

Confocal Raman AFM - A Powerful Tool for the Nondestructive Characterization of Heterogeneous Materials

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ABSTRACT

The combination of an atomic force microscope (AFM) and a Confocal Raman Microscope (CRM) has been used to study an emulsion consisting of alkyd and acrylic latexes. Alkyds and acrylics are used as binders in paints and coatings. These materials produce a shiny, hard finish that is highly water-resistant.

The high spatial resolution of the AFM enables the morphological characterization of the dried emulsion on the nanometer scale. Furthermore, when operating the AFM in Digital Pulsed Force Mode (DPFM), topographic information and local mechanical properties can be simultaneously recorded, allowing a comparison of the mechanical properties of the emulsion components.

Raman spectroscopy provides additional information on the chemical composition of materials. In combination with a confocal microscope, the spatial distribution of the various phases can be determined with a resolution down to 200 nm. Therefore, the topographically different structures observed in AFM images can be associated to the chemical composition by using the Confocal Raman Microscope (CRM).

Keywords: Confocal, Raman, AFM, Imaging

1 INTRODUCTION

The characterization of heterogeneous systems on the microscopic scale continues to grow in importance and to impact key applications in the fields of materials science, nanotechnology and catalysis. The development of advanced polymeric materials for applications such as these requires detailed information about the physical and chemical properties of these materials on the nanometer scale. However, some details about the phase-separation process in polymers are difficult to study with conventional characterization techniques due to the inability of these methods to chemically differentiate materials with good spatial resolution and without damage, staining or preferential solvent washing.

One technique that has been used successfully in the characterization of heterogeneity in polymers is Atomic Force Microscopy (AFM) [1-4]. AFM can provide spatial information along and perpendicular to the surface of a polymer film with resolution on 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 [5]. In these imaging modes the cantilever is oscillated at its resonance frequency with a free amplitude A_0 . While the cantilever is approaching the surface, the oscillating amplitude is reduced to a value A , which depends on the distance to the surface. 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. A phase image can be recorded simultaneously with the surface topography. 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 [6]. 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 properties [7-11]. Nevertheless, phase images are often used to characterize polymers at high resolution [12, 13].

If the AFM is operated in Pulsed Force Mode, information about the local mechanical properties of various regions on the sample surface can be obtained more quantitatively [14]. 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 applied force can be controlled using the beam deflection technique while the cantilever is approached to and retracted from the sample. The pulsed force curve shows the variation of the force signal as a function of time. Therefore it contains all information about the tip-sample interaction. The resulting pulsed force curve obtained during the whole cycle is recorded at every image point [15]. In this mode quantified material properties can be mapped together with the topography of the films [16].

Although these imaging modes have been successfully applied in the characterization of heterogeneous materials, the differentiation of materials is only possible by comparing their material properties, such as local stiffness. This is mainly due to the lack of information about the exact contact area between tip and sample. If a composite material consists of compounds with similar mechanical properties, a clear assignment of the phases to the corresponding materials by AFM is quite challenging. To discriminate between materials with similar mechanical properties additional spectroscopic information is useful. On the macroscopic scale, Raman spectroscopy has become widely used for the characterization of chemical and structural features of

polymeric materials [17]. The tremendous importance of the Raman effect lies in the fact that the difference in energy between the elastically scattered photons and the Raman shifted photons is caused by the excitation or annihilation of a specific molecular vibration. This energy shift is characteristic for the type and coordination of the molecules involved in the scattering process. Raman spectra provide qualitative and quantitative information about various polymer features [18-20] such as:

- chemical nature: structural units, type and degree of branching, end groups, additives
- conformational order: physical arrangement of the polymer chain
- state of order: crystalline, mesomorphous and amorphous phases
- orientation: type and degree of polymer chain and side group alignment in anisotropic materials.

However, in most spectroscopy setups the spatial resolution is very poor because the exciting laser spot diameter is on the order of 100 μm .

Optical microscopy, on the other hand, is capable of providing spatial resolution down to 200 nm using visible light excitation. In a confocal microscope, the light from the sample is detected through a pinhole in the back focal plane of the microscope, giving rise to depth resolution and a strongly reduced background signal [21]. By combining a high throughput confocal microscope with an extremely sensitive Raman spectroscopy system, it is possible to obtain Raman spectra from extremely small sample volumes down to $0.02\mu\text{m}^3$. To collect high resolution Raman images, the sample is scanned point by point and line by line through the excitation focus [22]. Thus, the Confocal Raman Microscope (CRM) combines the chemical sensitivity of Raman spectroscopy and the high resolution of confocal microscopy, providing an ideal tool for the characterization of materials in the sub-micrometer range. To achieve the highest resolution, the CRM is extended with AFM capabilities. By simply rotating the microscope turret, the user can link the chemical information obtained by confocal Raman spectroscopy with the ultra-high spatial and topographical information acquired by AFM.

The aim of this paper is to demonstrate the capabilities of the Confocal Raman-AFM in terms of the characterization of a polymeric emulsion consisting of alkyd and acrylic latexes.

