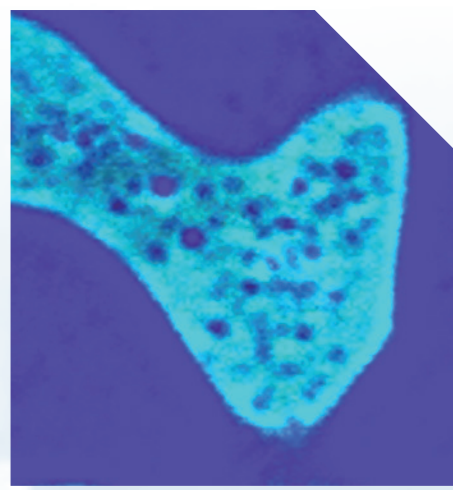
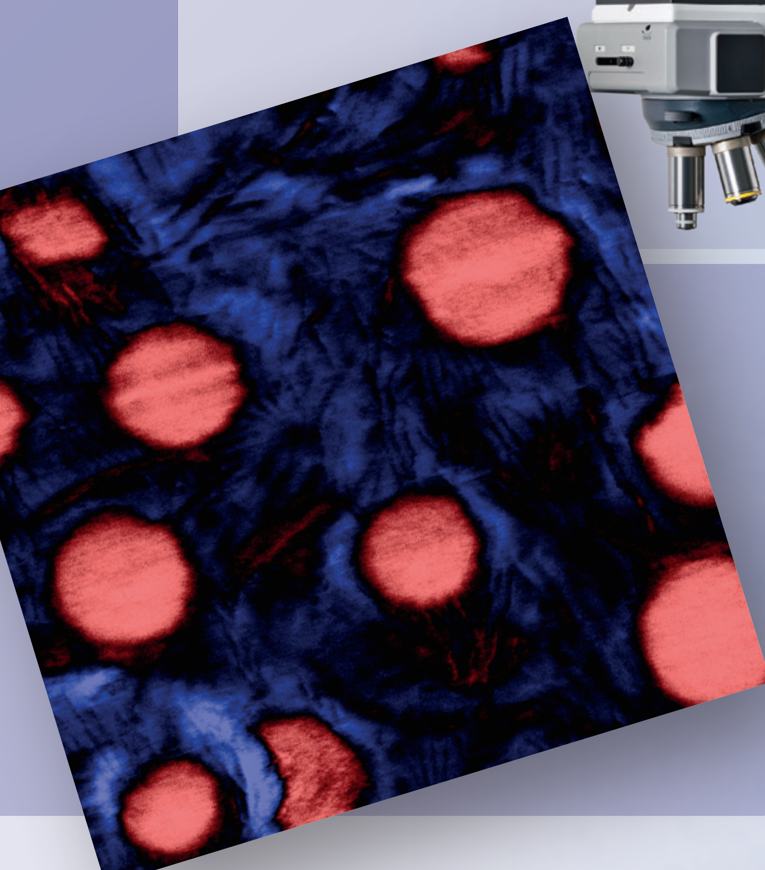
OXFORD INSTRUMENTS

TECHNICAL NOTE

Correlative Raman-AFM

Complementary Techniques from Oxford Instruments





https://raman.oxinst.com
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Correlative Raman-AFM: Complementary Techniques from Oxford Instruments

Oxford Instruments' product portfolio offers researchers a wide range of materials analysis solutions, several of which can be combined to obtain more comprehensive insight than possible with isolated techniques. A prime example of complementary methods is Raman imaging, pioneered by Oxford Instruments WITec, used in concert with atomic force microscopy (AFM), from innovators Oxford Instruments Asylum Research.

This technical note will describe the compatibility and benefits of respective instruments and portable coordinate systems from Oxford Instruments for characterising a polystyrene (PS)-polycaprolactone (PCL) polymer sample. It will highlight the distinctive approaches to handling data and show how the chemical sensitivity of Raman imaging and mechanical precision of AFM can be linked to reveal relationships between properties.

