

The Characterization of Polymer Blends Using a Combined Raman-AFM Microscope

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Key Words

Atomic Force Microscopy, Polymer Blends, Raman Microscopy

Introduction

The field of engineered polymers has become increasingly more important to industry over the last few decades. The goal of engineering a polymer is to impart specific, desirable properties to an existing material, depending on the intended use. The goal may be to strengthen the polymer, make it less brittle, more heat tolerant, or facilitate processing and manufacturability. Mixing two polymers, or blending, is one strategy to accomplish this goal. In a polymer blend, the complex interplay between two dissimilar polymers can result in materials possessing valuable properties, exceeding those of the individual component polymers.

For example High Impact PolyStyrene (HIPS) is an immiscible polymer blend consisting of polystyrene and polybutadiene. By blending a small proportion of polybutadiene into polystyrene, the formerly stiff and brittle polystyrene transforms into a more ductile and tough material. Mixing two different polymers is seldom complete, and phase separation or partial mixing often results when most polymers are blended. These polymer mixtures are referred to as immiscible blends. The shape made by the two phase separated polymers and their arrangement in the blend is termed the morphology of the blend. The morphology of a particular blend will impact the properties and will be influenced by the relative amounts of polymer components and mixing conditions.

Understanding and controlling the interaction between components in these heterogeneous materials requires interrogating these materials on a micron or even submicron scale. The development of atomic force microscopy (AFM) has opened new frontiers in the study of materials at the micron, submicron and even nanoscale. At these scales, AFM is used for high-resolution surface profiling and quantitative studies of local mechanical and electromagnetic properties. However, additional critical information may be obtained through the use of other analytical techniques such as extension of AFM measurements with a Raman instrument. The integration provides simultaneous, spatially coincident, and unambiguous molecular information that complements the topological, mechanical, and electromagnetic information that AFM provides.

Polymer Blends, AFM and Combined Raman-AFM measurements

Component distribution mapping and identification of multi-component materials becomes difficult as size begins to approach the micron and sub-micron scales, because x , y , and z . Although AFM provides highly detailed material property based information (i.e. surface topology, mechanical, electromagnetic) in the images it does not offer unambiguous identification of components and respective distribution. Component identification can be achieved with Raman microscopy, because individual polymers exhibit unique spectra, which are then used for identification and quantitation. The ability to identify individual components of polymer blends in combination with AFM imaging provides valuable information that explicitly establishes the chemical-morphology-property relationship in materials.

Integrated Raman-AFM instruments are capable of directly measuring chemical information that can be assigned to the features observed in the AFM images. The measurement taken by this integrated instrument is called co-localized Raman-AFM.



Figure 1: Thermo Scientific DXR Raman microscope integrated with an NT-MDT atomic force microscope

Raman-AFM Instrumentation

Co-localized Raman-AFM is a standard far field, diffraction limited, confocal Raman experiment measured at the sample. The Raman spectra are collected at the same time and are spatially coincident with the recording of the AFM measurement. Figure 1 shows the integrated Thermo Scientific™ DXR™ Raman microscope and NT-MDT NTEGRA Spectra AFM used to collect the co-localized Raman-AFM images in this application note. In the combined instrument, through-space optics are used to direct a collimated laser beam from the Raman microscope to the entrance of the AFM. The available excitation wavelengths for Raman-AFM measurements are 633nm and 532nm. In the AFM microscope, the beam is focused on the sample with a lens having numerical aperture (NA) of 0.75 and is positioned on the area of interest on the sample or at the AFM tip apex with

a piezo-driven mirror. The Raman scattered light from the sample positioned on the AFM unit is collected at 180 degrees and sent via the same through-space optics back to the spectrograph entrance on the Raman microscope. During the AFM measurement, the sample Z-axis position is adjusted as the sample is moved relative to the AFM tip and Raman laser. This Z-axis adjustment keeps the sample in constant, optimum Raman focus providing Raman measurements that are spatially coincident in the x -, y -, and z -planes with the AFM image.

Co-localized Raman-AFM Measurements

Raman spectroscopy provides valuable complementary information to the AFM image when the integrated instrument is operated in co-localized Raman-AFM mode. To illustrate this, a polymer blend of two immiscible components was prepared by mixing polystyrene (PS) and poly vinyl acetate (PVAC) together. Figures 2a-b show the Raman bands at the PVAC-specific region: 2839-2980 cm^{-1} and PS-specific region: 3000-3140 cm^{-1} , and clearly illustrates the distinct differences between the two polymers, which can be used to identify the distribution of the two polymers in the blend. The AFM height image of the PS/PVAC blend film on Si (Figure 2c) shows the perforated protrusions and the matrix. This morphology hints at a micro-phase separation of the individual constituents. A comparison of the intensity maps for the chosen Raman scattering bands points out that the protrusions are composed of PS and the matrix PVAC (Figures 2d-e). Numerous “droplets” are seen between the protrusions in the AFM height image but only the larger of these features are distinguished in the Raman map in Figure 2e since the smaller features are below the diffraction limit of the resolution of Raman microscopy.