2 EXPERIMENTAL

Atomic Force Microscopy: The Confocal Raman-AFM from WITec (www.witec.de) was used for AFM imaging in ambient conditions ($24 \pm 2^\circ\text{C}$). For high resolution imaging the AFM was operated in AC-Mode with a damping of $r = 50\%$ where topography and phase images are recorded simultaneously. For these experiments FM cantilever (Nanoworld) with a nominal spring constant of 2.8 N/m and resonance frequencies ranging between 70-80 kHz were

used. Additionally the samples were imaged in Digital Pulsed Force Mode to designate areas of different mechanical properties. The DPFM was operated with contact mode cantilever with a nominal spring constant $k \sim 0.2\text{ N/m}$ at a modulation frequency of 1 kHz, with cantilever oscillation amplitudes up to 300 nm.

Confocal Raman Microscopy: The Confocal Raman-AFM was used to collect single Raman spectra from the pure emulsion components and Raman spectral images from the emulsion. A Nikon 100x (NA = 0.90) objective was employed for all measurements. For excitation, a NdYag laser (wavelength of 532 nm) was used. The Raman spectra of the pure polymers were recorded with an integration time of 100 ms. Polymer blends were analyzed in Raman spectral imaging mode. In this mode, high resolution Raman images are obtained by collecting a complete Raman spectrum at every image pixel (up to $512 \times 512 = 262144$ spectra) with typical integration times below 100 ms/pixel. The analysis of spectral features (sum, peak position, peak width etc.) generates the Raman images.

3 RESULTS AND DISCUSSIONS

Figure 1 shows a $10 \times 10\mu\text{m}^2$ AFM phase image of a dried alkyd-acrylic latex droplet. Two different phases can be clearly distinguished: a texture less phase, which forms elliptical structures and another phase consisting of spherical particles. The diameter of these particles is approximately $250 \pm 50\text{ nm}$.

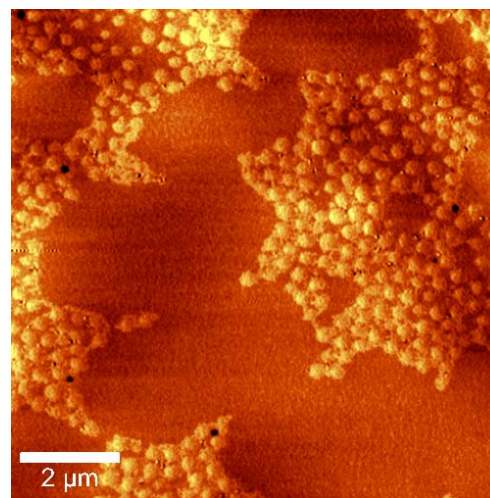


Fig. 1: High resolution AFM phase image of the dried emulsion of alkyd-acrylic latex.

The unique Raman spectra of alkyd and acrylic latexes are presented in Fig. 2. The variations in the Raman spectra make it possible to distinguish the two phases in the emulsion. The same sample area as shown in Fig. 1 was imaged in Raman spectral imaging mode by simply turning the microscope turret.

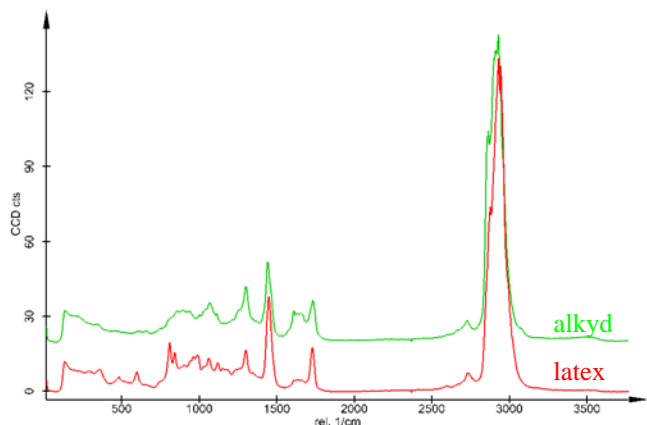


Fig. 2: Raman spectra of alkyd and acrylic latex.

In Raman spectral imaging mode, a complete Raman spectrum is recorded at every image pixel ($200 \times 200 = 40000$ spectra) with integration times below 100 ms. To assign the different polymers in the emulsion, not only were individual features (such as peak position, peak width, etc) of the Raman spectra employed, but the complete spectra of the materials by using basis spectra analysis. In this procedure each measured spectrum of the 2-dimensional data array is fitted by a linear combination of basis spectra using the least squares method [23]. Fig. 3 shows the color coded distribution of the two phases within the emulsion.

