ANALYTICAL SERIES

Transition Temperature Microscopy:

Probing Thermal Properties of Coatings and Multilayer Films at the Micro- and Nanoscale

by **Louis T. Germinario,** LG Analytical
Clifford K. Schoff, Schoff Associates
Kevin Kjoller, Craig Prater, and **Khoren Sahagian**
Anasys Instruments Corp.

Transition temperature microscopy (TTM) is a novel local thermal analysis technique that maps spatial variations in thermal properties on length scales from millimeters to nanometers. Traditional bulk thermal analysis provides a sample-averaged result and cannot generally supply sufficient information about complex structures or heterogeneities within films or coatings. There currently exists a nanoscale thermal analysis (nano-TA) technique in which a nanoscale thermal probe heats a localized region on the sample surface to measure its thermal properties, including thermal transition temperatures like crystalline melting points and glass transitions. TTM enables these nano-TA measurements to be carried out rapidly at a succession of points, thus creating automated high-resolution spatial maps of the thermal properties of a sample. In this article we also demonstrate how TTM can be used to characterize chemical and structural heterogeneities and thereby generate vital information in applications ranging from coating defects, to in-situ property measurement of individual layers in multilayered films, to the detection of gradients and interfaces.

INTRODUCTION

Thermal methods such as differential scanning calorimetry (DSC), modulated temperature DSC (MDSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) are well-established techniques for characterizing polymers, thin films, and coatings. However, a serious limitation of these conventional thermal methods is that they can only measure a sample-averaged response and cannot offer specific information on localized defects, structural non-uniformities, or chemical heterogeneities, nor can they give thermal property data of coatings or film surfaces or interfaces that are less than a few microns thick. This analytical limitation often impacts innovation in the coatings industry where new metrologies are needed for quantifying the impact of micro- and nanostructured additives on performance and explore solvent effects in high-solids, low-VOC coatings. Increased pressure to develop "green" or "sustainable" products provides increased impetus and urgency to develop tools to measure and quantify thermomechanical properties of films and coatings at increasingly smaller length-scales.

HOW TRANSITION TEMPERATURE MICROSCOPY WORKS

TTM extends into an imaging or microscopy mode, the current point-measurement technique of nanoscale thermal analysis (nano-TA), which makes use of a thermal probe to locally heat the surface of a sample while simultaneously monitoring the softening of the sample surface under the heated probe.[1-6] The nano-TA technique is similar to thermomechanical analysis with the important difference

that instead of heating the entire sample, as is done in a TMA experiment, nano-TA probes the thermal response of the material in contact with the probe and therefore can locally determine the transition temperature of the sample on the micro- or nanoscale. TTM plots an array of nano-TA measurements to obtain an image or map of the transition temperatures across the region of interest.

Figure 1 is an SEM image of the thermal probe used in TTM. Similar to probes employed for atomic force microscopy (AFM), the thermal probe is made using microfabrication techniques, allowing very small geometries and repeatable performance.[7] The apex of the probe which contacts the sample surface has a radius that is less than 30 nm and the probe incorporates an embedded miniature heater to perform a variety of transition temperature measurements. Because of its small size, the temperature of the probe can be changed quickly, allowing heating rates from 5°C/min to 10,000°C/sec. This enables the measurement time per point to be faster than one second, thus significantly improving throughput.

The basic principle of TTM is outlined in *Figure* 2. At each point of interest on the sample, the probe is brought into contact with the sample surface and heated, while simultaneously monitoring the thermal expansion of the sample under the probe. At a transition temperature, the surface softens, allowing the probe to penetrate slightly into the sample. The array of nano-TA measurements is automatically analyzed to determine the transition temperature at each point or pixel within the scanned region. Then a false color map is created where the pixels are shaded according to the measured transition temperatures. The resulting spatial map allows visualization of thermal gradients and can detect the presence of inhomogeneities in a wide range of samples. The TTM image can also be analyzed by plotting the transition temperature versus lateral position on the sample as well as selecting points from the image to generate a histogram of transition temperatures.

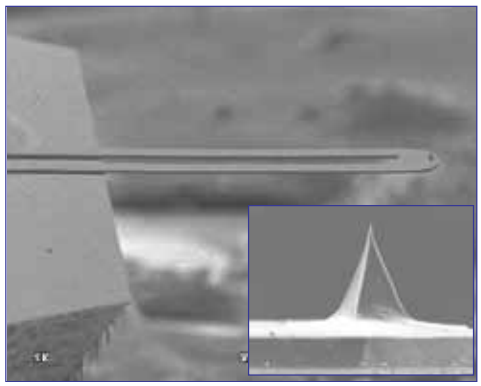

Figure 1—An SEM image of the microfabricated nanoscale thermal probe used for TTM measurements. The inset is a zoom of the tip which makes contact with the sample surface. These tips have a radius of <30 nm allowing for a lateral resolution of each point measurement of ~100 nm.