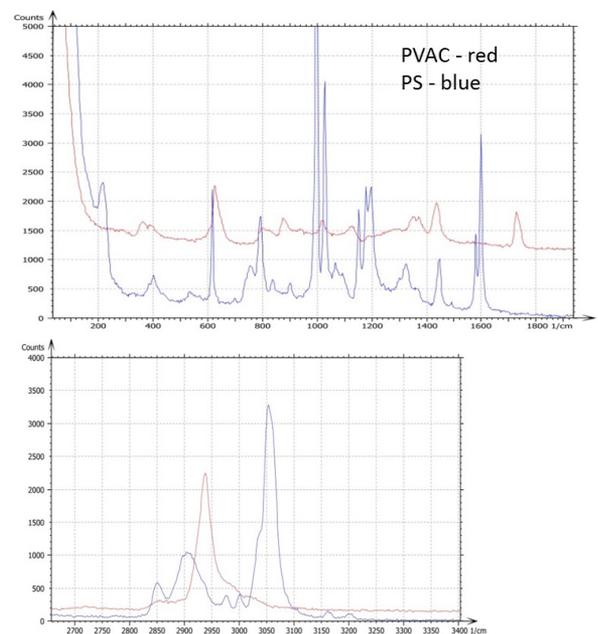


Figure 2a and 2b: (a) - (b) Raman scattering spectra of PVAC and PS polymers in two spectral regions.

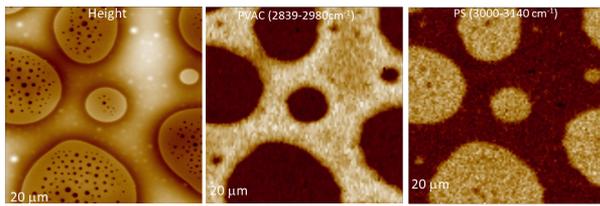


Figure 2c-e : (c) AFM height image of a film of the immiscible PS/PVAC blend. (d) - (e) Intensity maps of Raman scattering bands specific to PVAC and PS.

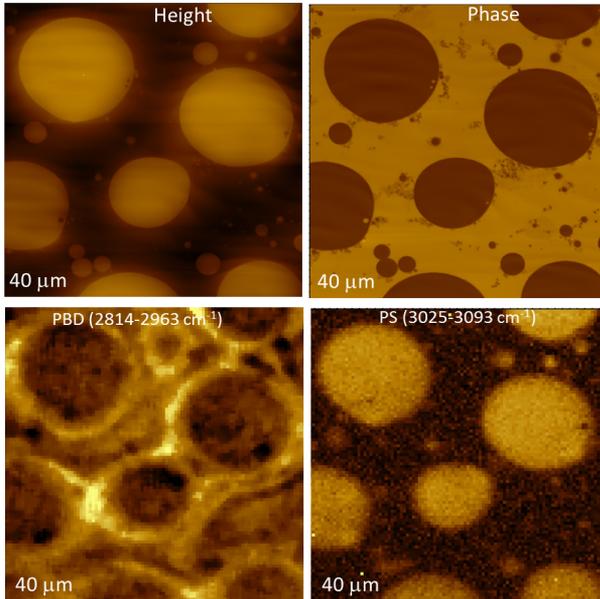


Figure 3a-d: (a) – (b) AFM height and phase images of a film of PS/PBD blend. (c) – (d) Maps of the intensity of Raman scattering bands specific to PS and PBD.

Prior to the development of Raman-AFM microscopes, compositional AFM imaging of polymer blends was performed using phase contrast imaging [1], which uses phase images to differentiate between individual components of polymer blends due to phase changes that the probe detects during interaction with dissimilar materials. The AFM height and phase contrast images of a film of an immiscible blend of PS and polybutadiene (PBD) blend are shown in Figures 3a-b. The binary contrast of the phase image suggests that the round elevated domains and surrounding matrix seen in the AFM height image can be assigned to different components of the blend. Generally, the assignment of the phase changes to the components with different stiffness or adhesion is difficult. However, correlations between mechanical properties of polymer materials and phase contrast microscopy have been found experimentally, and are often employed to classify locations with different phase contrast. As discussed above, the addition of Raman scattering measurements to AFM provides a direct means for chemical identification of the components of the polymer blends. The Raman maps of the scattering bands in the region of C-H bonds (2814 - 2963 cm⁻¹ PBD) and (3025 – 2094 cm⁻¹ PS) indicate that the matrix is com-

posed of PBD and the elevated protrusions are identified as PS (Figures 3c-d). A comparison of the phase image, shown in Figure 3b, and the Raman spectral map shown in Figure 3d, shows that phase imaging achieves higher resolution than Raman spectroscopy.

