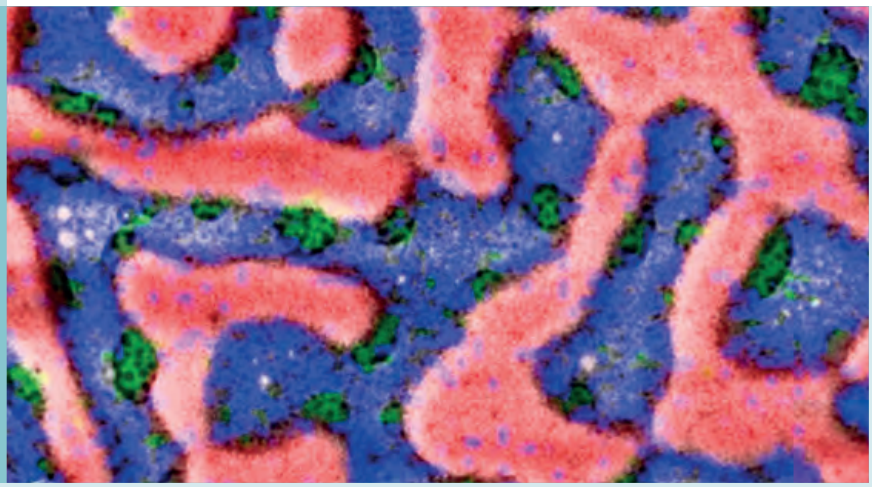
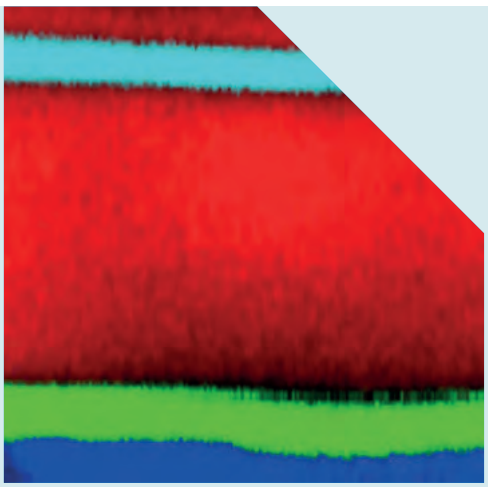
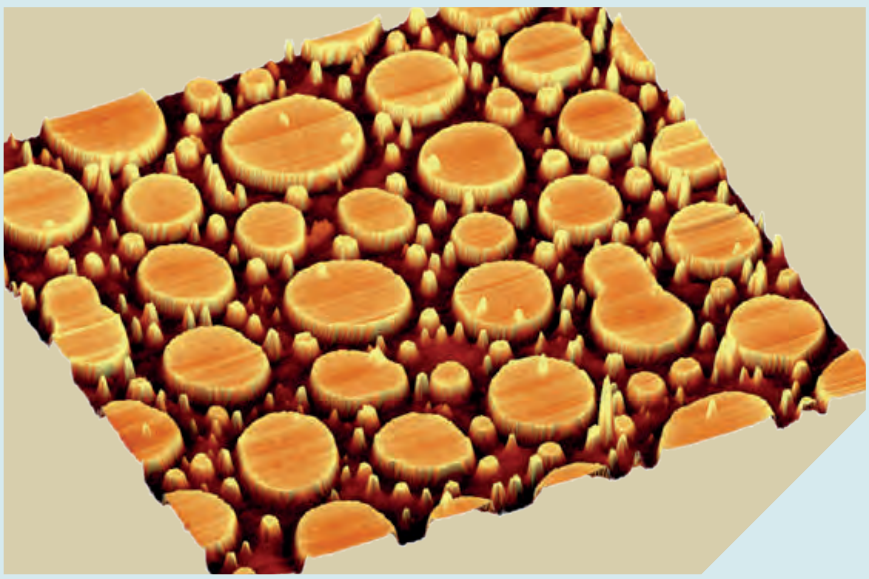
APPLICATION NOTE

Correlative Raman Imaging of Polymeric Materials







WITec GmbH, Lise-Meitner-Str. 6, 89081 Ulm, Germany
phone+49 (0) 731 140 700, fax +49 (0) 731 140 70 200
info@WITec.de, www.WITec.de

WITec
focus innovations

Lise-Meitner-Straße 6 · D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700 · Fax. +49 (0) 731 140 70200
www.witec.de · info@witec.de

Characterization of Polymer Blends with Correlative Microscopy: Confocal Raman Imaging and Atomic Force Microscopy

Polymers play an essential role in modern materials science. Due to their widely varying mechanical and chemical properties they are used in almost every field of application and remain a dynamic component of the development of new materials with demanding requirements. For many of these endeavors, knowledge of the morphology and chemical composition of heterogeneous polymeric materials on a sub-micrometer scale is crucial.

