Probing Polymer Material Properties on the Nanometer Scale

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Introduction

Polymers play an essential role in modern materials science. Because of the wide variety of mechanical and chemical properties of polymers, they are used in nearly every industry. Knowledge about their physical and chemical properties on the nanometer scale is often required. However, some details about the phase-separation process in polymers are difficult to study with conventional characterization techniques because these methods cannot chemically differentiate phases with good spatial resolution without damage, staining, or preferential solvent washing.

One technique that can characterize 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 this imaging mode the cantilever is oscillated at its 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 potencial. 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]. Because 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 [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 (PFM), 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 information about the tip-sample interaction. Figure 1 shows two 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.
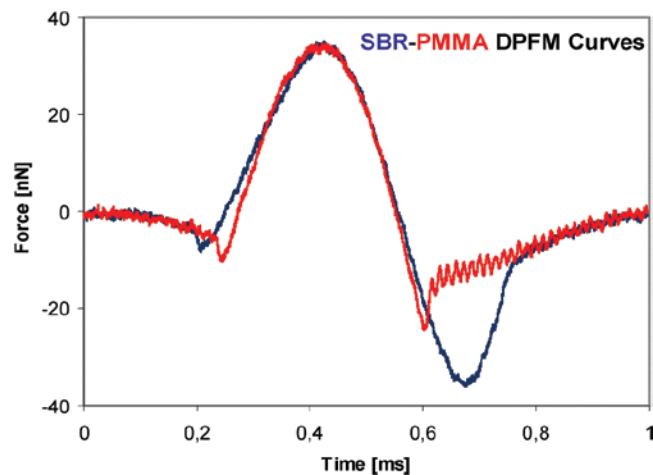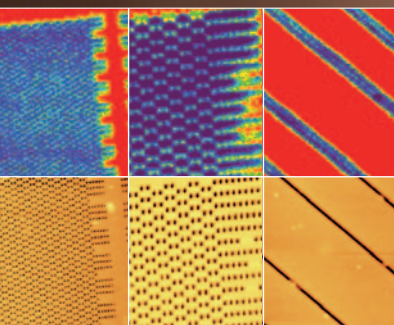

Figure 1: Characteristic PFM curves recorded on a stiff sample (red curve) and on a soft sample (blue curve).

In the Digital Pulsed Force Mode (DPFM), 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 sample [16]. Although these imaging modes have been successfully applied in the characterization of polymer blends, differentiation of phases is only possible by comparing their material properties, such as local stiffness. This is mainly because of the lack of information about the exact contact area between tip and sample.
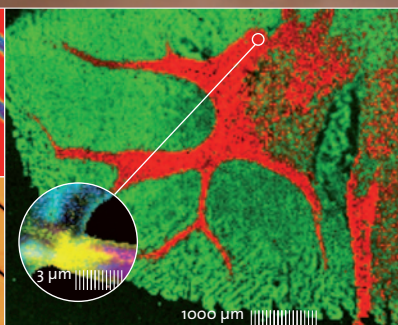
Raman spectroscopy is one of the standard characterization techniques used to uniquely determine the chemical composition of a polymer [17]. Modern polymer materials, however, are generally heterogeneous, in which various chemical components or polymorphs of the same chemical species can be present in a very small sample volume. For the analysis of such heterogeneous materials, the combination of Raman spectroscopy with confocal microscopy delivers information about the spatial distribution of the various chemical species with a resolution down to 200 nm. To collect high-resolution Raman images, the sample is scanned point-by-point and line-by-line through the excitation focus [18]. Thus, 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. To achieve higher image resolution, the confocal Raman microscope may be extended with the AFM. 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.
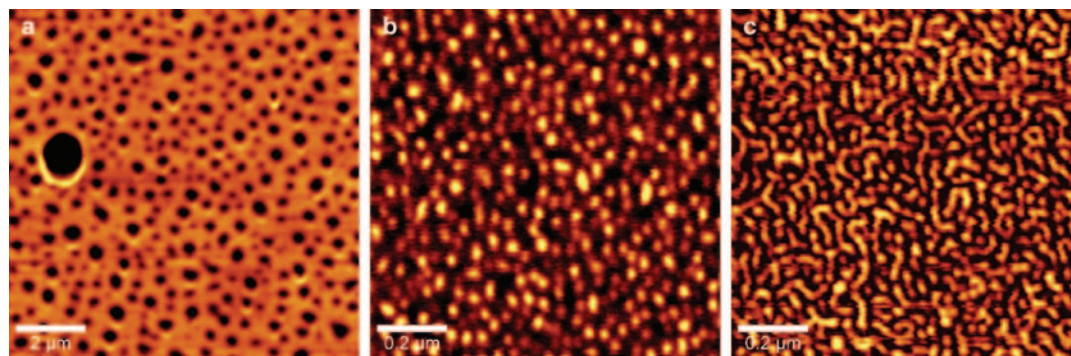
Figure 2: AFM images of pure polymer films spin-coated on glass substrates: a) PMMA topography image scan size: 10 × 10 μm², Δz = 130 nm, b) SBR phase image scan size: 1 × 1 μm², and c) SBS phase image scan size: 1 × 1 μm².