TTM APPLIED TO COATINGS AND MULTILAYER FILMS

Organic polymeric materials are widely used as coatings in a variety of markets and for numerous applications, primarily due to the relative ease with which the raw materials can be processed, versatility in form, and their tunable properties, which provide improved appearance and performance. These applications are becoming more sophisticated, and due to the multi-variate nature of coatings, their decreased dimensions often produce

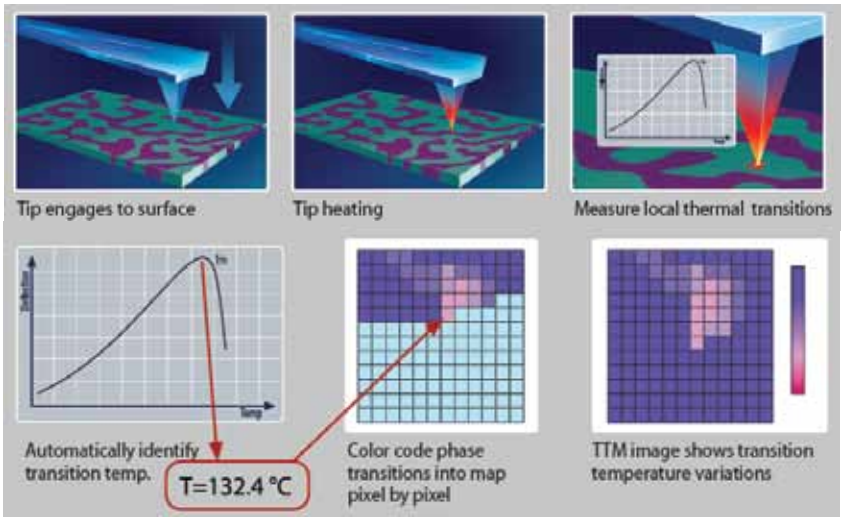

Figure 2—TTM maps local variations in melting temperatures and glass transition temperatures. A heated probe locally measures the temperature at which softening of the material occurs. Arrays of measurements can be made to assemble a spatially resolved image of the sample.

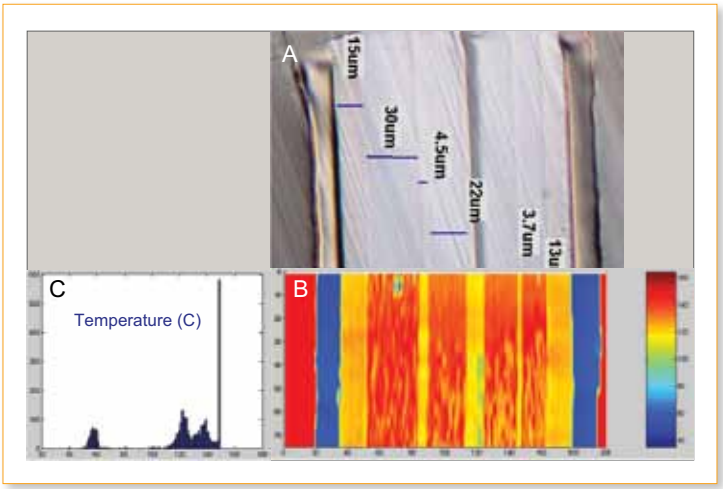

Figure 3—(A) An optical image of a cross-sectioned multilayer LCD film showing the various layers. (B) An 80 x 200 micron TTM image of the cross section shown in A, which is positioned so that the features are aligned with the corresponding optical image in A. (C) A histogram of the transition temperatures in the TTM image, allowing measurement of the average and distribution of transition temperatures in the various layers.

layers of polymers having different functions. In addition, the viscoelastic nature of most polymeric materials leads to a marked time and temperature dependence on performance.[8]

In this article, we discuss examples where TTM has been used as a tool for problem solving in coatings, multilayer films, and composites.

In-situ Analysis of Multilayer Films

The different layers in multilayered films are often engineered and designed to contribute to the final performance of the ensemble. However, no direct methods are currently available to study the thermal properties of the individual layers or interfaces once they are embedded in the composite stack. TTM can solve this problem by providing a convenient method for spatially resolving the thermal response of individual layers and their interfaces by generating transition temperature maps of areas scanned by the thermal probe. The intensity of each pixel within the TTM image can be compared to the optical or AFM image and provides a quantitative measure of the thermal characteristic of the individual pixel within the image. The spatial resolution of TTM is primarily limited by the diameter of the thermal probe and thermal response of the material in contact with the probe. Provided below are two examples of TTM analysis of individual layers within multilayered films and coatings

Flat-Panel Displays and Other Multilayer Materials

Polymers are an integral part of flat-panel displays and most often applied as thin films in order to provide their functionality. The critical property of flat-panel displays is clearly the optical dispersion characteristics of the materials, which combine to control resolution, brightness, and contrast. Since light scattering is impacted by the density distribution within films, density variations associated with chemical and structural heterogeneities will play a dominant role in the measured refractive index and performance. Moreover, the temperature dependence of density makes thermal property measurement more significant for both design of electronic displays and for failure analysis.

