Application Note 52670

Investigating Composite Materials utilizing a Combined Raman-Atomic Force Microscope

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Introduction

Material science has benefitted greatly from atomic force microscopy (AFM), a surface technique that characterizes materials down to the nanoscale dimension. The information gained can include surface roughness to sub-nanometer scale, visualization of surface structures to the atomic-scale, and nanometer-scale mapping of local mechanical and electromagnetic properties. The latter include, but are not limited to: stiffness, adhesion, elastic modulus, surface potential, dielectric permittivity, and piezo-response. Although these properties can provide compositional imaging of heterogeneous materials, the lack of local spectral information limits a comprehensive understanding of the morphology. Comprehensive characterization of materials however often requires additional techniques to gain a more thorough understanding of the materials. In this application note we discuss the benefits of including Raman spectroscopy as a technique to characterize materials. Specifically, this note discusses the characterization of a composite material using fully integrated Raman-AFM instrumentation.

Raman-AFM Instrumentation

The Thermo Scientific™ DXR™ Raman microscope with the NT-MDT NTEGRA Spectra AFM was used to collect the data in this application note (Figure 1). This fully integrated system is capable of providing simultaneous Raman and AFM data acquisition. The two instruments are directly coupled via free-space optics, making this a Class 3b laser system. The laser beam, originating from the Raman instrument, is introduced into the AFM microscope from above where it is directed to the sample via a high numerical aperture 100x objective. The Raman scatter from the sample on the AFM stage is collected with a backscattering geometry and is directed back into the Raman microscope's spectrograph, where it is dispersed and focused onto a CCD detector. The Raman-AFM supports two excitation wavelengths, 532 and 633nm. Control of all instrument parameters such as laser power at sample, exposure time, and signal averaging, data acquisition modes for both AFM and Raman set in a single software interface.

Figure 1: The Thermo Scientific™ Raman-AFM system

Combining AFM and Confocal Raman Studies

Composite materials like graphite-reinforced-polymers are widely used in a variety of application areas. The addition of graphite into polymer materials improves mechanical strength. The amount and orientation of the graphite into the materials has a pronounced effect on the ultimate performance of these materials.

AFM provides detailed information about the surface roughness of graphite. AFM topological maps can also provide valuable information about the distribution of graphite within the composite material, but AFM measurements are not always conclusive because the technique lacks specificity with respect to the chemical nature of the materials being investigated. Additionally, AFM is a surface technique, limiting sub-characterization to the surface only.

In contrast, Raman microscopy provides detailed chemical insight into materials. The technique interrogates materials on a molecular level and is highly sensitive to structure and bonding, making identification of materials based upon their chemical composition possible. In addition, Raman microscopy can analyze materials below the surface when used in confocal mode. Confocal Raman measurements provide unique chemical information by placing an aperture at the back focal plane of the microscope which improves the spatial resolution of the microscope and enables depth profiling by acquiring spectra as the laser focus is moved into a transparent sample. In the Raman-AFM system, the vertical displacement of the focus is performed with a piezo-scanner, effectively moving the sample through the focal plane of the objective.

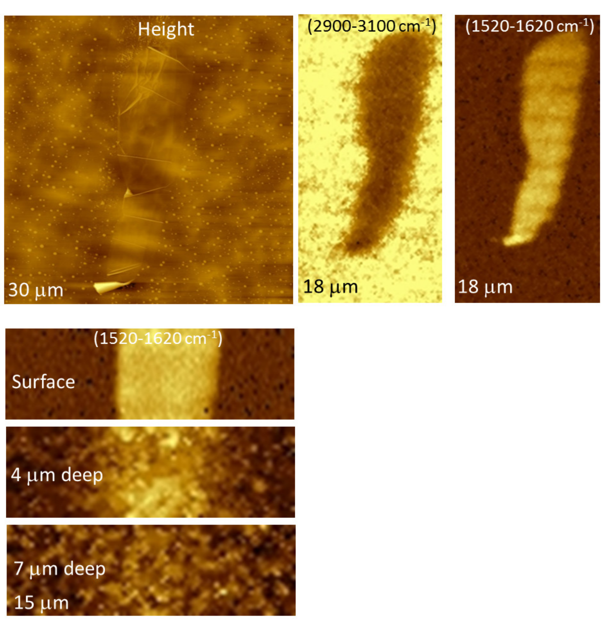

Figure 2: 2a-d. (a) Height image of Polyvinylidene fluoride (PVDF) film with a graphite flake. (b-c) Raman maps of PVDF and graphite. (d) The maps of the graphite band at different depth.

Figure 2a shows the topological AFM map of a sample containing graphite flakes on PVDF. The AFM topological image shows a polymer surface area with a flat-lying "flake" in the center. This height map demonstrates the detail that can be obtained by AFM illustrating the surface roughness of a sample. The flake is distinguished by submicron features that appear as "wrinkles" and by an absence of grainy structures. Surface roughness in composite materials is important as it influences the mechanical properties of the material. The surface roughness can increase the interfacial adhesion between materials of the composite thereby improving the mechanical properties of the composite. This topological map, however, does not distinguish the identity of the flake as graphite. For unambiguous identification of the feature, we turn to Raman microscopy.

Figures 2b-c are co-localized images from the same sample presented in figure 2a. Clear differentiation between the flake and PVDF is obtained in the Raman images at wavenumber regions specific for the PVDF and graphite components: the 2900 – 3100 cm^{-1} region (C-H) characterizes PVDF and the 1520-1620 cm^{-1} region (G-band) – graphite. Confocal Raman images taken at a series of depths are presented in figure 2d. The images show the intensity of the graphitic band of graphite occurring in the region of 1520-1620 cm-1 band and defines that the flake thickness is approximately 4mm. The confocal spatial resolution is dependent upon the excitation wavelength used and the numerical aperture of the objective lens. For this measurement the spatial resolution is ~2mm, limiting Raman's ability to be used as a sensitive probe for investigating surface roughness and illustrates the complementary relationship between AFM and Raman techniques.

Conclusion

It was demonstrated how highly detailed images can be obtained from a combined Raman-AFM microscope, capable of providing complementary information to the characterization of composite materials. Here, it was shown that AFM provides insight into the surface roughness and confocal Raman measurements provides detailed chemical identification and component thickness information.

References

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