WITec, headquartered in Ulm, Germany, is the leading developer of Raman imaging and correlative forms of Raman microscopy. Its reputation is founded on the exceptional speed, sensitivity, and resolution of the alpha300 series of Raman systems.

Asylum Research, of Santa Barbara, California, is renowned for advancing technologies that analyse mechanical, electrical, magnetic and thermal properties at the nanoscale, including its Cypher, Jupiter, and Vero lines of atomic force microscopes.

TrueOrigin and Ergo

Oxford Instruments WITec's data acquisition and processing software features the TrueOrigin portable coordinate system. Oxford Instruments Asylum Research's Ergo Advanced Automation software, based on the powerful AZtec platform, stores sample locations in a coordinate file. Both systems rely on three markers, relative to which any position on the sample can be located, and a region of interest (ROI) defined. This ROI can be quickly found again after the sample has been removed from the stage and returned to it, or even placed on another instrument. This is vital in user facilities where multiple experiments run concurrently, or laboratories in which different methods are applied and results are correlated.

The systems differ in that TrueOrigin uses physical markers on the sample holder or features on the sample itself to establish the location of the ROI. These are recognised by the software in the video image (Figure 1a). Ergo imports and exports numerical coordinates expanded into three categories: centre of stage, fiducial markers, and user positions (Figure 1b). The centre of stage does not necessarily correspond to the origin (0,0) in TrueOrigin. Fiducial markers are easily recognisable reference points on the sample that are determined relative to the centre of the stage, and functionally equivalent to the TrueSurface markers. The user positions constitute the ROI and are defined in relation to the fiducial markers. Therefore, Ergo uses a transformation between centre-relative and fiducial-relative positions, with the complete coordinate space saved as an .ess file.

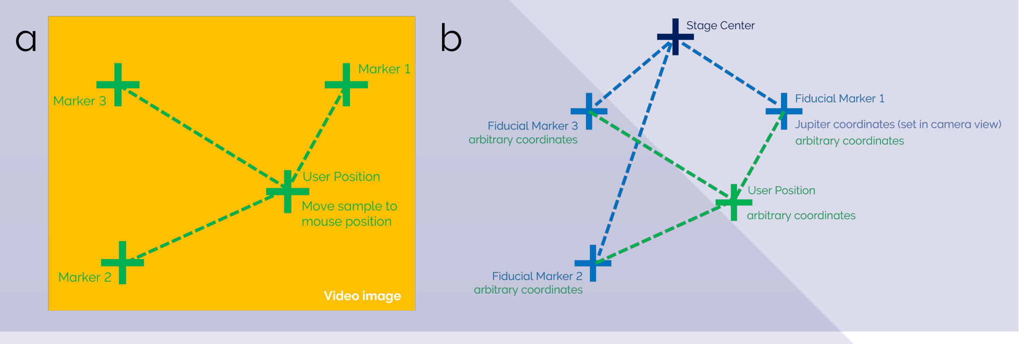

Figure 1: (a) TrueOrigin's video image-based coordinate system.**(b)** Ergo Advanced Automation's coordinate system, based on a transformation between two sets of three coordinates.

Sample, Instruments, and Correlative Approach

To demonstrate the unique benefits of correlative Raman imaging and AFM analysis, a polymer blend sample comprised of polystyrene (PS) and polycaprolactone (PCL) was chosen. It was prepared by a spin-coating procedure that typically generates "islands" of different polymer phases. Raman imaging can identify the composition of its components and visualise their distribution, while AFM can characterise the sample's surface morphology and mechanical properties.

