Multimodal Imaging of Polymeric Materials and Coatings

The combination of AFM and confocal Raman microscopy in a single instrument enables the non-destructive characterization of heterogeneous materials.

Ute Schmidt

Polymer blends are designed to address needs of different industries and in many cases the relationship between structure, morphology, and material properties is indispensable for optimization of material design. Since the beginning of plastics industry, it has been recognized that blending yields materials with property profiles superior to the features of the individual components.

A polymer blend is a macroscopically homogeneous mixture of two or more different species of polymer, which combine the useful properties of all the constituents. Its morphology indicates the size, shape and spatial distribution of the component phases with respect to each other. Characteristics of a polymer blend, e.g. mechanical, optical, rheological, dielectrical, and barrier properties are strongly influenced by the type and fineness of the phase structure. The aim of this article is to show how several analytical techniques can be combined in one instrument for the characterization of polymeric materials on the micro- and nanometer scale.

Methods

Atomic Force Microscopy (AFM)
Heterogeneity in polymers can be characterized with AFM [1]. This method provides spatial information along and perpendicular to the surface of a polymer film with a resolution in the order of 1 nm. The most commonly used AFM imaging mode for polymers is the intermittent contact mode also known as AC Mode or Tapping Mode [2]. In this imaging mode the cantilever is oscillated at its
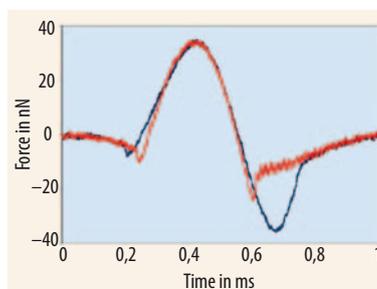
Ute Schmidt, WITec GmbH, Lise-Meitner Str. 6, 89081 Ulm, Germany ute.schmidt@witec.de

Fig. 1 Two examples of pulsed force curves: The red curve is characteristic for a stiff and non-adhesive material, whereas the blue curve highlights the characteristics of a soft and sticky sample.

resonance frequency with a free amplitude A_0. When the cantilever approaches the surface, the oscillating amplitude is reduced to a value A, which depends on the distance to the surface and the surface potential. The ratio $r = A/A_0$ defines the damping of the amplitude while the tip is in contact with the surface and is proportional to the applied force. By keeping the damping of the amplitude constant, the surface topography can be mapped and a phase image can be recorded simultaneously. In this image, the phase shift between the free oscillation in air and the oscillation while the

tip is in contact with the surface is recorded [3]. Since the phase shift depends as much on the viscoelastic properties of the sample as on the adhesive potential between the sample and the tip, the phase image outlines domains of varying material contrast without providing information about material properties [4]. Nevertheless, phase images are often used to characterize polymers at high resolution [5]. If the AFM is operated in Pulsed Force Mode (PFM), information about the local mechanical properties of various regions on the sample surface can be obtained more quantitatively [6]. In this imaging mode, a sinusoidal modulation is imposed on the cantilever typically with a frequency of 1 kHz, which is far below the resonance frequency of the cantilever. Thus, the maximum applied force can be controlled using the beam deflection technique while the cantilever is approached to and retracted from the sample. A complete pulsed force curve shows the variation of the force signal as a function of time and contains information about the tip-sample interaction (**Fig. 1**).
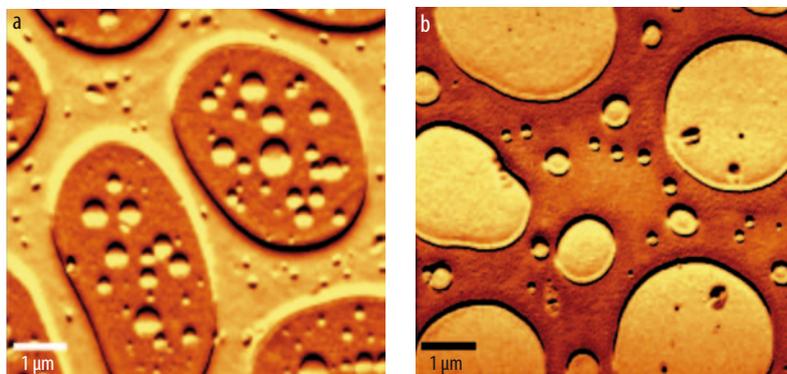

Fig. 2 Stiffness maps of PMMA-SBS (a) and PMMA- SBR (b). The blend PMMA-SBS shows the formation of elliptic features and a netlike structure with higher stiffness as shown by the bright and dark colors respectively (a). A much higher contrast between the bright round islands and the dark surrounding is found in the blend PMMA-SBR (b).