Certain properties, however, are difficult to study with conventional characterization techniques due to their inability to chemically differentiate materials with sufficient spatial resolution and without damaging, staining or otherwise treating them.

Correlative microscopy comprised of Atomic Force Microscopy (AFM) and confocal Raman imaging opens new avenues for the analysis of advanced polymeric materials when a detailed understanding of physical and chemical properties is required. While AFM records topographic information and local mechanical characteristics along and perpendicular to the surface of a sample with high spatial resolution, Raman imaging reveals its molecular composition.

Throughout all measurements the samples remained in place, allowing the images to be correlated. The WITec Project software enables a comprehensive evaluation of the acquired data and the generation of depth profiles.

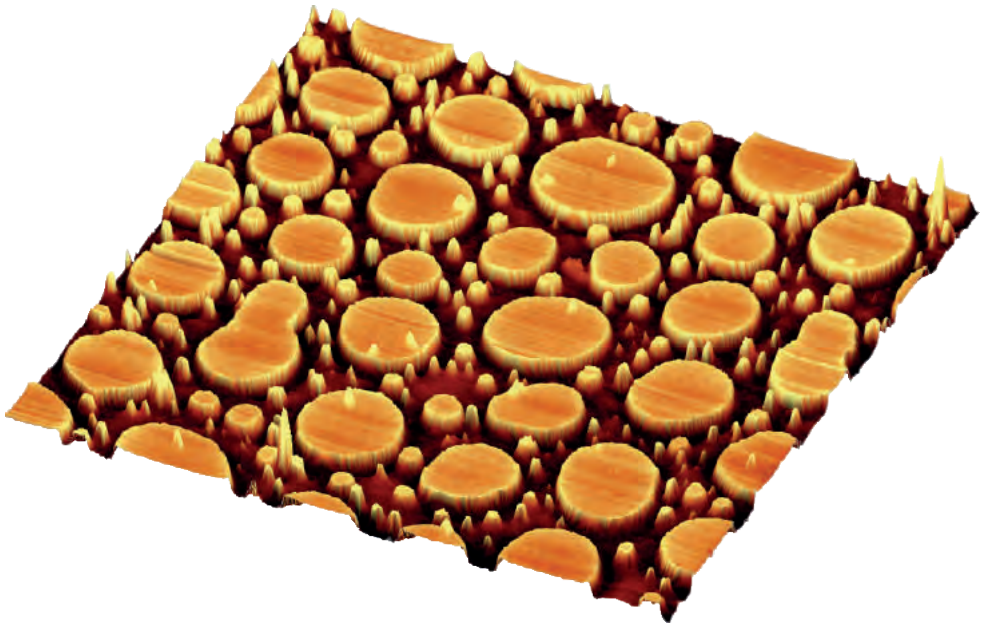
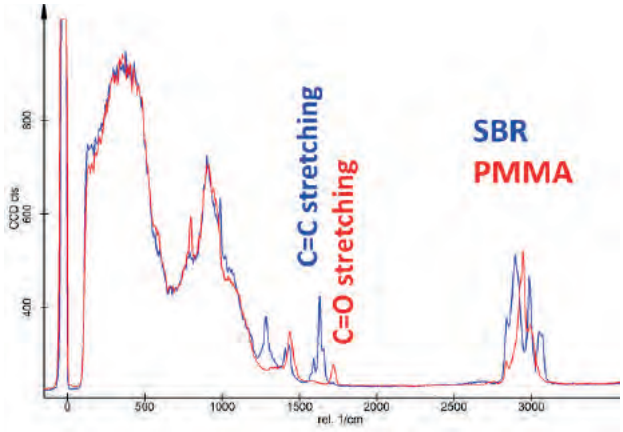


Fig. 1: AFM image of a PMMA-SBR blend. The scan area was 20 x 20 x 0.03 µm³.

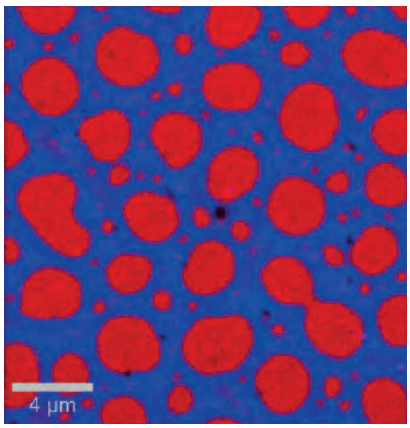
To demonstrate the capabilities of AFM-Raman correlative microscopy, thin films of a mixture of two polymers were studied. Polymethylacrylate (PMMA) and styrene-butadiene-rubber (SBR) were mixed and spin coated onto a glass cover slip. For imaging a WITec alpha300 RA microscope was used.