An alpha300 with a 532 nm excitation laser, a UHTS 600 spectrometer with an Oxford Instruments Andor Newton back-illuminated CCD camera, a ZEISS EC Epiplan-Neofluar DIC 100x (NA 0.9) objective, and measurement control and data evaluation software equipped with TrueOrigin was used for the Raman imaging measurements. AFM imaging was performed with a Jupiter and the Ergo software. The microscope was employed in AM-FM mode (Amplitude Modulation-Frequency Modulation), also known as viscoelastic mapping, which is one of the several options for nano-mechanical characterisation that belong to the NanomechPro Toolkit. AM-FM is a bimodal technique that benefits from the stability, ease-of-use, gentleness and resolution of AC (tapping) mode, and the sensitivity of higher eigenmode imaging. For this study, an Olympus AC160TS-R3 cantilever (f = 300 kHz, k = 26 N/m) was employed in air over a sample area of 10 µm (overview) and 1 µm (zoom-in) with a scan rate of 1 Hz.

Correlation was accomplished through screenshots, or more precisely, zoomed-in images of the TrueOrigin markers (viewed through the microscope's optics, Figure 2a) and the Ergo map (displaying all markers and user positions on the stage, Figure 2b). These images can be loaded into the TrueOrigin dialogue to align the markers and enable navigation of a common ROI.

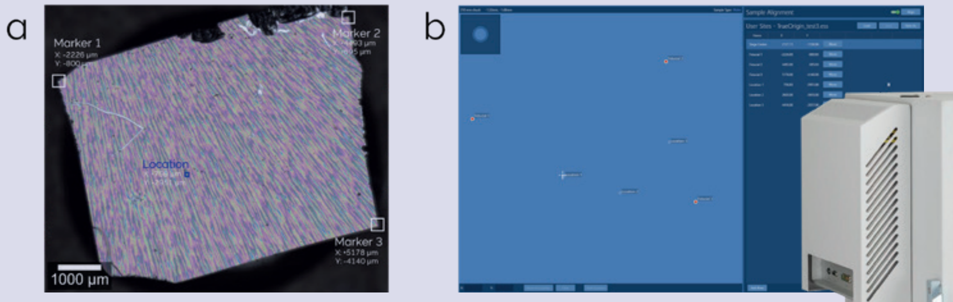

Figure 2: (a) The actual large scale stitching image used for the presented polymeric sample. The fiducial markers and the ROI (user position) are highlighted. **(b)** Screenshot of the corresponding markers as shown in the Ergo Advanced Automation software.

Results

The side-by-side comparison of topography and Raman images in Figure 3 demonstrates the ability to precisely locate sub-micron features, even after moving the sample between instruments. As shown in Figure 3a, the two polymeric phases of PS and PCL could be clearly distinguished based on their Raman spectra by using TrueComponent Analysis. With the straightforward alignment procedure described above, imaging of the surface morphology via AFM could be performed on the same ROI. Figure 3b shows that not only was it possible to clearly identify the PS and PCL phases through different channels including phase, frequency, and dissipation, but it was also possible to access relevant material properties such as Young's modulus. Concerning the latter, AM-FM clearly shows the higher storage modulus of PS (light brown) compared to PCL (dark brown). Additionally, thanks to the high spatial resolution and gentle nature of AC mode, it is possible to appreciate the fine fibrillar structure of PCL in multiple channels. In this way, AFM topography and viscoelastic mapping can be enhanced by the chemical identification and visualisation that Raman delivers.

