

$\mu$ TA™

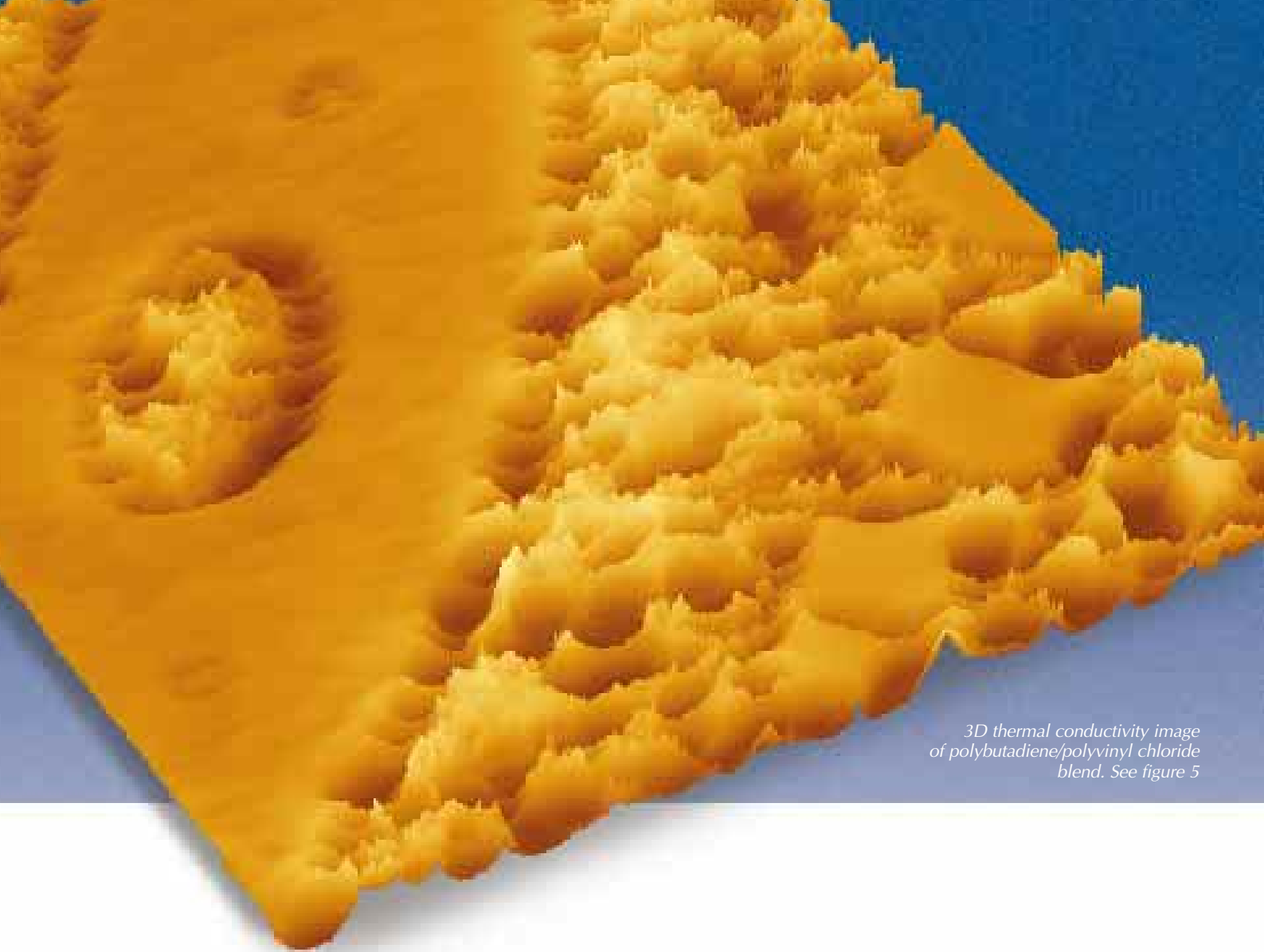
## 2990 Micro-Thermal Analyzer

*Characterizing  
the Nano-World*



**TA** Instruments  
Thermal Analysis & Rheology

A SUBSIDIARY OF WATERS CORPORATION



*3D thermal conductivity image of polybutadiene/polyvinyl chloride blend. See figure 5*

## Introducing $\mu$ TA: The Technique

Micro-Thermal Analysis ( $\mu$ TA™) is an exciting new innovation in the field of materials characterization. This invention combines the visualization power of atomic force microscopy (AFM) with the characterization capabilities of thermal analysis.