The mixture was analyzed with AFM in the AC Mode (Fig. 1). The topographic image reveals round spheres. Their chemical nature was determined by their Raman spectra.

Lise-Meitner-Straße 6 · D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700 · Fax. +49 (0) 731 140 70200
www.witec.de · info@witec.de



2a

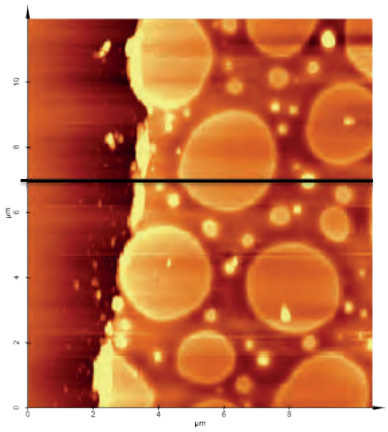


2b

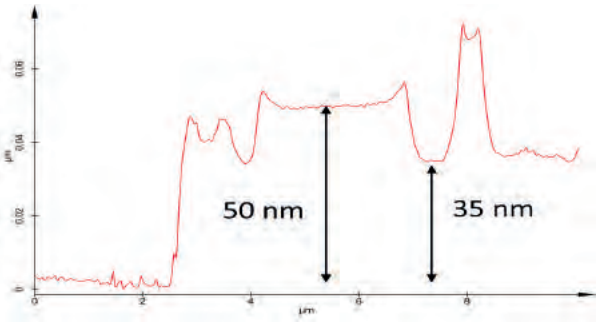
Fig. 2: Raman spectra (a) of PMMA (red) and SBR (blue). PMMA was identified by its typical C=O stretching band and SBR molecules by their C=C double bond stretching band. In the Raman image (b) PMMA appears as round spheres in the surrounding SBR.

The spectra of the molecules in these island-like structures contain a band at 1735 rel./cm (Fig. 2a red). This is associated with C=O double bond stretching, identifying the substance as PMMA. The area between the spheres consists of SBR. It was identified by a Raman band at 1640 rel./cm that is characteristic for the C=C double bonds of the SBR molecules (Fig. 2a, blue). The distribution of the polymer was visualized by Raman imaging (Fig. 2b).

To determine the thickness of the polymer blend, the film was scratched with a razor blade and imaged with AFM. The cross section marked with a black line in the AFM image (Fig. 3a) indicates that the PMMA islands are up to 70 nm high and protrude from the SBR film that is 30 nm high (Fig. 3b)



3a



3b

Fig 3: AFM image of a PMMA-SBR mixture spin-coated on glass (a). The film was scratched with a sharp razor and a depth-profile was measured (b) along the black line in the left figure.
Image parameters: scan range 10 x 12 x 0.6 µm³

Lise-Meitner-Straße 6 · D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700 · Fax. +49 (0) 731 140 70200
www.witec.de · info@witec.de

Correlative High-Resolution Raman-AFM-SNOM Imaging of a Three-Polymer Mixture

A three-component polymer blend was studied by using a combination of Atomic Force Microscopy (AFM), Scanning Near-field Microscopy (SNOM) and confocal Raman imaging.

While AFM operating in AC Mode recorded topographic information and local mechanical characteristics, SNOM detected optical properties with resolution far below the diffraction limit and Raman imaging revealed the molecular composition of the sample. Correlated AFM – SNOM – confocal Raman imaging, provides deep insight into the chemical and physical properties of polymer mixtures on a sub-micrometer scale.

The phase separation of a thin film blend of 1:1:1 polysterene (PS), styrene-butadiene-rubber (SBR) and ethyl-hexyl acrylate (EHA) was analyzed with a WITec alpha 300 RAS microscope featuring all three analysis methods integrated within one instrument. The sample, spin-coated onto glass, remained in place throughout, allowing for images to be correlated. Evaluation of the acquired data and generation of depth profiles was accomplished with the WITec Control software.

