

Application Note AN M110

Reverse Engineering of Materials and Polymers Using Infrared and Raman microscopy

Product development in the industrial world can be a long and expensive process. In a competitive market, the window of opportunity for significant revenue can close before a new competitive product could even exit the development cycle. The obvious solution to keeping up in a competitive market is to acquire the product in question, disassemble it, and analyze it. This reverse engineering process can greatly expedite the immediate introduction of competitive products into the marketplace. There are many tools for determining the physical properties of materials that will not be discussed here. The chemical properties can be readily determined by utilizing analytical tools such as gas phase chromatography, atomic absorption spectroscopy and many others. Molecular spectroscopy (infrared and Raman) is among the most powerful tools in the reserve engineering process. Each molecule has a unique infrared and Raman signature providing great specificity in the identification process. The distribution of components can also be determined by collecting area infrared and Raman images of the product in question.

Elastomers are used in a variety of products ranging from aircraft to common household products to toys. There are many different types of elastomers, usually tailored to meet the demands of the application. These can be broken down

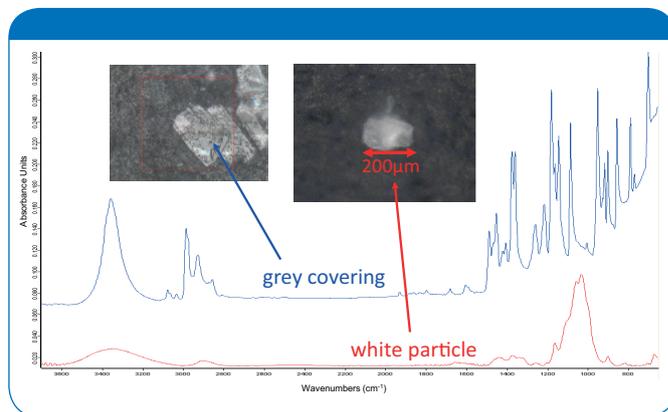


Fig. 1: Brightfield image of an elastomer with a gray coating (left image), a white contaminant particle (right image), and their respective infrared spectra.

into two different categories, unsaturated and saturated rubbers. Polyisoprene, polybutadiene, and nitrile rubbers are examples of common unsaturated rubbers and common saturated rubbers are silicone, polyacrylic, or ethylene propylene based. Figure 1 shows two pictures of the same elastomer with two contaminants. Contaminants can provide insight to the manufacturing process. These particles were analyzed using an attenuated total reflectance (ATR) objective with a germanium crystal mounted on a

HYPERION infrared microscope (Bruker Optics, Inc.) at 4 cm^{-1} spectral resolution. The field aperture on the microscope was projected through the ATR crystal to improve the spatial resolution to 4x better than the wavelength of light and used to define the analysis area ¹⁾. The resulting infrared spectra, also shown in Figure 1, were collected in 30 seconds and analyzed using a condensed phase database provided by Biorad Informatics ²⁾. The gray covering was exactly identified as tetramethyl-xylene-diol, a plasticiser, and the small white particle was identified as cellulose.

Multi-layer polymer films can be an important part of maintaining product integrity. Products from food, pharmaceuticals, consumer products, etc. are delivered in polymer film packaging. These films can be important for preventing exposure to oxygen, ultraviolet illumination, or other environmental factors depending on the product in question. The design and fabrication of polymer films is typically a complex and costly process that can affect actual and perceived product quality. For example, a product that suffers discoloration due to ultraviolet illumination may still be viable, but be undesirable from a consumer viewpoint. A polymer film from a food product was obtained and carefully sectioned. The brightfield image is shown on the left in Figure 2.

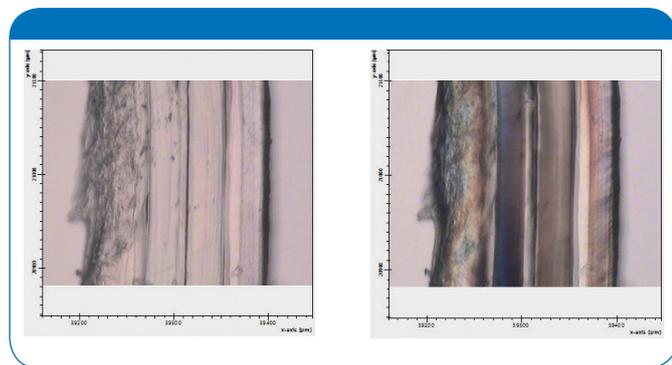


Fig. 2: Brightfield image (left) and polarized light image (right) of a multilayer polymer film after sectioning.