In Micro-Thermal Analysis, the AFM head is fitted with an ultra-miniature temperature probe which not only provides the heat source, but also measures the thermal response providing information similar to traditional thermal analysis, but on a microscopic scale. Patented modulated temperature technology is used to enhance the signal in a similar way to Modulated DSC®, and to provide depth profiling by varying the frequency over a wide range. This new technology has wide ranging applications including the characterization of phases, grains, and interface surfaces of polymers, pharmaceuticals, and foods.

Micro-Thermal Analysis can be used to characterize materials and surfaces, visualizing the spatial distribution of phases, components, and contaminants. The instrument images the structure of a 100 x 100  $\mu$ m region of the sample in terms of its topography, thermal conductivity, and thermal diffusivity. With a resolution of less than 1  $\mu$ m, any point (2 x 2  $\mu$ m) on the image can be selected for characterization of its calorimetric and mechanical properties.

Because of the small amount of sample actually affected for each measurement, heating and cooling rates are very high, providing the ability to make numerous measurements in a few minutes. Micro-Thermal Analysis is an important new addition to TA Instruments' wide range of thermal analysis and rheology products.

# TA Instruments

## $\mu$ TA 2990 Micro-Thermal Analyzer

The  $\mu$ TA 2990 is the product of TA Instruments' continuing dedication to innovation in materials characterization. The system has been designed with expansion and modularity in mind. Interchangeable probe tips, open architecture electronics, and a comprehensive suite of software provide a powerful tool today, with the potential to expand in the future as new measurement and analysis capabilities are added to the  $\mu$ TA 2990.

The  $\mu$ TA 2990 system consists of the AFM head with thermal probe, electronics control unit, and controller with data acquisition and analysis software. The AFM head can either be placed over the sample, for large samples, or onto a dedicated stage for imaging small samples.

Samples are easily mounted on 1 cm<sup>2</sup> metal disks, which are then held magnetically under the thermal probe. A 100x microscope connected to a CCD camera (charged coupled device) is used to view the surface of the sample and to help align the thermal probe over the area of interest. The thermal probe is then rastered (scanned) over the surface of the sample, simultaneously acquiring topography, thermal conductivity and thermal diffusivity images.

With a simple point-and-click of the mouse, the operator can select specific points of interest on the image for characterization

of calorimetric and mechanical properties. Because of the small sample size, heating and cooling rates are very high, (~500°C/min) providing the ability to make numerous measurements in a few minutes.

Powerful image analysis software is used to manipulate and display topographical, thermal conductivity, and thermal diffusivity images in a variety of ways, including leveling, shading, and display in 2 or 3 dimensions.