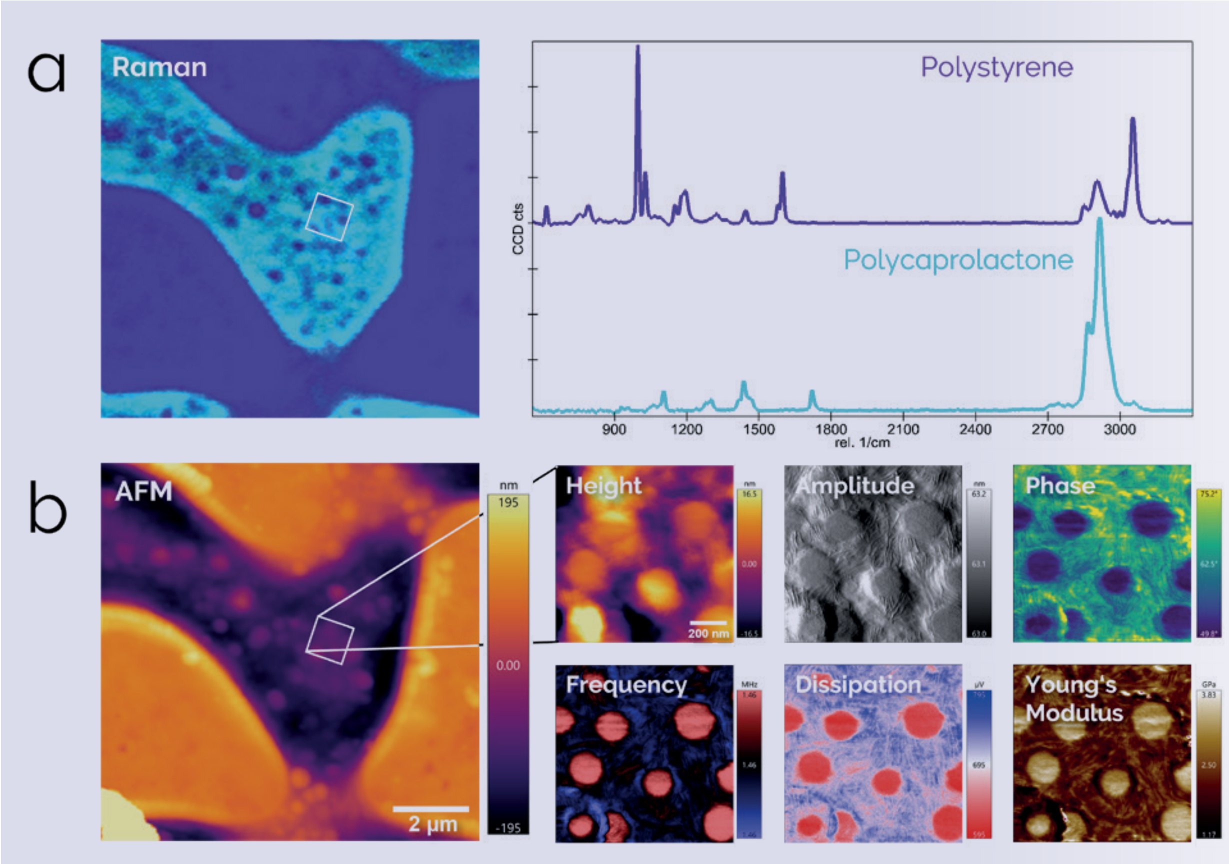

Figure 3: (a) Raman imaging of a polymer blend of polystyrene (PS) and polycaprolactone (PCL). The two phases of PS (purple) and PCL (cyan) are clearly distinguishable by their Raman signals, and are colour coded according to their corresponding spectra. **(b)** AFM topography (AC mode) of the same region measured in (a). The zoomed-in panels reveal additional information on the more heterogenous parts of the polymer mixture, including an estimation of Young's modulus (AM-FM).

Synopsis

The combination of Raman imaging microscopy, AFM topographic analysis and viscoelastic mapping applied to a PS-PCL polymer sample provided a more comprehensive characterisation than possible with any single method.

It revealed chemical, topographic and mechanical properties in vivid detail, and visualised the relationships between them. Oxford Instruments' TrueOrigin and Ergo Advanced Automation coordinate systems are user-friendly, readily compatible, and accelerate correlative measurements while ensuring sub-micron precision.

These technologies offer great utility to scientists in multi-user facilities and laboratories that investigate materials with an array of techniques.

OXFORD INSTRUMENTS

Raman and Correlative Microscopes

alpha300 S: Scanning Near-field Optical Microscope

alpha300 A: Atomic Force Microscope

alpha300 R: Confocal Raman Microscope

alpha300 R*i*: Inverted Confocal Raman Microscope

RISE®: Raman Imaging and Scanning Electron Microscope

alpha300 *apyron*™: Automated Confocal Raman Microscope

alpha300 *access*: Confocal Micro-Raman System

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