The aim of this paper is to demonstrate the capabilities of the confocal Raman-AFM for the characterization of thin heterogeneous polymer films. For this purpose we investigated two blends composed of immiscible polymers, which are either rubbery or glassy at room temperature.

Materials and Methods

Sample preparation. Two types of styrene-butadiene (SB) copolymers with a styrene content of 30% were acquired from Sigma Aldrich (www.sigmaaldrich.com). Triblock copolymer (SBS) with a molar mass MW of 74 kg/mol and statistical copolymer (SBR) with a molar mass MW of 380 kg/mol. These masses were measured using Gel Penetration Chromatography calibrated for polystyrene. Poly(methyl methacrylate) (PMMA) with a MW of 100 kg/mol was purchased from Polymer Standards (www.polymer.de). From these materials, polymer solutions were prepared by dissolving 10 mg of the polymer in 1 ml of toluene. Blends were prepared by mixing 2 ml of the PMMA toluene solution and 1 ml of the SBS or SBR solutions.

Thin films with a thickness of less than 100 nm were obtained by spin coating pure polymer solutions as well as blended ones on cleaned glass substrates (cover slides) using spinning velocities of 2000 rpm.

Atomic Force Microscopy. The confocal Raman-AFM alpha300 RA (www.witec.de) was used for AFM imaging in ambient conditions (24 ± 2°C). For high-resolution imaging, the AFM was operated in AC-Mode with a damping of r = 50%. In this imaging mode, topography and phase images are recorded simultaneously. Additionally, the samples were imaged in DPFM to designate areas of different mechanical properties. For all experiments "Arrow Force Modulation" cantilevers from Nanoworld (www.nanoworld.com) were used. The nominal spring constant of this cantilever is 2.8 N/m, and the resonance frequency ranges between 70–80 kHz. The DPFM was operated 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 polymer and Raman spectral images from the films of polymer blends. A Nikon 100× (NA = 0.90) objective was employed for all measurements.

For excitation, a frequency doubled Nd:YAG laser (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 imaging mode. In this mode, Raman images are obtained by collecting a complete Raman spectrum at every image pixel (up to 512 × 512 = 262144 spectra) with typical integration times below 50 ms/pixel. Spectral features (sum, peak position, peak width, etc.) were used to generate the Raman images (maps).

Results

The AFM topography image recorded on the glassy PMMA film (Figure 2a) reveals a porous structure that is not covering the glass slide completely. The pores are about 100 nm deep, with diameters ranging from 100–500 nm, leading to a net-like morphology of the film.

The SB films appear smooth without any corrugations in topography. However, high-resolution AC Mode phase images reveal a phase-separated structure in the rubbery polymers. In the phase images, brighter areas can be assigned to the harder (glassy) polystyrene domains, whereas the rubbery butadiene domains appear dark. In SBR, where small polystyrene blocks are statistically distributed, this phase forms spheres with a diameter of about 25 nm (Figure 2b). The long polystyrene blocks, present in the triblock copolymer SBS, aggregate to a wormlike structure as shown in Figure 2c. These variations in the polymer nano-structure are in good agreement with previously reported data [19, 20].