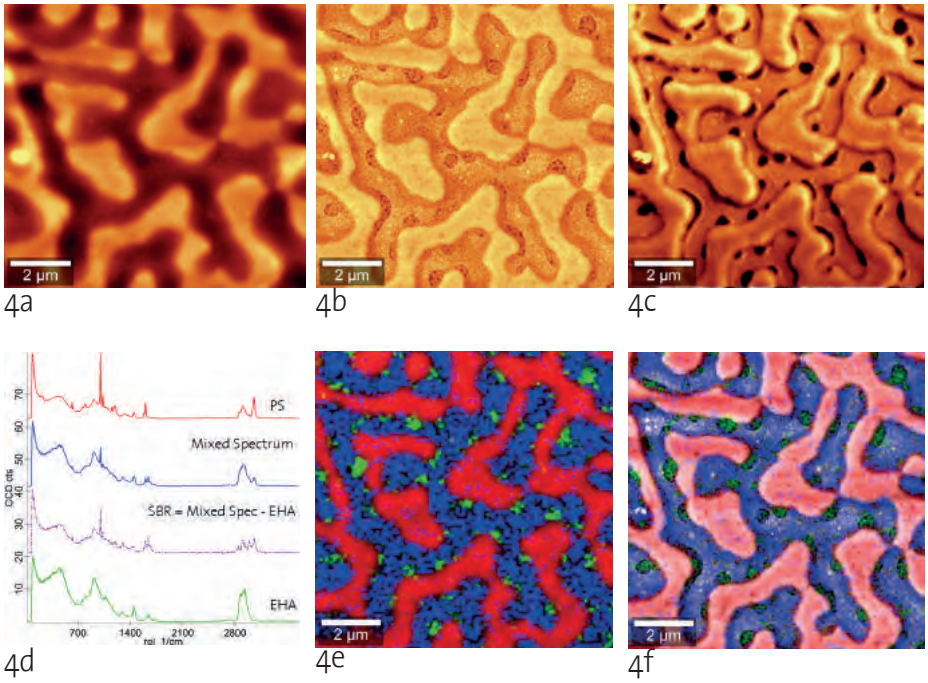


Fig. 4: Correlative, high-resolution AFM – SNOM – confocal Raman imaging of a 1:1:1 mixture of PS, SBR and EHA. Using AFM in tapping mode the sample's topography (a) and its phase image (b) were measured simultaneously. With SNOM the transparency of the same area was determined with the dark spots being opaque (c) Concurrently with the AFM and SNOM measurements the Raman spectra (d) were recorded for each pixel of the area and displayed as a false color image (e): red = PS, green = EHA, blue = mixed spectrum of SBR and EHA, violet: SBR).
The overlay of the AFM phase and Raman images is shown in Fig. 4f.

The topography of the sample measured with AFM reveals a three-level structure (Fig. 4a) while the simultaneously recorded phase image (Fig. 4b) shows a fine netlike texture at the lowest topographic level, material containing small spheres in the intermediate layer and an amorphous pattern in the uppermost substance. The SNOM image acquired from the same sample section indicates that the thinnest areas of the samples are opaque (Fig. 4c). These areas contain EHA only, as can be seen in the Raman image (Fig. 4e) that was generated from the Raman spectra (Fig. 4d). The uppermost features of the sample appear to be PS, which is known to form spheres. The perfect correlation of topography, phase separation, SNOM and molecular composition is illustrated by the overlay of the AFM phase and Raman images (Fig. 4f).

All correlated structural, physical and chemical data lead to the conclusion that the EHA forms the lowermost layer on the microscope slide. It is covered by a layer of SBR as indicated by the blended (EHA-SBR) Raman spectrum. PS spheres are submerged in and protrude out of this double-layer polymer film.

The combination of AFM, SNOM and confocal Raman imaging in a single instrument enables easy-to-use, nondestructive, physical and chemical characterization of heterogeneous materials at very high resolution.

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focus innovations
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www.witec.de · info@witec.de

Confocal Raman Imaging for Depth Profiling of Polymer Films and Coatings

A full analysis of a heterogenous polymer blend not only includes the two-dimensional arrangement of its individual components but also their distribution in the third dimension. A comprehensive, three-dimensional characterization of polymers such as films and coatings can be achieved with confocal Raman microscopy. Films and coatings play an important role in many fields of application such as food packaging, drug delivery and medical devices or adhesives.

While the resolution of two-dimensional Raman imaging is limited by diffraction, the quality of depth resolution relies on the confocality of the microscope. WITec confocal Raman microscopes combine a highly sensitive confocal microscope and a high-transmission Raman spectroscopy system. The WITec Control software can extract a variety of properties from a single measurement such as peak width, center of mass or peak position of certain Raman lines. For depth profiling measurements, the focal plane can be moved in the z-direction when performing either x-z scans or generating x-y image stacks in the z-direction. Here, the microscope's capabilities are demonstrated by imaging the inner polymer coating of an orange juice container and of polymer layers on paper.