A polymer multilayer from a liquid crystalline display (LCD) was microtomed to gain access to the different layers within the LCD stack and the cut surface was then imaged using TTM. *Figure* 3A shows an optical image that reveals the multiple layer construction of the LCD stack, ranging in size from a few microns to many tens of microns. Below this image is *Figure* 3B, which is the corresponding color-coded TTM image that is scaled to track with the optical image. This figure clearly illustrates the variations in thermal properties across the different layers that are not evident in optical micrographs. Similar analyses could be performed on automotive or other multilayered coatings by sectioning with a microtome and using TTM to characterize the different layers and interfaces within the coating. Estimates could be made of the degree of cure of the different layers from measured softening point values. In addition, TTM can be combined with spectroscopic methods such as IR microscopy or confocal Raman to better understand and study diffusion and molecular migration effects on cure rates and performance.[9]

TTM can also detect the presence of thermal gradients and thermal transitions within layers. In addition, TTM images can provide a quantitative measure of the spatial distribution of thermal inhomogeneities, in the form of thermal property maps. Such features are usually not visible or detectable in optical images. Transition temperatures can also be displayed in the form of a histogram that provides a plot of the measured distribution of thermal (and hence, mechanical) properties over the sample. This superposition of thermal analysis and microscopy makes the TTM technique unique in its ability to generate high-resolution thermal property maps.

In-situ, Time-Resolved Cure-Rate Measurements in Automotive Refinish Coatings

Automotive refinish clearcoats are crosslinked coatings that are usually cured through a reaction between two or more components. The primary function of clearcoats is to protect themselves and the coatings under them against environmental influences and provide scratch, mar, and chip re-

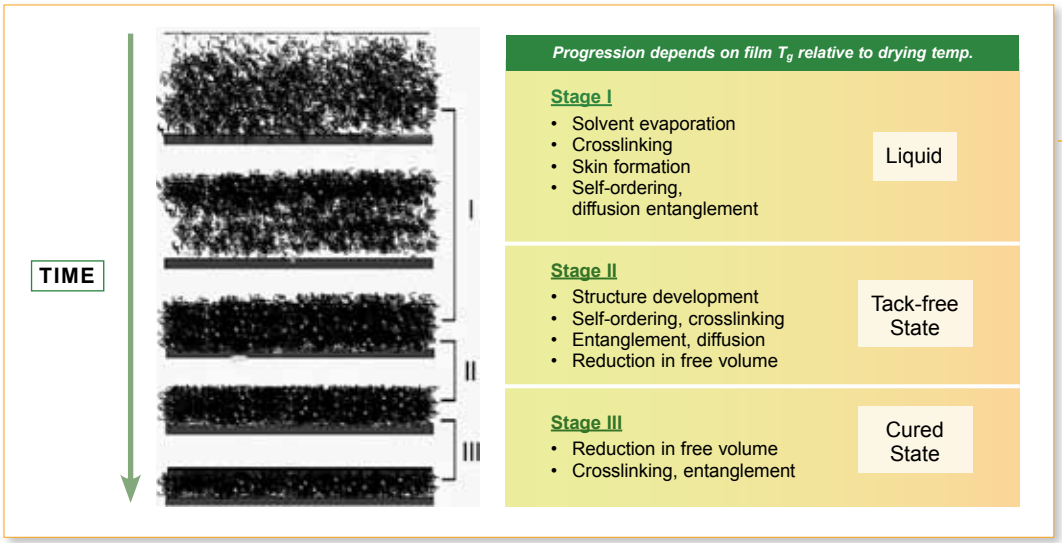

Figure 4—Film formation dynamics.

sistance, as well as erosion and solvent resistance, while still maintaining a high gloss and excellent appearance.[10] Due to the fact that the clearcoat is the first line of defense against environmental influences, understanding surface, near-surface chemical, and mechanical property development as a function of composition, cure time, and environmental exposure is fundamental to improving their performance. Furthermore, the demand for lower VOC systems in the automotive refinish industry means that new resins, solvents, and additives are being introduced. This, coupled with demands for attaining fast cure at ambient temperature to reduce the investment in drying equipment and the time of repair, points to the need for a thorough understanding of the dynamics of film formation.

Figure 4 is a schematic of the different stages in the film formation process and is provided to show its complexity and time dependence.