A non-destructive characterization with respect to the chemical composition of the polymers is possible using spectroscopy methods such as Raman spectroscopy (Figure 3). All polymer samples show characteristic band structures in the range 2800–3100 cm⁻¹, which is associated with C-H stretching and peaks at 1460 cm⁻¹, which is characteristic for C-H bending vibrations [21]. In addition, each polymer sample reveals additional characteristic peaks associated with molecular vibrations observed for the different polymers as summarized in Table 1 [25]. In PMMA, a band appears at 1730 cm⁻¹, which is correlated to the C=O stretching. The Raman spectra collected from the SB films show Raman bands characteristic for C=C stretching at 1635–1650 cm⁻¹. For the polymers SBS and SBR,

Table 1: Characteristic Raman Bands from Measured Spectra of Pure Polymer Films.

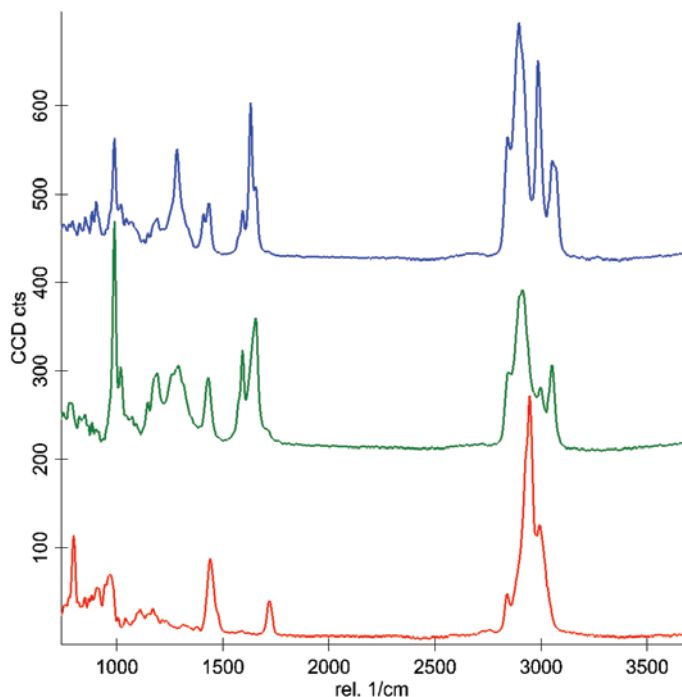| Raman Band (cm⁻¹)	Molecular Vibration	Observed in Raman Spectrum of:
1460	C-H bending	PMMA, SBS, SBR
1635–1650	C=C stretching	SBS, SBR
1730	C=O stretching	PMMA
2800–3100	C-H stretching	PMMA, SBS, SBR

Figure 3: Raman spectra collected from the pure films of polymers spin-coated on glass substrates: PMMA (red), SBR (blue), and SBS (green).

Raman bands can be found at the same wavenumber, indicating the same chemical composition. However, variations in the intensity of peaks, for example, at 1635–1650 cm⁻¹, reflect the structural differences of the two films as observed in the AFM images.

To gain more information about the mechanical properties of SBS and SBR, the two types of styrene-butadiene (SB) were blended with PMMA into PMMA-SBS and PMMA-SBR. In this case PMMA acts as a common reference for further DPFM measurements. For the unique identification of the polymeric species within the blend, the thin films of the polymer blends were first analyzed using Raman imaging. Areas of 20 × 20 μm²

of each blend were scanned and arrays of 200 × 200 spectra were recorded with an integration time of 50 ms per spectrum. To assign the different polymers in the film, the spectra shown in Figure 2 were used as basis spectra for the spectral analysis tool of the WITecProject software. In this procedure, each measured spectrum of the 2-dimensional spectral array is fitted by a linear combination of basis spectra using a least squares method. The weighting factor is proportional to the quantity of the material and is stored in the corresponding Raman image. A color-coded Raman image for each blend is shown in Figure 4; the color in the corresponding image matches the color of the spectra shown in Figure 3. The blend SBR-PMMA reveals round islands of PMMA with diameters ranging from 0.5–2 μm surrounded by the SBR phase. In the PMMA-SBS blend, PMMA forms a netlike structure, filled with the SBS phase. In both blends the distribution of PMMA and SB is complementary, proving that the polymer phases are immiscible and form an interface with the glass substrate.

