Technical Note: 51740

Raman Mapping of Single-walled Carbon Nanotube Distribution on Phase Separated Polystyrene and Polymethylmethacrylate

Paulette Guillory, Timothy O. Deschaines, Thermo Fisher Scientific, Madison, WI, USA

Key Words

- Nicolet Almega XR
- Carbon Nanotubes
- Chemical Imaging
- Polymers
- Raman Mapping
- Raman Spectroscopy

Introduction

Phase separated polystyrene (PS) and polymethylmethacrylate (PMMA) polymers were vapor deposited onto silicon. To ensure that these materials were indeed phase separated, dispersive Raman mapping was used to show the distribution of the polymers. The size of the structures varied from 10-50 microns in width. Single-walled carbon nanotubes (SWCNT) were then vacuum-deposited onto the surface. While modeling suggested that the SWCNT would preferentially deposit onto the polystyrene, this could be easily verified by using Raman spectroscopy. The mapping data shows where the SWCNT were deposited and their coverage onto the silicon/polymers. Using Raman spectroscopy offers several advantages over FT-IR analysis, including higher spatial resolution (down to 1 micron or smaller) and no need for a reflective substrate for the analysis. Dispersive Raman analysis has long been considered an optimum method for carbon nanotube identification and classification.

Dispersive Raman spectroscopy, also called visible Raman spectroscopy, uses visible (400-785 nm) lasers for the excitation of the sample. The use of visible lasers allows for higher spatial resolution (down to less than one micron) and higher sensitivity of the Raman emission compared to FT-Raman, since Raman emission is proportional to $1/\lambda^4$. Raman spectroscopy is sensitive to both chemical and physical properties of materials and the unique selection rules of Raman give a molecular fingerprint of the material which is well suited to identification of materials. Raman spectroscopy is highly sensitive to molecular backbone and branching structures which make it well suited for polymer identification

Experimental

The Thermo Scientific Nicolet Almega XR, shown in Figure 1, was used for this analysis. The Nicolet™ Almega™ XR is a dispersive Raman instrument that can be configured as a dual-laser system, with high spectral resolution. The Almega also offers high spatial resolution (down to 1 micron) and advanced chemical mapping and imaging capabilities. The Almega XR uses a research-grade microscope that features brightfield and darkfield illumination, as well as visible polarization, fluorescence and differential interference contrast illumination enhancements. Both brightfield and darkfield illumination modes were used to visually analyze the samples in preparation for data collection. Data collection, processing, and analysis was performed using the Thermo Scientific OMNIC

Figure 1: Nicolet Almega XR Dispersive Raman spectrometer

software suite, including OMNIC™ Atlμs™. The DXR Raman microscope is also ideal for this application especially because of its precise laser power control which is beneficial when working with carbon nanotubes.

Data and Analysis

The Almega XR was used to analyze and identify the regions containing the polymers and the SWCNT. OMNIC Atlμs mapping software was used to "draw" the regions in the mapping window. Area mapping can be used to create a chemical image of the map area. This chemical image can be used for component identification, location and concentration analyses.

The chemical image, shown in Figure 2a, was collected using the 532 nm laser, with 8 second exposures per step, for a total of 1271 collection points. The chemical image shows the spectral intensity of a specified spectral band, in this case the 1605 cm^{-1} Raman band. The intensity of the Raman band is shown in varying colors, with red being the most intense and blue indicating virtually no spectral intensity for that Raman band. The band at 1605 cm^{-1} is the carbon–carbon stretching frequency that is prominent for the polystyrene structure. Figure 2b shows the chemical image overlaid onto the visual image captured by the video camera. The red, green and yellow regions indicate high intensity of the 1605 cm^{-1} band signifying polystyrene and the blue areas show little intensity showing little to no polystyrene. Figure 2c shows the spectrum at the crosshairs (in Figure 2a), along with a polystyrene reference spectrum.