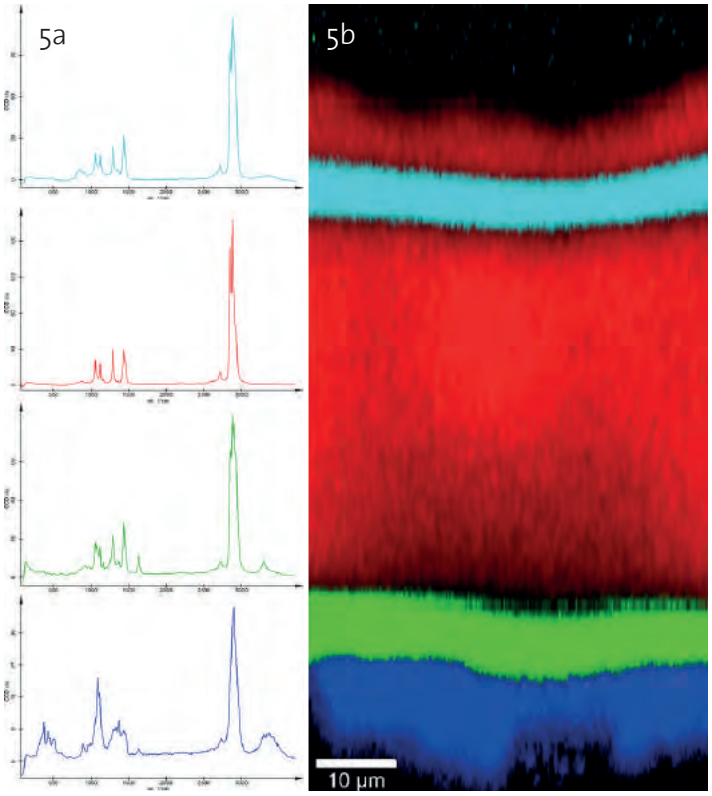
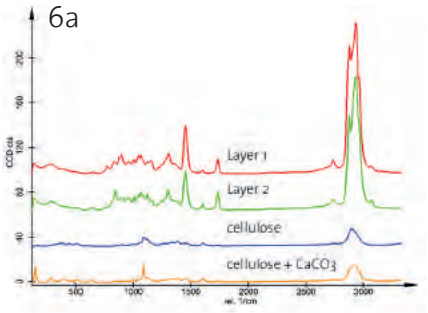
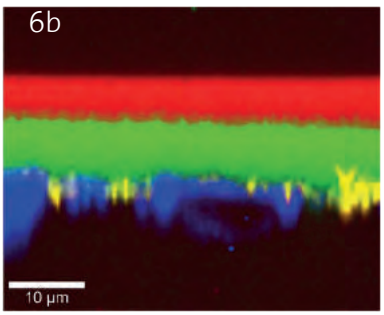


Fig. 5: Raman spectra (a) and corresponding color-coded Raman image (b) of the inner coating of an orange juice container. Image parameters: scan range 50 x 100 µm², 200 x 120 pixels (=24,000 spectra), 50 ms/spectrum acquisition time.

The inner plastic film of a paper beverage container was investigated by performing an x-z scan with a scan range of 50 x 100 µm². Within the acquired multi-spectrum file, four distinct spectra were observed, each representing a specific chemical compound within the beverage container coating (Fig. 5a). The Raman image generated from the spectra shows that the coating is about 80 µm thick and consists of five layers of different thicknesses made up of four compounds (Fig 5b).





In another experiment, confocal Raman depth scans provided insight into the layered structure of polymers that were applied to the surface of paper in order to make it adhesive. The two polymers identified by their Raman spectra (Fig. 6a) are immiscible and form a sharp interface with the paper beneath (Fig. 6b).

Fig.6: Raman spectra (a) and color-coded Raman depth profile (b) of adhesive polymeric layers on a paper substrate. Image parameters: 50 x 40 µm², 150 x 50 pixels (= 7500 spectra), 0.1 sec/spectrum acquisition time.

application note

Lise-Meitner-Straße 6 · D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700 · Fax. +49 (0) 731 140 70200
www.witec.de · info@witec.de

WITec alpha300 Confocal Raman Microscope Series

alpha300 series: modular and flexible design guarantees advanced confocal Raman imaging with multiple correlative microscopy technique options, such as AFM, SNOM, SEM (RISE), fluorescence, photoluminescence and topographic Raman imaging (TrueSurface).