The coating initially goes through a liquid phase as it is deposited, to tack free, and then to the final fully cured state. This progression depends primarily on the solvent evaporation rates, speed of chemical reactions, rates of diffusion, and the T_g of the independent systems which comprise the film. *Figure* 5 demonstrates how nano-TA can be used to follow the cure kinetics taking place at the coating surface. *Figure* 5A displays the temperature ramps taken on an acrylic clearcoat at three different times after the coating was deposited. The softening temperature can be easily measured from these curves and, if plotted versus cure times (*Figure* 5B), provides critical information on crosslinking rates and reaction kinetics. The ability to measure chemical kinetics opens new opportunities to explore the effects of composition, additives, and processing conditions on the speed of film drying, and mechanical property development at surfaces and interfaces. The ability to measure

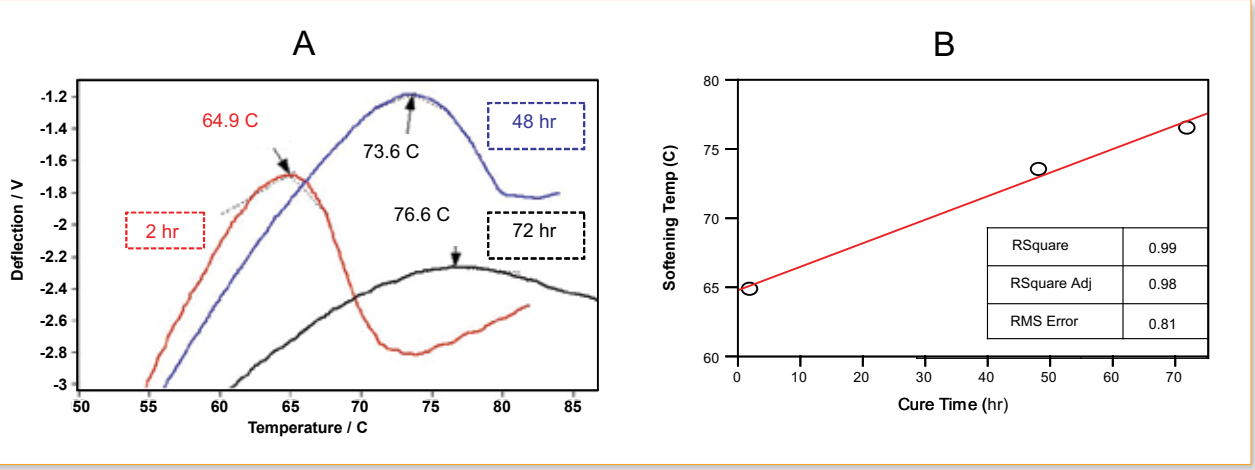

Figure 5—Nano-TA measurements of a clearcoat measured at three different times after deposition (A) and the plot of softening temperature vs cure time (B).

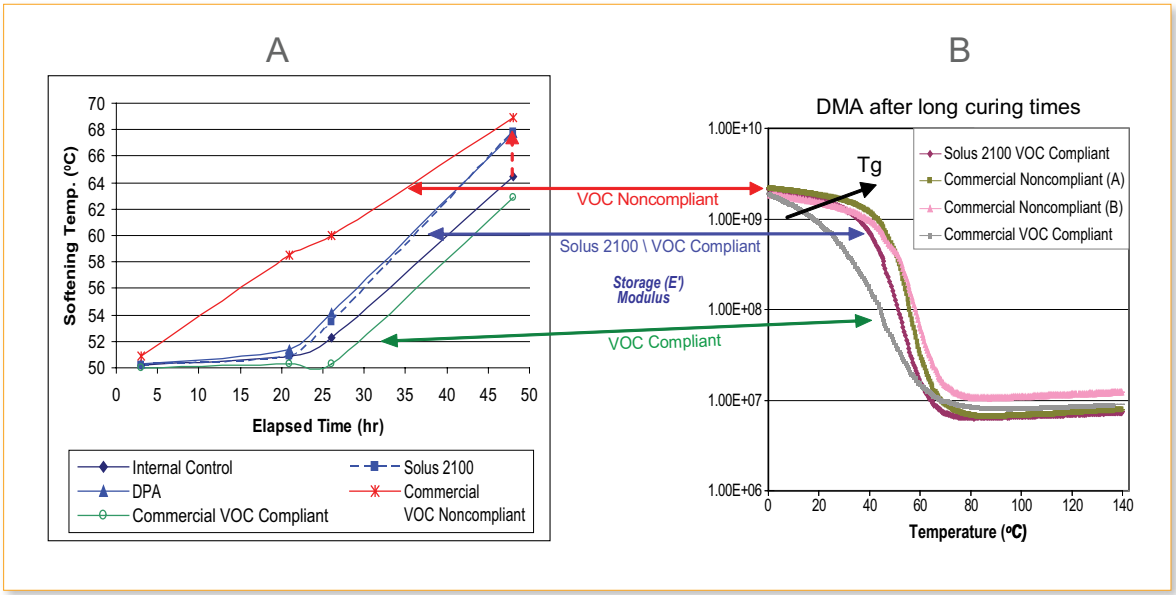

Figure 6—(A) Time resolved nano-TA measurements allow the study of real-time dynamics of a coating's cure rate. (B) Comparison with DMA of comparable coatings that were removed from substrates before testing. DMA and nano-TA results showed excellent correlation for the temperature dependent properties of the VOC-compliant and VOC non-compliant films.