Thermo SCIENTIFIC

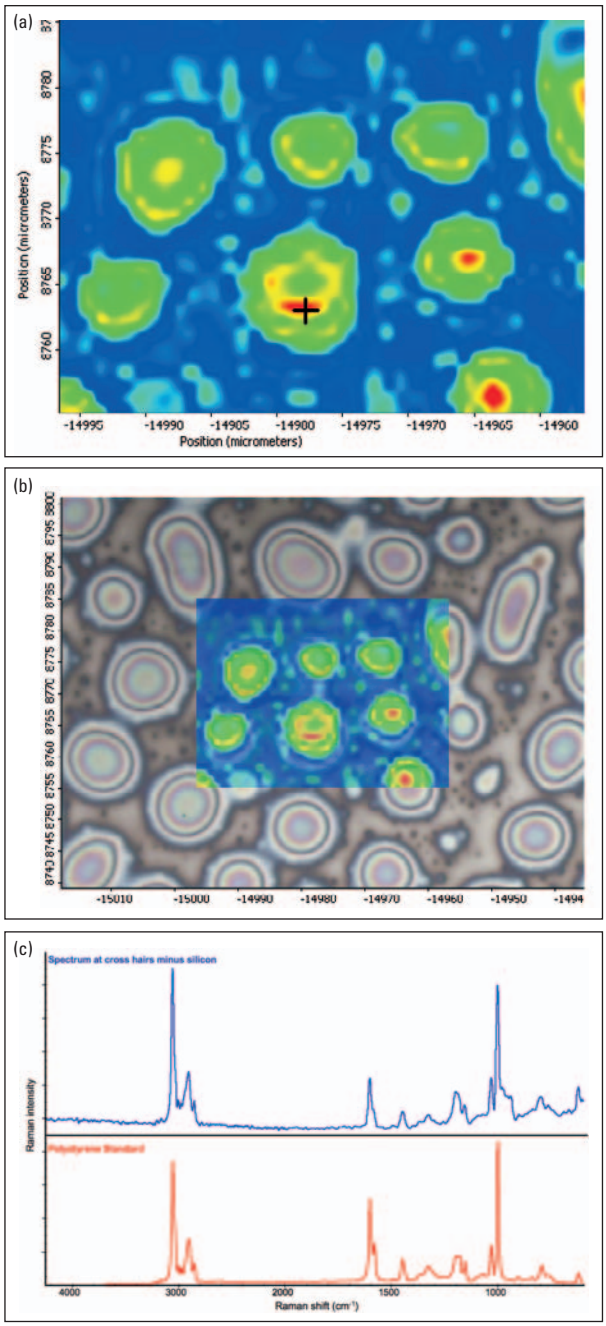

Figure 2: a) Chemical map, or chemigram, of the polystyrene and polymethylmethacrylate sample. Regions that are red, yellow, and green represent higher peak intensity for the 1605 cm^{-1} band associated with polystyrene. b) Overlay of the chemical map and the visual image of the sample. c) Comparison of the sample spectrum (from the location of the cross-hairs in Figure 2a) with the silicon spectrum subtracted, and the spectrum from a polystyrene standard.

Single-walled carbon nanotubes (SWCNT) have distinctive spectra, shown in Figure 3, dominated by a broad Raman band at approximately 1598 cm^{-1}. This band is associated with the G band or Tangential mode which corresponds to the C-C stretching mode in the graphitic plane. There is a small band at 1327 cm^{-1} that is associated with the D band, or the defect mode that represents the presence of disordered carbon. Finally the bands at 267, 248 and 185 cm^{-1} are the radial breathing modes (RBM) and these frequencies can be used to estimate the diameter of the carbon nanotubes.

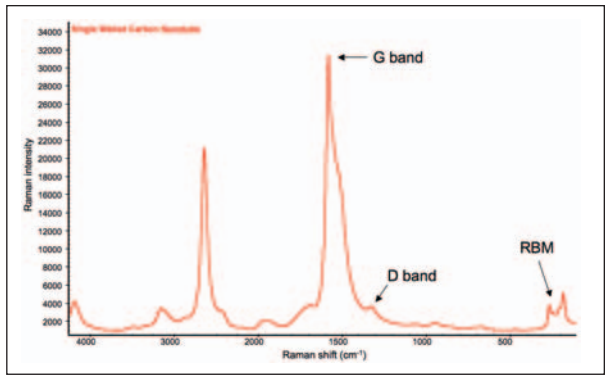

Figure 3: Spectrum of a single-walled carbon nanotube sample, with arrows indicating the locations of the G band, the D band, and the radial breathing modes (RBM).