In Figure 5, DPFM-AFM images of these heterogeneous blends are shown. On a scan area of 7 × 7 μm², the image of the PMMA-SBR blend (Figure 5a) reveals elevated circular islands with diameters in the range 500 nm to 2 μm (topography image). These islands are in good agreement with the PMMA phase resulting from Raman imaging (Figure 4a). The PMMA-SBS blend forms a netlike elevated structure (Figure 5b). This elevated topographic structure is in good agreement with the PMMA structure found in the Raman image in Figure 4b. In between the elevated features, a lower polymeric phase can be seen in both blends. Because SB and PMMA are immiscible, the different topographic structures can be associated with the various polymer phases. This gives strong evidence for the formation of a phase-separated morphology of the films due to dewetting.

Simultaneously recorded stiffness maps (Figures 5c and 5d) allow the assignment of topographical features to different polymer phases. The elevated topographic features also show higher stiffness (bright colors in the stiffness map) compared to the lower topographic regions, which have lower stiffness. Based on macroscopic mechanical properties, the stiffer phase corresponds to PMMA, which is in the glassy state at room temperature [22]. 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 [23].

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) using the relation [24]:
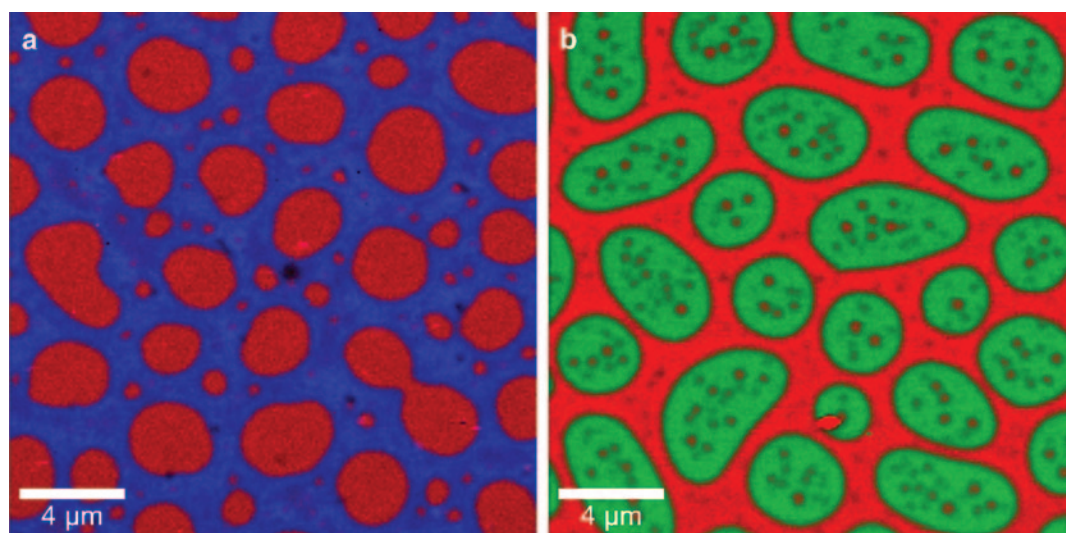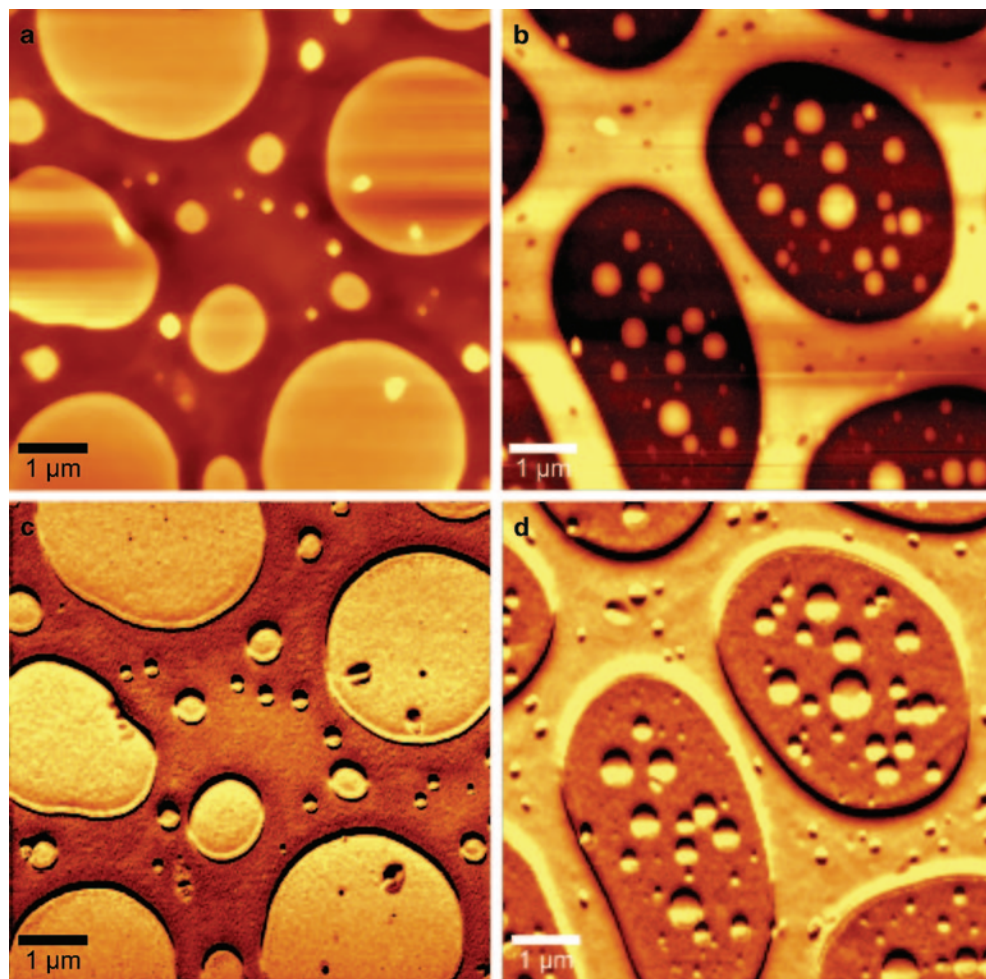

Figure 4: Color-coded Raman images of thin films of polymer blends: PMMA-SBR (a) and PMMA-SBS (b). The color in the image matches the color of the spectra shown in Figure 2.

Figure 5: DPFM measurements on polymer blend PMMA-SB: topography of blend a) PMMA-SBR, Δz = 40 nm and b) PMMA-SBS, Δz = 70 nm; simultaneously recorded stiffness maps c) PMMA-SBR and d) PMMA-SBS.

AFM phase images allow the identification of two styrene-butadiene copolymers (SBR and SBS) with different chain-microstructures. Well-separated domains are formed when these polymers are blended with PMMA and spin—coated on a glass substrate. The comparison of their mechanical properties estimated from DPFM local stiffness maps shows that SBS is 3.5 times stiffer than SBR. This is in good agreement with the observed fine structure on the nanometer scale, where within the triblock copolymer, the harder styrene blocks form more extended domains.