rates of chemical processes can also yield information about the reaction mechanism, transition states, as well as provide mathematical models that can be used to quantify and describe the time scales of the chemical reactions.[11]

As can be seen in *Figure* 5A, the transition temperature (which is a direct function of the crosslink density) shows a linear correlation with cure time. Since the molecular structure and thermodynamics near the air-surface interface usually differ from the bulk, this can lead to significant deviations in glass transition temperatures and modulus as measured by methods such as DSC or TMA.[12,13]

Figure 6 is another example of how nano-TA can be used to measure and quantify the effect of additives on mechanical property development of coatings, as a function of drying time and composition. This figure shows an increase in softening temperature (or crosslink density) over time for the five different coating products tested by nano-TA. These consist of a commercial VOC noncompliant formulation; a commercial VOC-compliant and a VOC-compliant internal control with two different additives, Eastman Solus™ 2100 (a performance additive for high solids 2K coatings); and a developmental performance additive (DPA).

Nano-TA of the VOC noncompliant coating, which is a low-solids, high-solvent formulation, shows a linear increase in softening temperature with cure time, while all of the VOC- compliant formulations (high-solids and low-solvent content) display ~24-hr lag or transition period during which time there is no measurable increase in softening temperature. After the 24-hr lag time, the rate of increase of softening temperature, or film cure (drying) rate, for the VOC-compliant coatings increases at a faster rate than the commercial VOC noncompliant formulations (*Table* 1). Because nano-TA can be applied on in-situ coatings, the softening temperatures can be monitored over time and thus provide cure-rate information from surfaces that are difficult to measure by other techniques.

Comparison of nano-TA with DMA of films 60–70 µm thick, having similar compositions, but peeled from substrates before testing, provides a measure of the temperature dependence of the storage modulus of the fully cured films, as a function of testing temperature. The DMA results (*Figure* 6B) compare favorably with the nano-TA results (*Figure* 6A) and show the VOC-compliant films as having the lowest softening temperatures, while the VOC noncompliant coatings (low-solids, high-solvent content) display the highest storage modulus at ambient temperatures and highest softening temperatures, above T_g. These data offer unambiguous evidence that addition of Solus 2100 to the

Table 1—Nano-TA measure of drying rates or rate of increase of softening temperature.

Formulation	Drying Rate (°C/hr) 24-48 hr
Internal control	0.519
Solus 2100	0.607
DPA	0.633
VOC noncompliant	0.391
VOC compliant	0.499