An area map of the silicon PS/PMMA sample with SWCNT added was also analyzed. A correlation profile of the SWCNT spectrum was calculated from the map data. The correlation profile calculates the correlation coefficient between the map spectra and the specified reference spectrum; in this case the SWCNT spectrum was used. The correlation intensities, seen in Figure 4, are the correlation coefficient values. A higher intensity value indicates a greater similarity to the SWCNT reference spectrum. A correlation value of 1.0, or a red color, indicates the spectrum from that region of the map and the reference spectrum are nearly identical. As can be seen in Figure 4, the SWCNT preferentially aggregate to the PS versus the PMMA portions of the sample, although not all PS has SWCNT association. If we zoom

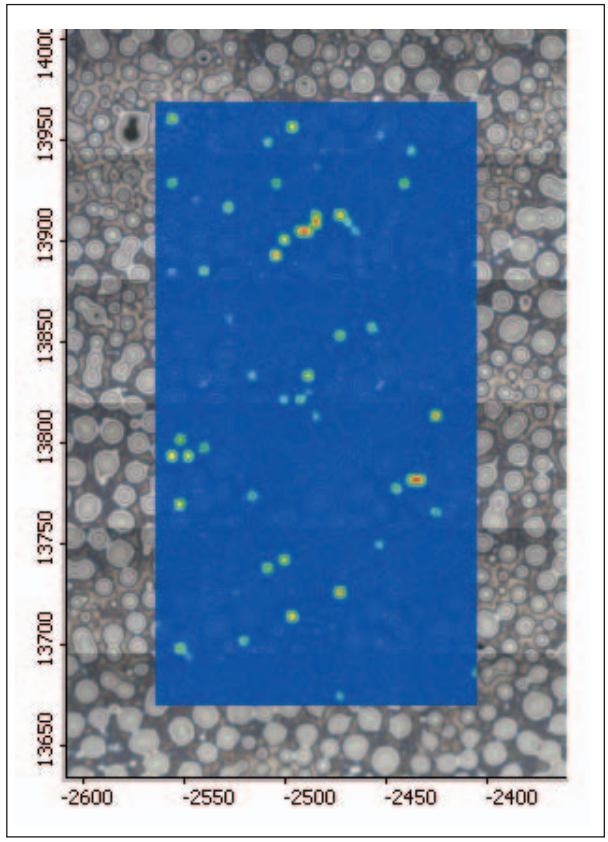

Figure 4: An overlay of the chemical map and the visual image of the sample. The red, yellow, and green areas on the chemical map represent degrees of correlation to a single-walled carbon nanotube (SWCNT) sample spectrum, with red representing the highest correlation.

to a smaller region of the sample we can see the finer detail of the chemical image, shown in Figure 5, which is approximately from the center of the image of Figure 4. The crosshairs in the chemical image show an area that has a high correlation to the SWCNT spectrum shown in Figure 3. If we look at the spectrum with silicon subtracted, we see that it is indeed very similar to the SWCNT spectrum, shown in Figure 6. The spectrum also shows a small amount of the PS spectral features as well.

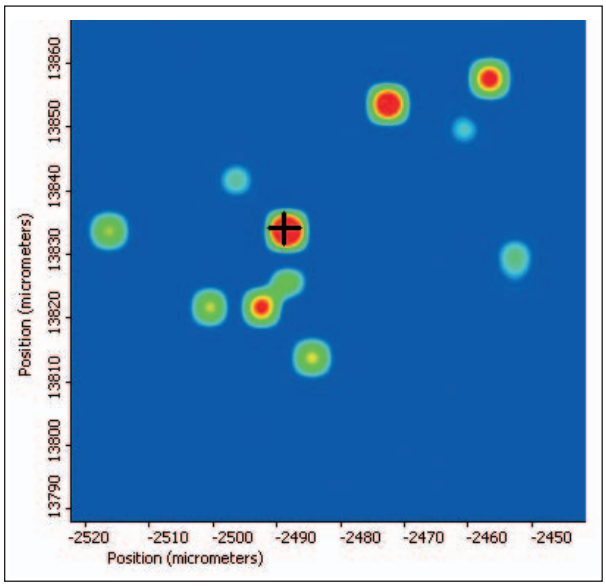

Figure 5: A close up of the chemical map from Figure 4, with red areas representing the highest correlation to the SWCNT spectrum.

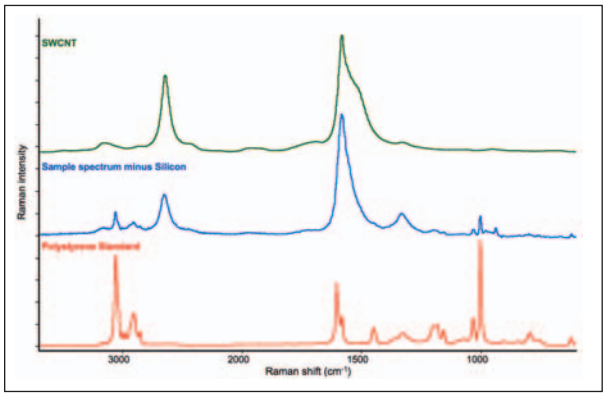

Figure 6: A comparison of the sample spectrum (taken from the location of the cross-hairs in Figure 5) to the reference single-walled carbon nanotubes sample, and the polystyrene standard.