Raman spectroscopy allows the identification of chemically unique materials. In combination with a confocal microscope, the distribution of various polymer phases within the films can be determined. The analyzed thin polymer films (thickness < 200 nm) show clear Raman spectra of the corresponding polymers, indicating that a small sample volume (below 0.02 μm³) is enough to identify the chemical composition of the film. The analysis of the Raman spectral images obtained from the blended films show that there is no overlap of basis spectra at any image point. This indicates that the studied polymers do not cover each other but have formed an interface with the glass substrate while dewetting.
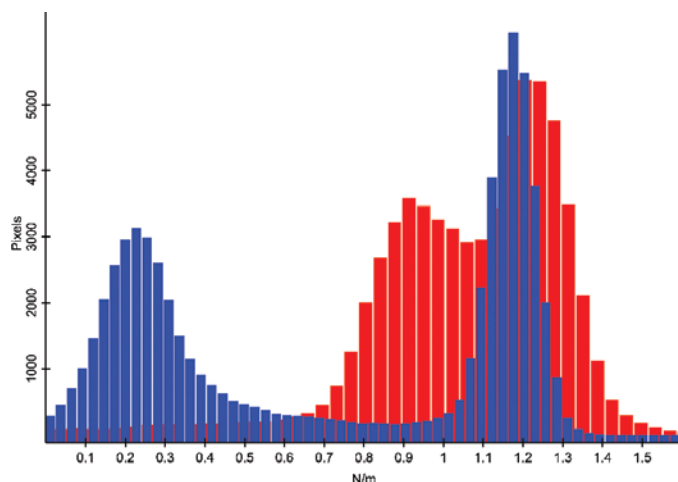
$$\text{Stiffness} = kSV_{\text{stiffness}}/[M(1 - \cos(2\pi f\Delta t) - SV_{\text{stiffness}}] \qquad (1)$$

where k is the spring constant of the cantilever, S is the sensitivity of the laser detection system, M is the modulation amplitude, f is the modulation frequency, and Δt is the repulsive tip penetration time.

After unit conversion of the stiffness maps, the histograms shown in Figure 6 are obtained. Both histograms show two peaks. The one 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 0.7 ± 0.1 N/m, and for SBR the average stiffness was 0.2 ± 0.1 N/m. Because 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. By comparing the stiffness data obtained for the PMMA-SB films, values indicate that SBS is stiffer than SBR by a factor of 3.5.

Discussion

The combination of Confocal Raman Microscopy with AFM was used for the characterization of polymer blends. AFM images reveal the topographic structure of polymer films with a resolution down to a few nano-meters. The high-resolution

Figure 6: Histogram of stiffness distribution of PMMA-SBR (red) and PMMA-SBS (blue).

Conclusion

The combination of AFM and confocal Raman microscopy in a single instrument enables the nondestructive characterization of heterogeneous materials. Surface topography can be imaged at high resolution while the various materials contributing to the surface composition can be chemically identified.

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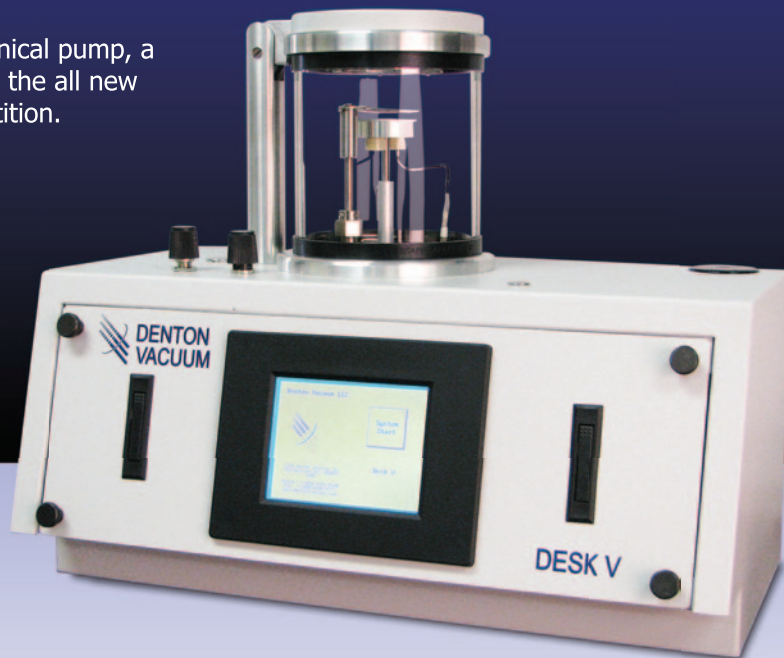
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