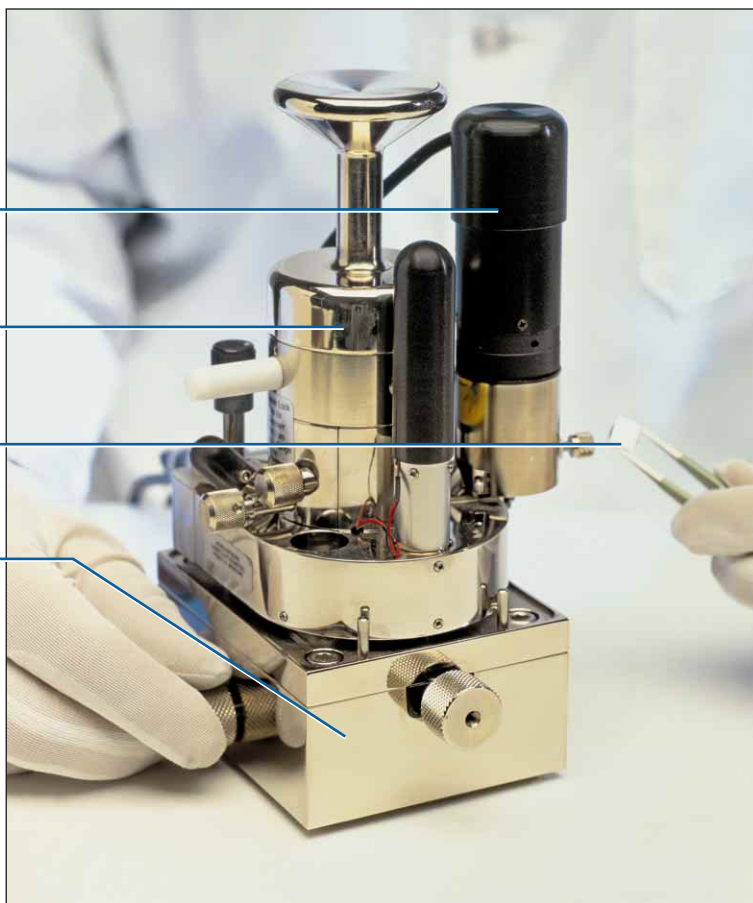
Thermal Solutions™ for Windows NT® software is used to analyze the thermal analysis data collected for each point of interest. Both analyses (image and thermal) can be run simultaneously on the Windows NT desktop with the ability to easily import results into standard 3rd party Windows® software (e.g. word processors, graphic packages, & spreadsheets) for publication quality report generation etc.

**Optical microscope  
with CCD camera**

**Atomic Force Microscope**

**Sample**  
*ready to be mounted on stage*

**Stage**



*Photo courtesy  
of the photographic unit at  
Lancaster University*

# Principles of Operation

The  $\mu$ TA 2990 uses a contact mode AFM method to raster the surface of the sample (Figure 1). As the probe scans the surface, it is deflected by changes in surface topography. A laser beam is reflected by a mirror on the probe to a four quadrant photo-detector. Changes in probe position (caused by surface topography) will generate a change in voltage at the photo-detector. These voltage changes are used to digitally generate a "picture" of the topography of the sample.

In addition to topography, the  $\mu$ TA 2990 images the thermal conductivity and thermal diffusivity of the near-surface. This is accomplished through the use of a patented probe design that incorporates a tiny resistance thermometer made from a Wollaston wire, enabling the probe to act as a heater and a thermal sensor simultaneously.

While scanning the surface to make topographical measurements described above, the temperature of the probe is modulated by a few degrees at frequencies in the kHz range. The average of the DC signal is a function of the thermal conductivity, and the response to the AC modulation signal is a function of the thermal