Image analysis is a powerful tool for obtaining useful information from the video or chemical image, including; distribution of chemical or visual features in a sample, the size of the features, or the percentage of the mapped portion of the sample. The image analysis can be done on the raw or unprocessed data. In this case the chemigram data can be referred to as the raw data as this is the mapping data in its original form. The image analysis can also be performed on the output of a profile or other mathematical treatment, such as Principal Component Analysis (PCA) or Multivariate Curve Resolution (MCR). In the latter two cases, the information that the image analysis provides will be based upon the mathematical treatments.

Image analysis was performed on the chemigram data of the PS/PMMA sample with SWCNT. Figure 7a shows a chemical image from the sample, while Figure 7b shows the image analysis of that chemical map. The image analysis shows the area coverage of the PS band located at 3056 cm^{-1} on the chemical image. The colored regions in Figure 7b demonstrate the regions of the chemical image that are the PS spectra. Each region is given a different color and each color/region has an area value. According to the area data in Table 1, the percent coverage of the PS is approximately 38% of the chemical image size. Assuming the coverage of the PS in the region in the chemical image would directly extrapolate to the coverage of PS in the entire sample, it can be said the sample contains surface coverage of 38% PS.

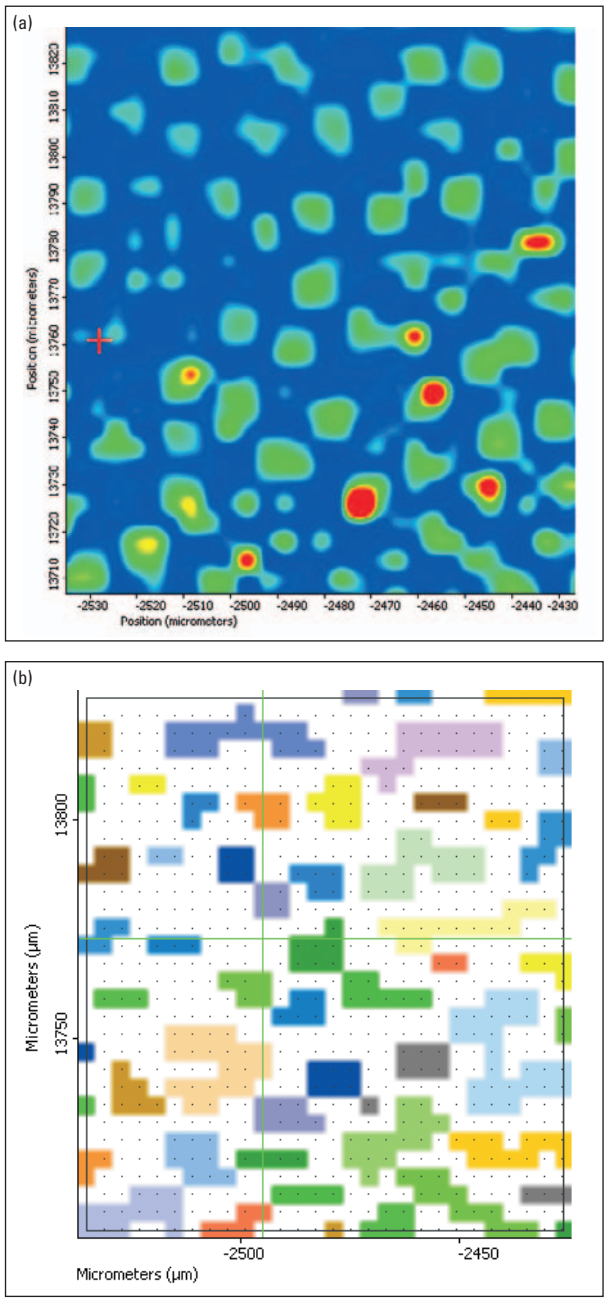

Figure 7: a) Chemical map of the sample, with the red, yellow, and green areas representing polystyrene regions. b) Image analysis of the chemical map shown in Figure 7a, with colored areas representing locations of polystyrene in the sample.

	Polystyrene	SWCNT
Total Feature Area (sq. microns)	5357.29	358.16
Total Image Area (sq. microns)	14177.17	6837.39
Feature Percentage (%)	37.79	5.24

Table 1: Percentage of sample area covered by polystyrene and single-walled carbon nanotubes.