The differences in the spatial resolution of AFM and conventional Raman mapping is also illustrated by studying a film of a heterogeneous blend of Polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA). The Raman spectra of the polymers (Figure 4a), contain a number of bands which can be used for component identification in binary blends made from these materials. We have chosen the band of 770 cm⁻¹ – 800 cm⁻¹ (C=O) for identification of PVDF and the band of 1700 cm⁻¹ – 1760 cm⁻¹ for identification of PMMA. Both bands are well resolved in the Raman spectrum of the film of PMMA/PVDF blend in Figure 4b.

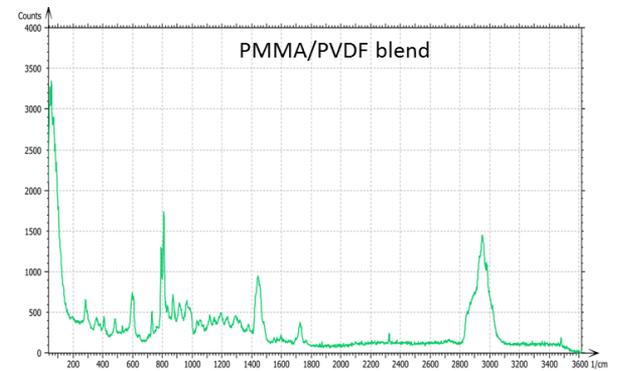
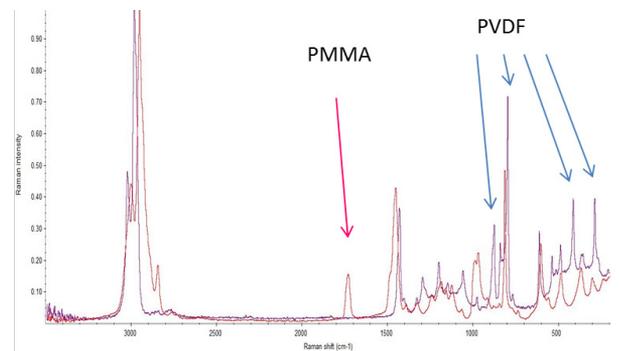


Figure 4a-b: (a) Raman scattering spectra of PMMA (red) and PVDF (blue). (b) Raman scattering spectrum obtained on a film of PMMA/PVDF blend.

The Raman-AFM data obtained from this film are shown in Figure 5a-c. The AFM height image shows that the film is characterized by a combination of small sub-micron particles which densely cover the entire area, and larger round-shaped domains with dimensions in the few micron range. The Raman scattering maps show variations of intensity of PMMA- and PVDF-related bands and distinguish only the round-shaped domains and areas in between. These domains are identified as PVDF and the surrounding matrix is composed of PMMA, respectively. Small particles covering the surface are not apparent in the Raman scattering maps, making their identification quite challenging. In this case we would expect that tip-enhanced Raman scattering (TERS) measurements will be able to provide more detail about the identity of these smaller particle by virtue of the sub-100nm spatial resolution capabilities of the TERS technique.

Conclusion

Polymer blending is making possible materials with drastically improved performance characteristics. The complete characterization of polymer blends requires multiple techniques to understand the complex interplay between components in these mixtures. Atomic force microscopy and Raman spectroscopic mapping provide complementary topological, mechanical and chemical information that is crucial to understanding the chemical, mechanical and morphological relationship of polymer blends. Specifically, integrated Thermo Scientific Raman-AFM system provides a valuable tool for the characterization of polymer blends. The co-localized Raman-AFM measurement demonstrates that vital chemical information is provided to the resulting images that is otherwise critically lacking in a stand-alone Raman or AFM measurement.

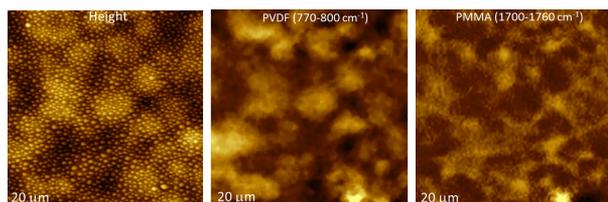


Figure 5a-c: (a) AFM height image of a film of PMMA/PVDF blend. (b) – (c) Maps of Raman scattering intensities of the PVDF- and PMMA- related bands, respectively.

References

1. S. Magonov, in Encyclopedia of Analytical Chemistry (R. Meyers, Ed.), pp. 7432-91, John Wiley & Sons Ltd, (2000).



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