Confocal Raman Microscopy

Raman spectroscopy is one of the standard characterization techniques used to uniquely determine the chemical composition of a polymer [7]. Modern polymer materials, however, are generally heterogeneous, in which various chemical components or polymorphs of the same chemical species can be present in a very small sample volume. Domains of different components in polymer blends are formed during phase separation and are typically a few hundred nanometer in size. For the analysis of such heterogeneous materials, the confocal Raman microscope combines the chemical sensitivity of Raman spectroscopy with the lateral resolution of confocal microscopy, providing an ideal tool for the characterization of materials in the sub-micrometer range. Raman imaging contributes to the analysis of multi-component polymer systems by visualizing the distribution of individual components based on the unique Raman spectra for different polymeric materials. To collect high-resolution Raman images, the sample is scanned point-by-point and line-by-line through the excitation focus [8]. In this way domains can be visualized with a resolution down to 200 nm [9]. In the past few years new instrument developments allow the recording of a complete Raman spectrum in less than one millisecond from a very small sample volume, thus the acquisition time for two dimensional arrays of tens of thousands of Raman spectra was reduced to a few minutes [8, 10]. Powerful software packages, which allow a fast evaluation of such 2D spectral arrays makes Raman imaging indispensable for the morphological characterization of polymer blends.

True Surface Microscopy

This new imaging technique was developed for confocal Raman measurements on rough surfaces over large areas. It allows for confocal Raman imaging guided by the surface topography obtained by an integrated non-contact optical profilometer. Large-area topographic coordinates from the chromatic confocal profilometer measurements can be precisely correlated with the large area confocal Raman imaging data. This allows for true surface Raman imaging on heavily inclined or rough surfaces, holding the true sample surface in focus, which maintains highest confocality.
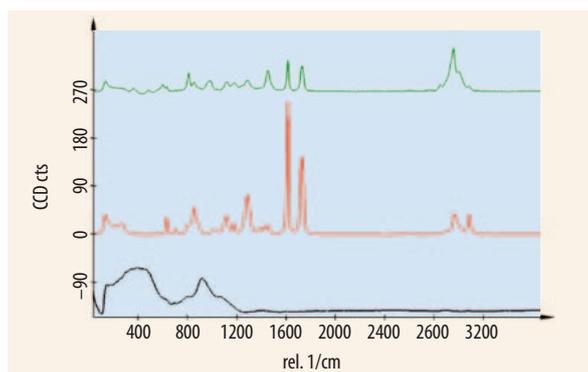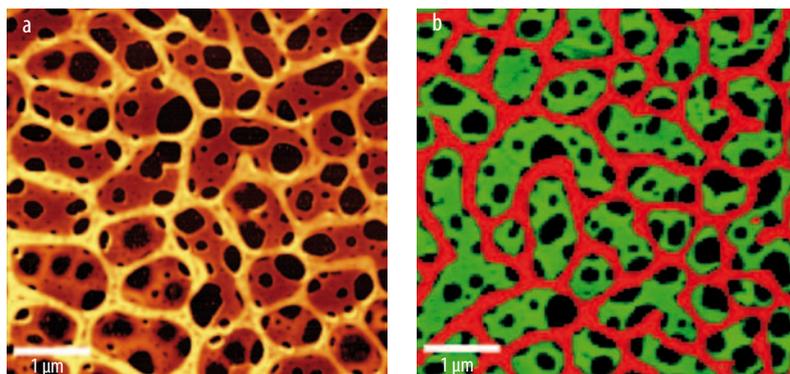

Fig. 3 Histogram of stiffness distribution PMMA-SBR (red) and PMMA-SBS (blue). The peak that appears for both blends at 1.15 ± 0.1 N/m can be correlated to the stiffer PMMA. The other at lower stiffness values can be assigned to the SB phase. For SBS the average stiffness was 0.9 ± 0.1 N/m, for SBR 0.2 ± 0.1 N/m.

In summary, the combination of confocal Raman microscopy with AFM and true surface microscopy enables the characterization of materials at high submicron resolution as well as on mm-rough surfaces across large areas. In the following, different thin films of polymer blends composed of immiscible polymers are investigated using a combined confocal Raman AFM. With the combination of these measuring methods information on the nanometer and micrometer range can be achieved. The capabilities of true surface microscopy are demonstrated with the confocal Raman imaging of a skittle.

Results And Discussion

In the first example, the mechanical properties of two styrene-butadiene (SB) polymorphs (the triblock copolymer SBS and the statistical copolymer SBR) are evaluated using AFM-PFM measurements. The investigated polymers were acquired from Sigma-Aldrich. As a reference PMMA from Polymer Standards was used. From these materials, polymer solutions were prepared by dissolving 10 mg of the polymer in 1 ml toluene. Blends were prepared by mixing 2 ml of the PMMA toluene solution and 1 ml of the SBS or SBR solutions. Thin films of PMMA-SBS and PMMA-SBR were prepared by spin coating of the corresponding solutions on glass slides. **Fig. 2** shows the