Determination of the number of layers using the brightfield image is difficult, but the polarized light image greatly enhanced the contrast and revealed six layers. Many polymer films and fibers are anisotropic thereby greatly improving the contrast. Infrared chemical images from the film were collected in transmittance also at 4 cm^{-1} spectral resolution using a 64×64 pixel focal-plane array (FPA) detector on the same infrared microscope. The resulting chemical images are shown in Figure 3, where each image represents the integration of absorption bands across the full image. The total data collection time was less than 1 minute for a total of 4096 spectra. Each layer is readily identified by comparison of the corresponding infrared spectrum with known references. Layers 1, 3, 5, and 6 were readily identified as polyethylene and layers 2 and 4 as polyamide. Layers 5 and 6 appear indistinguishable under normal brightfield illumination, but were resolved under polarized light. The infrared spectra of layers

5 and 6 are identical. It may be that these layers vary in density by a small amount. Lastly, there is some channeling present in the infrared spectra from layer 2, as evidenced by the superimposed sine wave that is highlighted in Figure 4. The thickness of the film is subsequently calculated to be 27 microns from the sine wave using Equation 1, where N is the number of fringes, n is the refractive index of the compound(s), and $\Delta\nu$ is the spectral range.

$$\text{Equation 1: Thickness} = N / (2n\Delta\nu) \text{ } ^3)$$

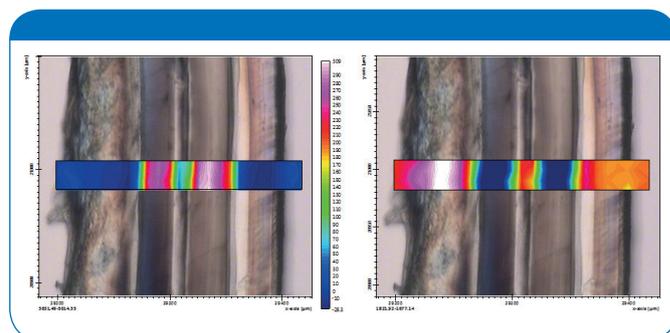


Fig. 3: Infrared chemical images collected from a multilayer polymer film. The left image resulted from integrating the infrared spectra from $3631\text{-}3014\text{ cm}^{-1}$ and the right image from $1822\text{-}1677\text{ cm}^{-1}$.

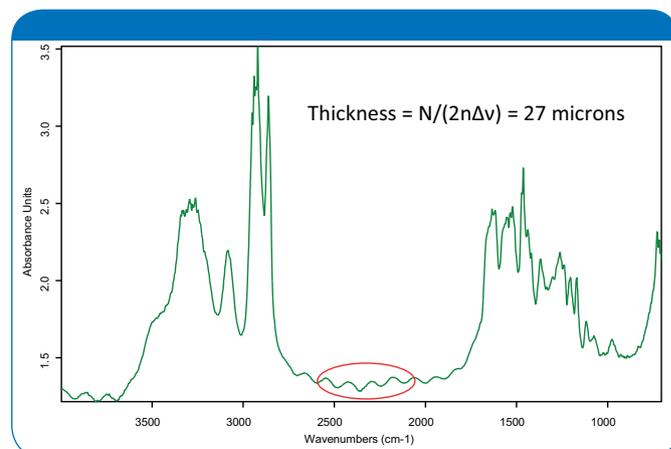


Fig. 4: A representative infrared spectrum from area 2 is shown with the channeling interference highlighted.

In contrast to the previous example that required thin sectioning, confocal Raman provides the ability to profile the depth directly from the top. This allows multilayer films to be analyzed very quickly without any sample preparation. Figure 5 shows the depth image collected from a polymer film using a SENTERRA II confocal Raman microscope (Bruker Optics, Inc.). The z-axis step size was set to 0.5 microns and the data was collected at $\sim 3\text{ cm}^{-1}$ spectral resolution for 15 seconds per point for a total depth profile of 20 microns. A $100\times$ dry objective with an NA of 0.9 was used with 532nm laser excitation. The total time for the data collection was 10 minutes. The depth of field for Raman microscopy is predominantly limited by the numerical aperture of the objective and in this case is about 1 micron ⁴⁾.