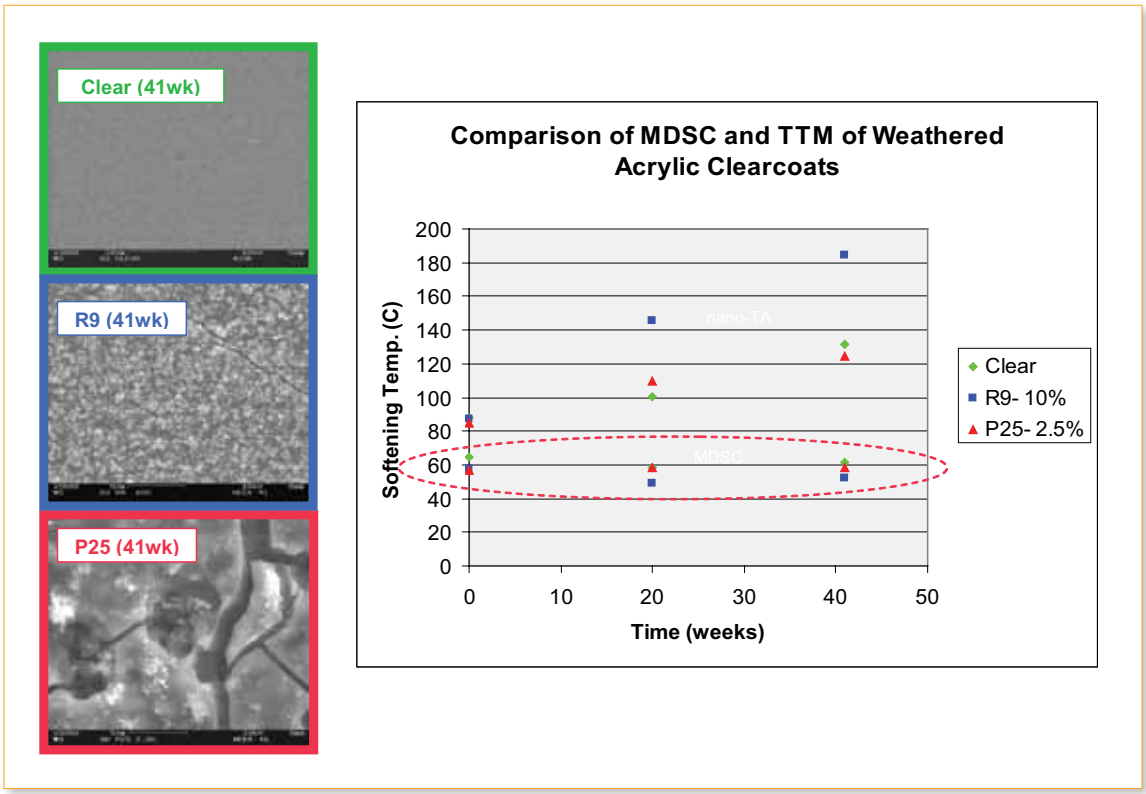

Figure 7—Comparison of softening temperatures measured for outdoor exposed (0, 20, and 41 weeks) clear and TiO_2 filled (P25 and R9) acrylic urethane coatings using nano-TA and MDSC. Surface morphology was also analyzed by SEM.

VOC-compliant, internal control formulation gives a measurable improvement in mechanical properties as measured by nano-TA for surface mechanical property development and DMA for mechanical property development of the fully cured films, and bridges the gap in performance between the VOC compliant and VOC noncompliant coating formulations. DMA results further support the trend for increased crosslinking by the increased T_g and increasing modulus above T_g.[14]

The major advantages of nano-TA over DMA are its surface sensitivity, ability to measure coatings on their substrates, and provide time-resolved thermomechanical property data for films that are not self-supporting. In this set of experiments, nano-TA confirmed the benefits of Solus 2100 addition to VOC compliant formulations in accelerating both drying rates and mechanical property development at the air/coating interface.

Surface Property Measurements

Photodegradation and weathering effects on coatings is another area of potential application of the nano-TA method. Acrylic urethane coatings were exposed 20 and 41 weeks to UV-A and UV-B.[15] Samples were scraped from surfaces and analyzed by modulated DSC (MDSC), while nano-TA analysis was performed, in-situ, on the weathered surfaces. To make a valid comparison of nano-TA with MDSC, the glass transition onset temperature was calculated from the MDSC curve and used to compare with the nano-TA softening temperature. Although a more appropriate comparison with nano-TA would have been conventional TMA, this method was not available.

Nano-TA, due to its surface sensitivity, was able to provide a measure of the weathering phenomenon, while the DSC method could not differentiate the surface from the matrix (*Figure* 7). These data further reinforce the need for surface sensitivity and value of combining imaging with thermal analysis.

Shown in *Figure* 7 are SEM images of weathered films used for comparison of nano-TA and MDSC measurements. Three different types of photo-degraded acrylic polyurethane coatings were analyzed after outdoor exposure for up to 41 weeks. Since the nano-TA technique is a surface property measurement, the effect of weathering is easily detected as an increase in softening temperature as a function of outdoor exposure time. MDSC, being a bulk measurement, is not capable of differentiating surface effects from bulk and cannot detect the surface chemical and structural degradation suffered by the coatings as shown by the scanning electron micrographs.

Biaxially Oriented Polypropylene Films

Biaxially oriented polypropylene (BOPP) is extensively used in the packaging industry with constructions that can be either heat sealable or