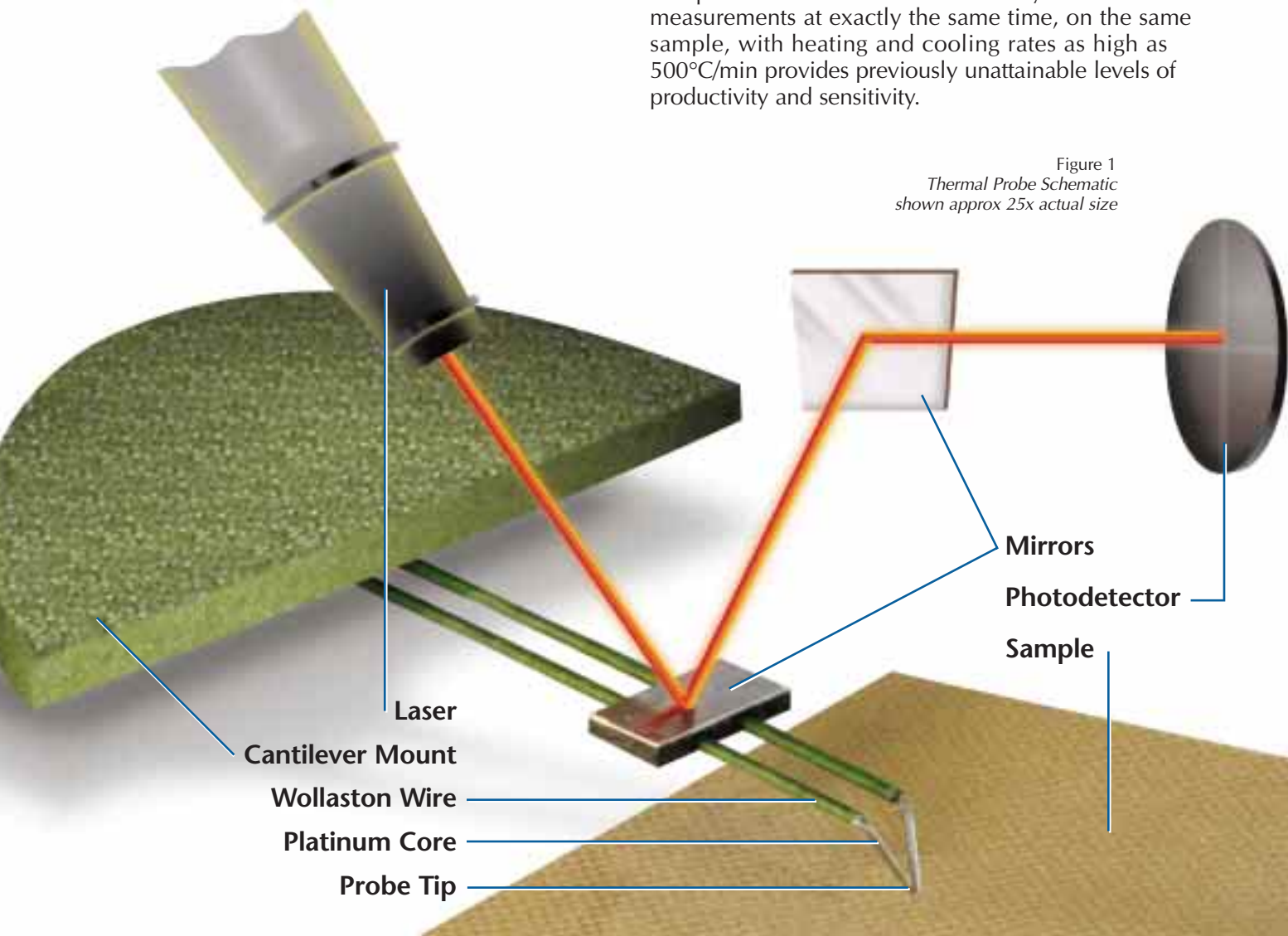
diffusivity of the near-surface. Using this technique, all three images, topography, thermal conductivity, and thermal diffusivity are obtained simultaneously (Figure 2).

The images are then used to select specific areas, domains, contaminants, or features that can be characterized by simply positioning the probe and performing a localized thermal analysis experiment. The temperature of the thermal probe is programmed in the same way as in Modulated DSC<sup>®</sup>. Patented modulated temperature technology is essential to enhance the signal, because of the small sample size.

In the  $\mu$ TA 2990, this patented technology is also used to provide depth profiling capability. As the frequency of modulation decreases, the volume (or depth) of the sample being modulated increases in proportion to the sample's thermal conductivity. The amplitude and period of modulation are user selectable, just as they are in a standard MDSC<sup>®</sup> experiment. This provides the unique ability to characterize the sample at varying depths.

The  $\mu$ TA 2990 can simultaneously make  $\mu$ MDTA and  $\mu$ TMA measurements. This ability to make two measurements at exactly the same time, on the same sample, with heating and cooling rates as high as 500°C/min provides previously unattainable levels of productivity and sensitivity.