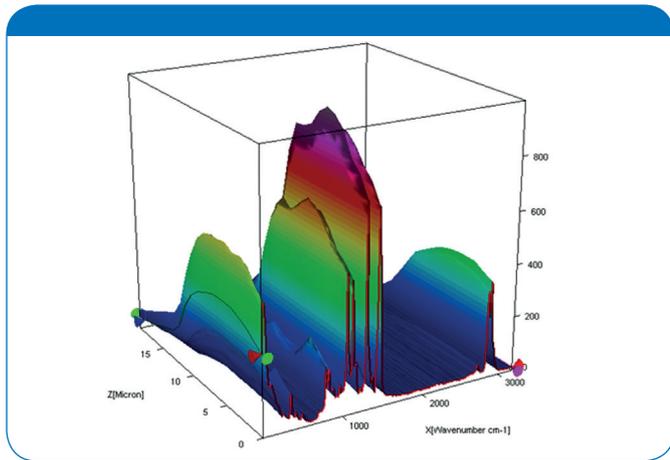


Fig. 5: A Raman depth profile image collected from a multilayer polymer film. The z-axis represents the depth of field.

In assessing the depth profile image six layers were readily detected. The same procedure can be performed for a variety of applications including profiling coatings on optics, documents, paint layers, lubricants, etc. In some cases the signal drops off as a function of depth, due to scattering and refraction. This is easily corrected by performing a min-max normalization on the image, which is easily performed when necessary.

Another application of interest is the analysis of the solid state vibrational modes of materials. These modes are lower energy and accessed in the far infrared region of the spectrum, typically $200\text{--}50\text{ cm}^{-1}$. Many times materials that will have very similar middle infrared or Raman spectra may have significant differences in their solid state modes. Products that fall into this category are pharmaceutical products (tablet and powders), inorganic compounds, polymer films, and other products possessing varying degrees of crystallinity or amorphous structure. Figure 6 shows the phonon region of the Raman spectra collected from two adjacent layers in a multilayer polymer film. While the resulting bands from the rest of the spectra range are virtually identical, these differences in the phonon region make it possible to confirm that there are two separate layers rather than one larger layer. For polymer and pharmaceutical products, variations in temperature and humidity at the time of formation

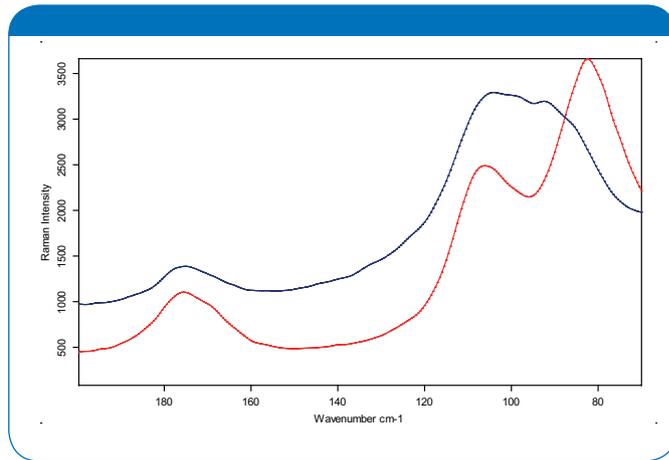


Fig. 6: Raman spectra collected from adjacent layers in a multilayer polymer film.

can affect structure. This may affect important product characteristics such as translucence, tensile strength, solvation, etc.

In conclusion, infrared and Raman spectroscopy have proven to be valuable tools in the characterization of materials and products. The capabilities of infrared and Raman microscopes continue to improve providing greater sensitivity and spatial resolution in characterizing small samples.

Tague Biographical Sketch

Dr. Tague is the Applications Manager for Bruker Optics, Inc. He received his Ph.D. from the University of Utah and B.S. from the University of Texas at San Antonio both in Chemistry. He is also a member of the Advisory Boards of the Metropolitan Museum of Art and EOS Photonics.

References

- [1] S.B. Ippolito, B.B. Goldberg and M.S. Unlu, J Appl Phys 97,053105, 2005.
- [2] <http://www.biorad.com>.
- [3] Fourier Transform infrared Spectroscopy, P.R. Griffiths and J.A. de Haseth, Wiley and Sons, 1986.
- [4] <http://www.olympusmicro.com/primer/digitalimaging/deconvolution/deconresolution.html>.

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