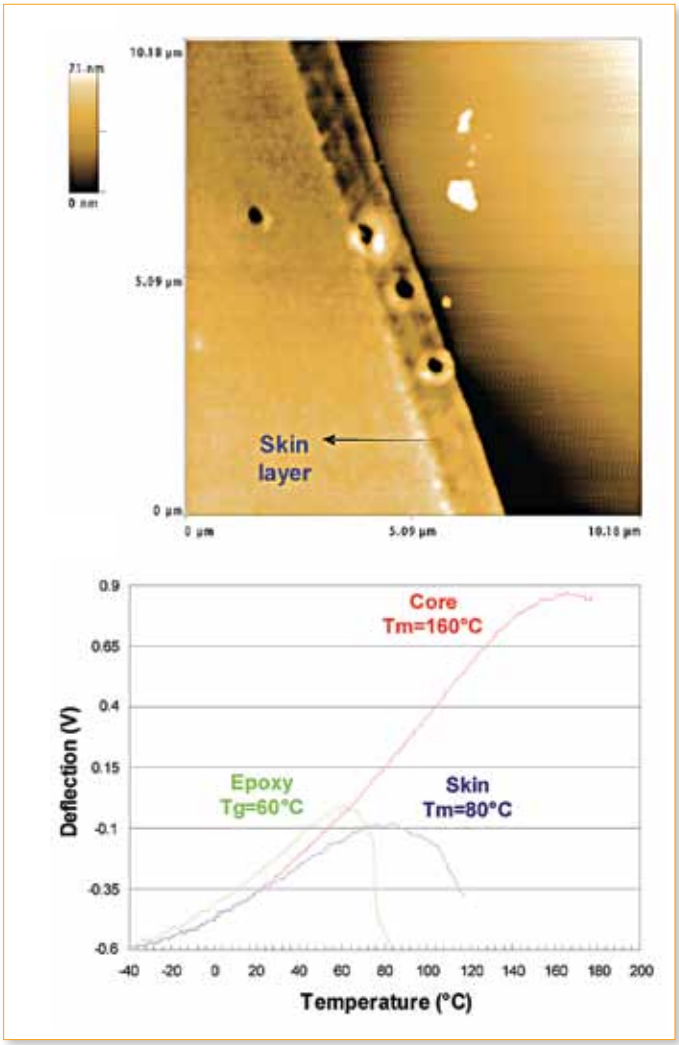

Figure 8—An AFM image (left) and nano-TA measurements (right) of a microtomed multilayer BOPP film.

nonheat sealable. These films can be composed of either uni- or multilayered structures and have typical total thickness of only 15–25 µm. The most common multilayer films consist of a three-layer structure: one thick core layer that is composed of a polypropylene homopolymer, sandwiched between two thin (usually ~1 µm thick) skin layers. Each layer has its own contribution to the film's property. In the standard three-layer structure, the core layer mainly provides the film's rigidity, whereas the skin provides sealing and/or surface properties.[16,17] *Figure* 8 is an example of a cross section of an epoxy embedded film and demonstrates an in-situ localized nano-TA measurement of the transition temperature of the skin layer, core layer, and embedding epoxy used to support the multilayer BOPP film.[18]

Analysis of Processing Defects in Fiber-Reinforced Composites

Transition temperature microscopy provides a new analytical window for testing heterogeneous, fiber-reinforced structures, since interfacial bonding is critical to performance. For example, a polyester fiber-reinforced composite was prepared for cross-sectional analysis in order to measure the fiber's internal morphology and diameters. The fiber sample was embedded in epoxy, cured, and sectioned by microtomy. Inspection of cross sections by optical microscopy, shown in *Figure* 9, revealed the presence of a skin layer around the microfibers. This skin layer was later identified as an unintended artifact that was formed during the microfiber embedding process and was the result of the use of "aged" epoxy resin and catalyst that had hydrolyzed during storage. To explore the chemical and thermal properties of the micron-sized skin layer surrounding the fibers, a TTM image was generated. The TTM map displayed in *Figure* 9 identified the skin layer as having a significantly higher transition temperature than either matrix or fiber. A plot of transition temperatures displayed in the TTM image as a histogram, identifying the presence of three distinct transition temperatures in the composite structure. The highest thermal transition is centered at ~170°C and is associated with the microfiber skin layer, or ring-like artifact surrounding the microfibers. The TTM data also suggest that the microfibers contain either a structural or compositional gradient with its surface having the lowest softening temperature (~80°C), and a core which softens at ~100°C. The combination of optical, TTM mapping, and a summary of transition temperatures in the form of a histogram provided a most useful approach for unraveling the complexities associated with the fiber-reinforced composite.

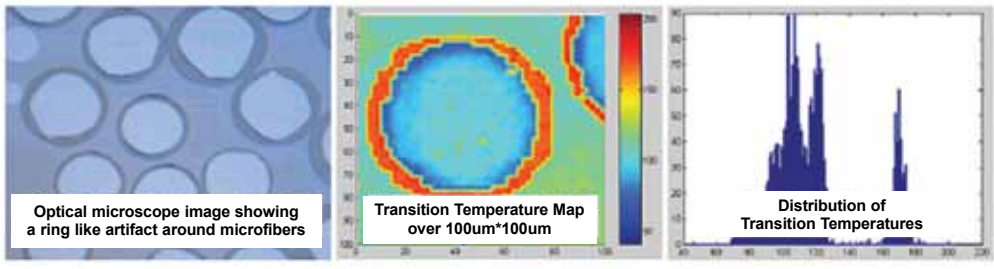

Figure 9—An optical microscope image (left), TTM image (center), and histogram (right) of a fiber reinforced composite sample.

CONCLUSION

Transition temperature microscopy (TTM) is a technique that combines the benefits and advantages of microscopy with nanoscale thermal probe technology. The addition of a probe with an integrated heater to an optical microscope or a conventional AFM adds a new dimension and the valuable capability of spatially resolved thermal analysis. This combination facilitates the characterization of complex, heterogeneous, and multilayered structures by providing high-resolution thermal property mapping. The ability to heat and test very small regions of a sample surface enables the TTM technique to be uniquely valuable in applications ranging from coating defect analysis to in-situ characterization of reinforced composites and time-resolved dynamic measurements for coating design. This technique is made possible by the recent advances in microfabricated thermal probe technology, which permit scientists to heat and measure thermal properties from regions on the nano- and microscale.