Figure 1  
Thermal Probe Schematic  
shown approx 25x actual size



# What $\mu$ TA can tell you

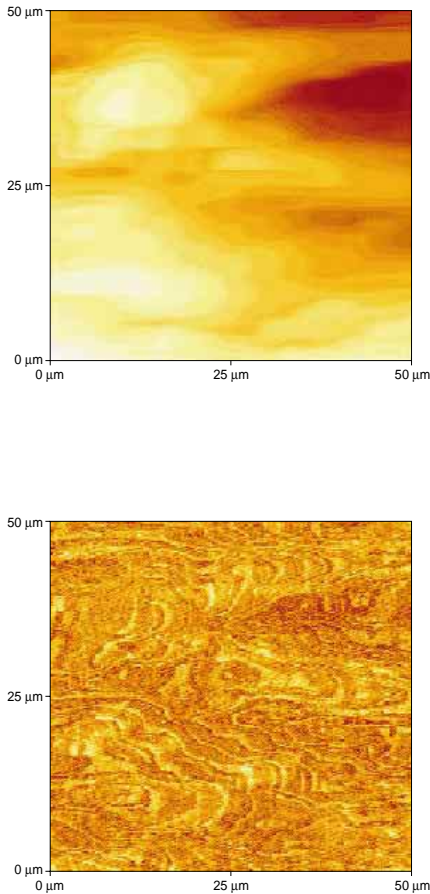


Figure 2  
As the thermal probe scans the surface, three images are obtained simultaneously. Shown clockwise from top are Topography, Thermal Conductivity and Thermal Diffusivity images for a thermoplastic polymer.

- **Surface Visualization**

Image contrast based on surface Topography, Thermal Conductivity and Thermal Diffusivity of the near-surface region

Differentiate and study polymer phases due to their thermal properties

“Look into” a sample by varying frequency of modulation

- **Surface Characterization**

Identify phases by measuring the material’s thermal properties

Measure Melting, Glass Transitions, Domain Size, Structure and Morphology

- **Spatial Distribution of Phases**

Measure Size and Distribution as a function of temperature

Differentiate phases based on thermal conductivity and diffusivity and study how these phases change with temperature

Detect how material properties change at interfaces

- **Thermal Properties of small samples/ small areas**

Measure changes in thermal properties across the surface of a sample

Measure transitions in ultra small, or thin samples, or samples buried within larger components

Understand the effects of processing or end-use conditions on a material’s structure

Differentiate between surface and bulk properties

## $\mu$ MDTA™

### Micro-Modulated Differential Thermal Analysis

Thermal transitions are measured in a way that is analogous to Modulated DSC. Because of the small sample sizes involved, these transitions would be barely detectable without the use of the patented modulated temperature technology. Results from  $\mu$ MDTA experiments can be readily compared with data from conventional DSC or MDSC, and can be used for identifying the individual phases of a sample from the onset and peak transition temperatures.

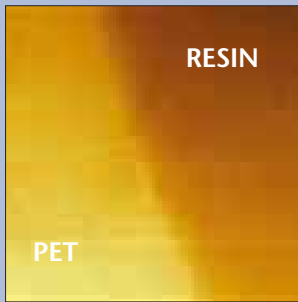
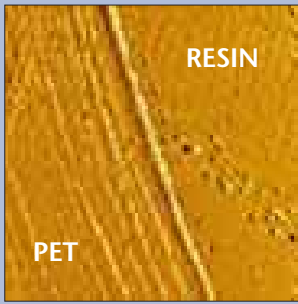
## $\mu$ TMA™

### Micro-Thermomechanical Analysis

As the probe heats the sample, expansion or softening can be measured by displacement in the Z-axis. This measurement is analogous to conventional thermomechanical analysis (TMA), and can be used for measuring expansion, softening, melting and glass transitions.

# Applications

Figure 3  
Topography (top)  
and Thermal Conductivity (bottom)  
images for a PET/Resin composite



## Analysis of Blends

Figure 3 shows the Topography and Thermal Conductivity images for a PET/Resin composite. At room temperature, both polymer phases are below their T<sub>g</sub>. Note that in the topographical image, there is very little contrast between the two polymer phases. The thermal conductivity image, however, shows clear differences between the PET and resin. Thermal imaging often yields this improved phase contrast, providing a superior way to visualize micro-phases, domains, and other spatially resolved components.

Characterization of the phases using micro-thermal analysis provides further differentiation and understanding. Figure 4 shows  $\mu$ TMA data for the PET and resin. The different properties can be clearly seen and serve to identify each phase. These curves can easily be compared and overlaid with curves generated by traditional thermal methods for additional confirmation and identification.

