised at nanoscale resolution with its routine imaging modes, which allows the user to select the spatial locations at which to investigate the thermal properties of the surface. The user then obtains this information by applying heat locally via the probe tip and measuring the thermomechanical response. There have been several examples in the literature of the application of sub-100nm LTA in the field of Polymers and Pharmaceuticals [3-6].

However a question that frequently arises is the correlation of the results from nano-TA to Bulk Thermal Analysis. One potential concern is that the probe size makes the contact pressure using nano-TA around 10 MPa (two orders of magnitude higher than the contact pressure using bulk TMA). This increase in contact pressure and the nanoscale contact radius give rise to questions regarding the concept of traceability to the bulk measurements. This does not necessarily mean that local and bulk measurements will or should agree, since the thermal effects at the nanoscale could have their own dynamics. In order to understand these aspects, recent work has been performed to understand the correlation between bulk techniques and the nano-TA measurements and this Application note summarizes the results. (This work was first published as a featured article in the Nov. 2007 issue of American Laboratory and this Application Note has been excerpted from that article with kind permission of the publishers)

Experimental setup

Experiments were performed using a Veeco Multimode AFM equipped with an Anasys Instruments (Al) nano-TA module and Al nanoscale thermal probes. All images were recorded using tapping mode AFM. The nano-TA data presented are of the probe cantilever deflection (while in contact with the sample surface) plotted against probe tip temperature. Events such as melting or glass transitions that result in the softening of the material beneath the tip, produce a downward deflection of the cantilever. In order to confirm the tested points of interest, images are routinely recorded after performing the temperature ramp.

Results and discussion

Calibration

Metal calibration standards which are standard in traditional bulk Thermal Analysis cannot be used in nano-TA since heat diffusion due to high thermal conductivity means that local probes cannot heat bulk metals fast enough to cause melting. Organic crystals are difficult to prepare in smooth enough form to be readily useful, and some materials may have safety issues. Hence, semicrystalline polymer melting standards are used for calibration because they can be prepared as pressed or extruded films. Three materials covering the range from 50°C to 250°C are poly(caprolactone) (PCL), high-density polyethylene (HDPE), and poly(ethylene terephthalate) (PET). These are provided as thin film samples by Anasys Instruments Corp., 121 Gray Ave, Suite 100, Santa Barbara, California 93101 www.anasysinstruments.com Instruments, and the onset melt temperature has been measured using a DSC as the reference temperature for the nano-TA calibration.

Figure 1 depicts heating rate-dependent deflection curves for these semicrystalline materials (left) and additional amorphous or thermoset systems (right). The curves in Figure 3 show deflection of the cantilever due to expansion of the surface underneath the probe until the material yields under the contact pressure through the transition. Each curve in the plot is an average of 3–5 measurements. Heating rates span two orders of magnitude, from 0.1/sec (bridging typical TMA and DSC rates) to 10 °C/sec. The small thermal volume of the probe makes very high heating rates (of up to 10,000 °C/sec) accessible. In general, the crystalline materials have onsets that are relatively invariant to heating rate, while the amorphous materials show greater rate dependence as the onsets move to higher temperatures at higher rates. This is as expected for a softening or glass transition of amorphous material.

Comparison of nanoscale LTA to DSC and TMA measurements

In Figure 2a, the plots provide a least-squares fit of the LTA onset measurements obtained at the three heating rates to the DSC onset values obtained at 10 Ki/min. All the fits are good, with correlation coefficients exceeding 0.99. The LTA measurements tend to have positive offsets at all rates relative to the DSC onset measurement. Using a slope and minimum offset criteria, the best correlation of LTA to DSC is for the onset obtained at the lowest heating rate, 0.1 °C/sec.

In a similar fashion, the LTA results are compared with the TMA onset measurements in Figure 2b. This plot provides a least-squares fit of the LTA onset measurements obtained at the three rates to the TMA onset values obtained at 5 °C/min. Again, the fits are very good, with correlation coefficients exceeding 0.96. The LTA measurements tend to have slightly negative offsets at all rates relative to the TMA onset...
measurement obtained at 5 ºC/min. Using slope and minimum offset criteria, the best correlation of LTA to TMA is for the onset obtained at a heating rate of 1 ºC/sec. As can be seen from the data, the correlation is good between bulk techniques and the LTA technique. The offsets of the LTA data relative to the bulk methods suggest that there is something perhaps more subtle about the LTA response. In the case of the DSC, LTA seems to respond at a higher temperature than DSC. This may be due to the nature of heat flow in the material as being sourced from the tip versus the ambient. It is clear that lower LTA heating rates are closer to the bulk DSC onset temperatures. In the case of the TMA, LTA seems to respond at a slightly lower temperature than TMA. This may be sourced in differences in contact pressure and/or enhanced deflection sensitivity. Both of these offsets require further investigation. It is clear that the absolute values are different but not out of the range of the difference between two traditional bulk techniques DSC and TMA.

Conclusions
The authors compared data taken on a number of homogenous polymeric samples using a variety of experimental conditions with both traditional thermal analysis techniques and localized nano thermal analysis. This study has demonstrated a very high degree of correlation between nanoscale and bulk thermal analysis. For DSC measurements, correlation was >99.5% for the most optimum conditions and for TMA measurements, the correlation was >98%. The variation between nano-TA and bulk methods is small enough to be comparable to the variation between the standard bulk thermal techniques of DSC and TMA. This verifies the capability of the nano thermal technique to obtain accurate, relevant thermal analysis information while also allowing analysis of localized areas on the sample or very small quantities of material. This greatly extends the utility of thermal analysis to polymer blends, composites and surface properties of materials.

References

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