Fig. 4 Confocal Raman AFM Imaging of a polymer blend PET-PMMA: topography (a), color coded Raman image (b), and Raman spectra of PMMA (green), PET (red) and glass (black) (c).
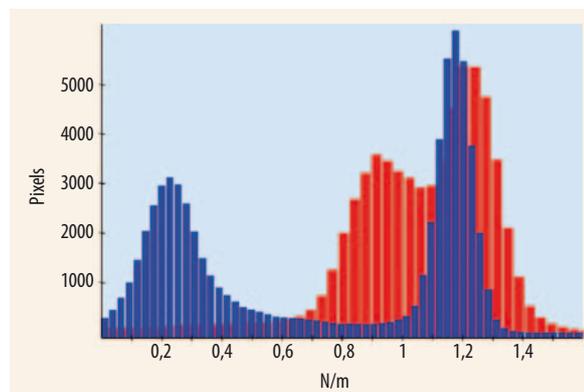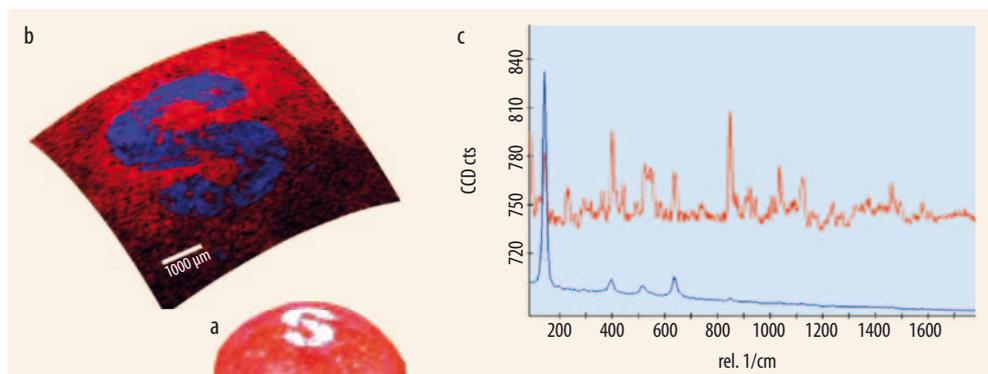
Fig. 5 TrueSurface Microscopy image of a skittle: photograph (a), color coded true surface image (b), and Raman spectra of TiO² in the writing on the skittle (blue spectrum) and sugar coating of the skittle (red spectrum).

Summary

The combination of AFM and confocal Raman microscopy in a single instrument enables the non-destructive characterization of heterogeneous materials. The surface topography can be imaged at the highest resolution and various materials contributing to the surface composition can be chemically identified. Confocal Raman imaging of large surface areas is possible by combining a profiler and confocal Raman imaging, thus keeping the sample in focus during measurements.

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stiffness maps of the two polymer blends obtained from AFM-PFM measurements. Based on macroscopic mechanical properties, the stiff phase corresponds to PMMA, which is in the glassy state at room temperature [11]. The softer phase can be assigned to SB, which has a glass transition temperature far below room temperature, thus leaving it in a rubbery state [11]. To quantify the stiffness maps, the measured voltages of the stiffness output ($V_{stiffness}$) of the DPFM electronics are converted into the physical unit of the local stiffness (N/m) [12]. After unit conversion of the stiffness maps, the histograms shown in **Fig. 3** are obtained. Both histograms show two peaks. Since the average stiffness of PMMA in both blends is the same, it can be used as an internal reference for the comparison of the stiffness properties of SBS and SBR, revealing that SBS is stiffer than SBR by a factor 3.5.

Generally, a differentiation based on mechanical contrast of polymeric phases in thin films is difficult or impossible without film destruction, if the two materials have similar elasticity modulus. In this case the combination of AFM with confocal Raman microscopy can provide more insight in to the phase allocation in such polymer blends. **Fig. 4a** shows the AFM topography image of a thin film of the polymer blend PET-PMMA. A three level structure is visible, although only two materials were spincoated on the glass substrate. The same film was also imaged in Raman imaging mode by acquiring a 2D spectral array of 200 × 200 Raman spectra, with an integration time of 0.1 s per spectrum. The 40 000 Raman spectra were clustered into three most similar Raman spectra. The resulting spectra (**Fig. 4c**) and correspond to the unique Raman spectra of PMMA (green), PET (red) and glass (black). The distribution of the three phases is shown in the color coded confocal Raman image presented in **Fig. 4b**. By comparing these two images, it became clear, that the topographic elevated net-like structure corresponds to PET, the intermediate structure corresponds to PMMA and the black holes in the topography image are uncovered glass areas. This example reveals, that the combination of AFM and confocal Raman imaging is a powerful tool for both, the precise determination of the film morphology, build up in three topographic levels of only a few tenth of nanometer thickness and the non-destructive identification of the blend components through Raman spectroscopy and their distribution within the film.

The analysis of large sample areas with a surface roughness which exceeds the focal length of a high numerical aperture objective can be performed with true surface microscopy. **Fig. 5** shows a large area confocal Raman image of a skittle. Such Raman images can be acquired only if the topographic coordinates of the skittle are followed while recording the 2D array of Raman spectra.