## Characterization of Interfaces and Morphology

When two or more polymers are combined (either physically or chemically), the microstructure and morphology have a direct impact on the material's final mechanical and chemical properties. Knowledge of the size and distribution of these phases can lead to a better understanding, and ultimately optimization, of mechanical properties. An evaluation of the structure as a function of time or temperature leads to a better understanding of degradation, oxidation, aging and weathering. Optimization of these characteristics leads to an improved product with more consistent lifetime properties.

Figure 5 shows thermal conductivity images for polybutadiene (PB) blended with a) polyvinyl chloride (PVC) and b) polyethylene oxide. In 5a, it can be seen that the PB forms domains within a PVC matrix. At room temperature, PB has higher thermal conductivity than PVC. This is represented by the lighter colored domains within a darker colored PVC matrix. In Fig 5b, a totally different morphology is present with the PEO forming domains within the darker colored PB matrix.

Figure 4  
Micro-Thermomechanical Analysis of  
PET (top) and Resin (bottom)

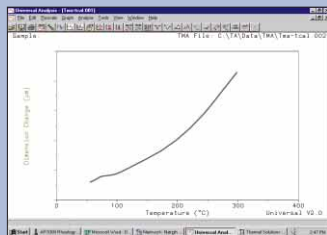
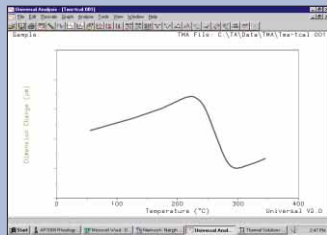


Figure 5  
Thermal conductivity images of PB blended  
with PVC (left) and PEO (right)

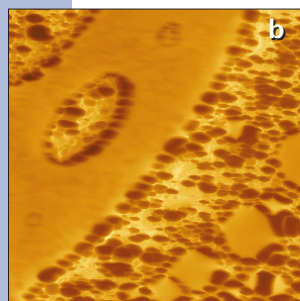
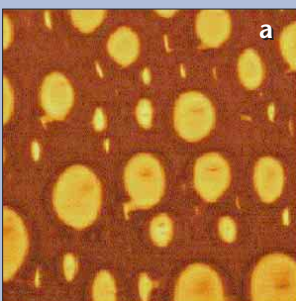


Figure 6 takes the study of the PVC/PB sample further by evaluating the effect of temperature on the polymer blend. At ambient temperatures, the rubbery PB matrix contains PVC domains. As the sample is heated through to 70°C the PVC passes through its T<sub>g</sub>, becoming softer, and the domains are less well defined. At even higher temperatures (>95°C), the matrix becomes almost liquid.

## Depth Profiling

Controlling the frequency of temperature modulation provides the ability to vary the depth to which the sample is analyzed. The thermal conductivity of the sample determines the depth to which temperature modulation extends, and therefore the depth to which the sample is analyzed. This approach provides a non-destructive technique for looking just below the surface of a material. By comparing these sub-surface images with those obtained from the surface, the effects of wear, oxidation and degradation can be determined. Figure 7 shows images of a polymer film coated on a substrate with high thermal conductivity. The film has circular craters formed during the manufacturing process. The imaging of the crater shows that the polymer is thick enough to prevent sub-surface imaging at 30kHz, but at 1kHz, the  $\mu$ TA2990 “looks” through the polymer layer and “sees” the high thermal conductivity substrate.

Figure 6  
Polybutadiene and polyvinyl chloride blend  
heated from ambient to over 95°C