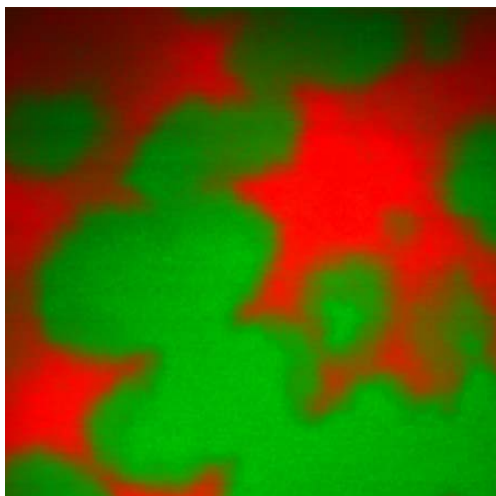


Fig. 3: Color coded Raman spectral image of the emulsion.

This image indicates that the two phases are immiscible and form well separated domains within the emulsion. The featureless elliptic structures from the AFM phase image can be associated unambiguously to the alkyd phase. The net formed by the small latex particles (Fig. 1) appears as second phase in the Raman spectral image in Fig. 3. Furthermore, by investigating the tip sample interaction, one can obtain not only the high resolution topographic

structure of the surface, but also information about the local mechanical properties of the sample components. Fig. 4 shows pulsed force mode (PFM) images of the emulsion.

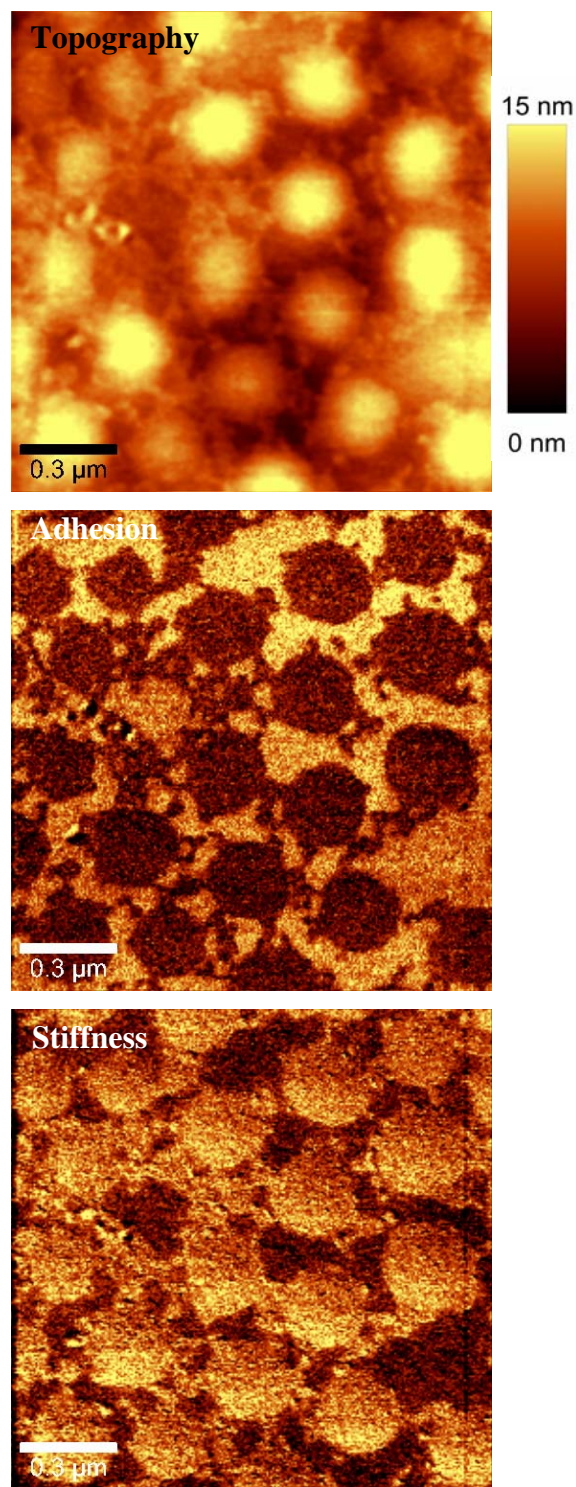


Fig. 4: Pulsed Force Mode images of the emulsion.

The topography image shows that the spherical acrylic latex particles are surrounded by a chain-like network. The simultaneously recorded adhesion and stiffness images show only a very small difference in adhesion (20%) between alkyd and acrylic latex and an even smaller stiffness difference of 2%. The detection of such small differences in material properties is only possible if a flexible cantilever with a spring constant below 0.5 N/m is used. The phase contrast observed in AC mode (Fig. 1) can be associated with the stiffness difference measured in pulsed force mode.

4 CONCLUSIONS

The Confocal Raman-AFM is a breakthrough in microscopy. It combines three measuring techniques in one instrument: a high resolution confocal optical microscope, an extremely sensitive Raman spectroscopy system, and an Atomic Force Microscope (AFM). Using this instrument, the high spatial and topographical resolution obtained with an AFM can be directly linked to the chemical information provided by confocal Raman spectroscopy. By simply rotating the microscope turret, the AFM is transformed into a confocal Raman microscope. With the confocal Raman microscope, it is possible to obtain Raman spectra from extremely small sample volumes and to collect high resolution Raman spectral images.

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