ACKNOWLEDGMENTS

The authors express their gratitude to Drs. Aaron Forster and Stephanie Watson (NIST) for supply of weathered, acrylic-polyurethane coatings. We also thank Dr. Deepanjan Bhattacharya and Chip Williams of Eastman Chemical for the supply of acrylic clearcoats.

References

1. Zhou, J.N., Douglas, J.F., Karim, A., Snyder, C.R., Soles, C.L., and Berry, B., "Nanoscale Thermal and Mechanical Probe Determination of Softening Transitions in Thin Polymer Films," *Nanotechnology*, 19, 495703 (2008).
2. Harding, L., King, W.P., Craig, D.Q.M., and Reading, M., "Nanoscale Imaging of Partially Amorphous Materials using Local Thermomechanical Analysis and Heated Tip Pulsed Force Mode AFM," *Pharm. Res.* (2007).
3. Nelson, B.A. and King, W.P., "Thermal Analysis with Nanoscale Spatial Resolution using Heated Probe Tips," *Rev. Scientific Instruments*, 78, 023702, (2007).
4. Nelson, B.A. and King, W.P., "Temperature Calibration of Heated Silicon Atomic Force Microscope Cantilevers," *Sensors and Actuators A*, 140, 51-59 (2007).
5. Germinario, L., "Nano Thermal Analysis of Polymers, Thin Films, and Coatings," *Microscopy and Microanalysis Conf.*, Fort Lauderdale, FL, 2007.
6. King, W.P, Saxena S., Nelson, B.A., Weeks, B.L., and Pitchimani, R., "Nanoscale Thermal Analysis of an Energetic Material," *Nano. Lett.*, 6 2145–9 (2006).
7. King, W.P., et al., "Atomic Force Microscope Cantilevers for Combined Thermomechanical Data Writing and Reading," *Applied Phys. Lett.,* 78, p. 1300-1302 (2001).
8. Struik, L.C.E., *Physical Aging of Amorphous Polymer and Other Materials,* Elsevier, Amsterdam, 1978.
9. Dupuie, J.L., et al., "Clearcoat Analysis in Isolated and Multilayer Paint Systems by Confocal Raman Microscopy," *Polym. Degrad. Stab.,* 57, 339-348 (1997).
10. Schmidt, E.V., *Exterior Durability of Organic Coatings,* FMJ Intern. Publ., Redhill Surrex, 1988.
11. Germinario, L.T. and Shang, P.P., *J. Thermal Analysis Calorimetry,* Vol. 93, 1, p. 207–211 (2008).
12. Herminghaus, S., Jacobs, K., and Seemann, R., *Euro. Phys. J.,* 12, 101-110 (2003).
13. Forrest, J.A. and Dalnoki-Veress, K., *Advance in Colloid and Interface Science,* 94, 167-197 (2001).
14 Menard, K.P., *Dynamic Mechanical Analysis: A Practical Introduction,* CRC Press, p. 107, 1999.
15. Watson, S., et al., "Effects of Pigment and its Dispersion on UV Degradation of Epoxy and Acrylic Urethane Polymer Systems," in *Nanophase and Nanocomposite Materials V*, Komarneni, S., Kaneko, K., Parker, J.C., and O'Brien, P. (Eds.), *Proc. Mater. Res. Soc. Symp.*, Volume 1056E, 2008.
16. Van Assche, G., Ghanem, A., Lhost, O., and Van Mele, B., *Polymer*, 46 (18), 7132-7139 (2005).
17. Abad, M., Ares, A., Barral, L., et al, *J. Appl. Polym. Sci.*, 85 (7), 1553-1561 (2002).
18. Gotzen, N.-A. and Van Assche, G., et. al, *ICNT Conference*, Basel, Switzerland, 2006.

AUTHORS

Louis T. Germinario, LG Analytical, 2012 Buckingham Court, Kingsport, TN 37660. Email: germ@chartertn.net.

Clifford K. Schoff, Schoff Associates, 4736 Magnus Dr., Allison Park, PA 15101. Email: c_schoff40@msn.com.

Kevin Kjoller, Craig Prater, and Khoren Sahagian, Anasys Instruments Corp., 25 W. Anapamu, Ste. B., Santa Barbara, CA 93101. Email: kevin@anasysinstruments.com.

This article was partially excerpted from the poster entitled, "Transition Temperature Microscopy: A New Technique for Probing Nanoscale Thermal Properties of Polymeric Materials" (K. Kjoller, et al.), presented at the European Polymer Forum, Graz, Austria, July 12-16, 2009.