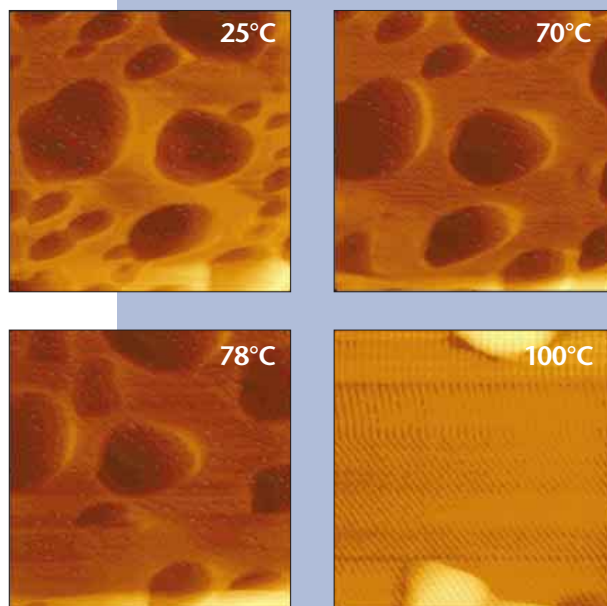
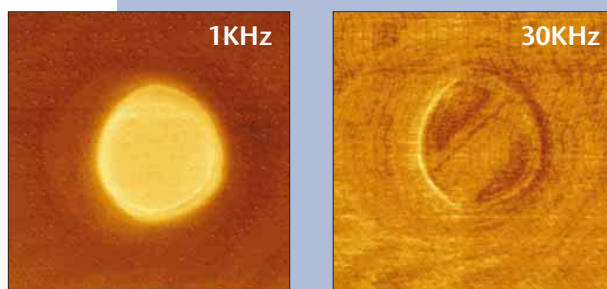


Figure 7  
Images of polymer film at 30kHz (right) and  
1kHz (left) illustrate depth profiling capability



## Features and Benefits

- Patented Wollaston wire thermal probe permits fast heating rates (~500°C/min) for high productivity.
- Patented modulated temperature technology provides the ability to obtain  $\mu$ MDTA and  $\mu$ TMA information simultaneously on precisely the same point on the sample.
- Depth profiling of a sample by varying frequency of modulation
- Obtain topographical, thermal conductivity and thermal diffusivity images simultaneously. Use these images to select points for immediate thermal characterization.
- Real-time, closed loop linearized scanners provide accurate measurements in all dimensions, and accurate probe placement at specified locations
- Easy sample preparation: take the  $\mu$ TA 2990 to large samples, or bring small samples to the  $\mu$ TA 2990.
- Integrated 45° view optical microscope permits easy alignment of the thermal probe within a specific area of the sample.
- Multiple sample stages optimized for ambient or sub-ambient measurements

## Specifications

<i>Manual X-Y translation stage</i>	Range 6mm x 6mm Resolution <1µm
<i>Scanner X-Y Range</i>	100µm x 100µm Linearized using TrueMetrix™
<i>Scanner Z Range</i>	>10µm Linearized using TrueMetrix™
<i>Optical microscope</i>	Integral 100x, CCD camera with 9" monitor
<i>Sample Size:</i> ~ without base ~ with base	Unlimited 22mm diameter, up to 5mm high.
<i>Visualization Modes</i>	Topography, Thermal Conductivity, and Thermal Diffusivity
<i>Characterization Modes</i>	µMDTA™ µTMA™
<i>Temperature Range</i> Standard With Cooling Stage	ambient to 500°C -70°C to 300°C
<i>Heating/Cooling Rates</i>	0 to 500°C/min

*Specifications are subject to change.*

The TA Instruments µTA 2290 is the result of continuing cooperative technical developments with:

- *Dr. Michael Reading of Loughborough University, UK*
- *Dr. Hubert Pollock and Dr. Azzedine Hammiche of Lancaster University, UK*
- *TopoMetrix Corporation, California USA*
- *Linkam Scientific Instruments Ltd., UK*

## TA Instruments Commitment

The µTA 2990 system is designed and engineered to assure easy, reliable, trouble free operation. It is supported by a full range of services, including an applications laboratory, publications, training courses, seminars, applications CD's, and internet website, and a telephone Hotline for customer consultation. Highly qualified service personnel specializing in thermal analyzer/rheometer maintenance and service are available throughout the world. All of these items reflect TA Instruments commitment to providing innovative thermal analysis & rheology products and related services that deliver the maximum value for your investment.

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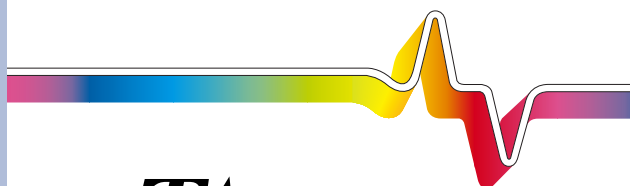
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