Image analysis was also performed on the correlation profile using the SWCNT spectrum. Figure 8a shows the correlation profile of SWCNT on an area of the sample, while Figure 8b shows the image analysis for coverage of the SWCNT. Each of the colored regions in Figure 8b shows where the SWCNT spectrum is located. These regions match up exactly with the chemical image, Figure 8a. Table 1 shows the area percentages, and we see the SWCNT has coverage of approximately 5% for this region.

Conclusion

Raman spectroscopy is well suited for the analysis of carbon nanotube materials. Carbon nanotubes have strong, characteristic Raman spectra, and changes to the functionality of the carbon nanotube structure can be easily seen in the shifting of peak location and changes in intensity of the corresponding Raman bands. Raman is a useful surface analysis technique. For materials that are vapor deposited onto a substrate, Raman enables the easy and non-destructive analysis of the surface modifications. Silicon is a Raman scatterer, and can exhibit strong bands. But silicon has only a few Raman bands, which are easily subtracted from the sample spectra. The use of chemical mapping is an invaluable tool for this analysis, allowing for the determination of the location and identity of the polymer species, as well as the analysis of the carbon nanotubes. Image analysis gives invaluable information as to the area coverage of the different species.

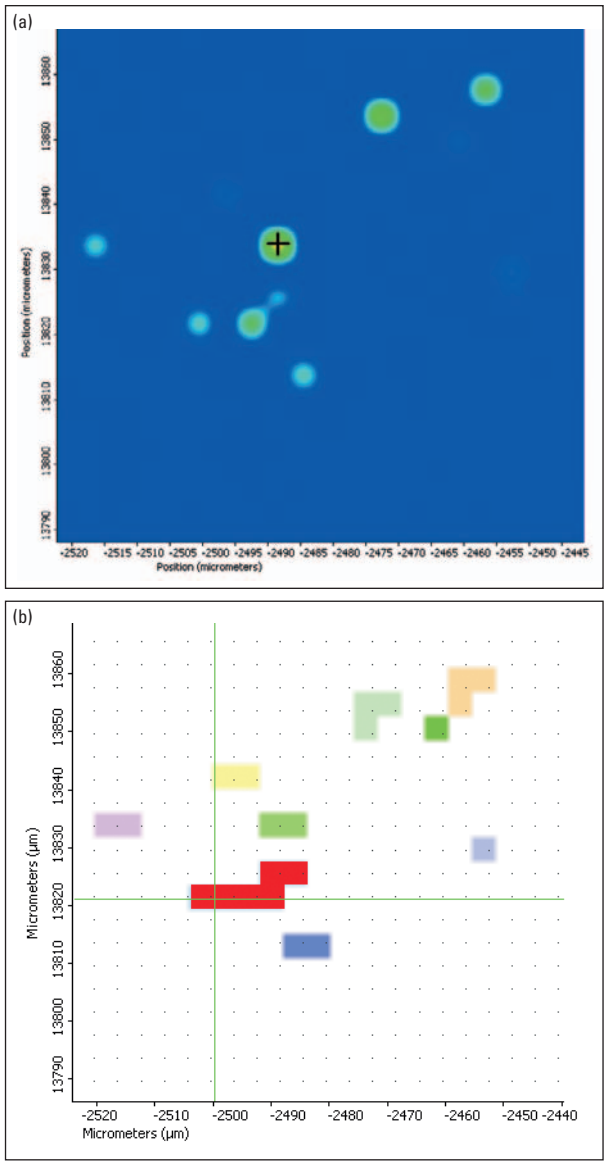

Figure 8: a) The correlation profile of SWCNT coverage on an area of the sample, regions that are yellow and green represent locations correlating to SWCNT. b) Image analysis of the profile from Figure 8a, with colored regions representing locations where SWCNT were on the sample.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa-Other
+27 11 570 1840
Australia
+61 2 8844 9500
Austria
+43 1 333 50 34 0
Belgium
+32 2 482 30 30
Canada
+1 800 530 8447
China
+86 10 8419 3588
Denmark
+45 70 23 62 60
Europe-Other
+43 1 333 50 34 0
Finland/Norway/ Sweden
+46 8 556 468 00
France
+33 1 60 92 48 00
Germany
+49 6103 408 1014
India
+91 22 6742 9434
Italy
+39 02 950 591
Japan
+81 45 453 9100
Latin America
+1 608 276 5659
Middle East
+43 1 333 50 34 0
Netherlands
+31 76 579 55 55
South Africa
+27 11 570 1840
Spain
+34 914 845 965
Switzerland
+41 61 716 77 00
UK
+44 1442 233555
USA
+1 800 532 4752

www.thermo.com

TN51740_E 02/09M