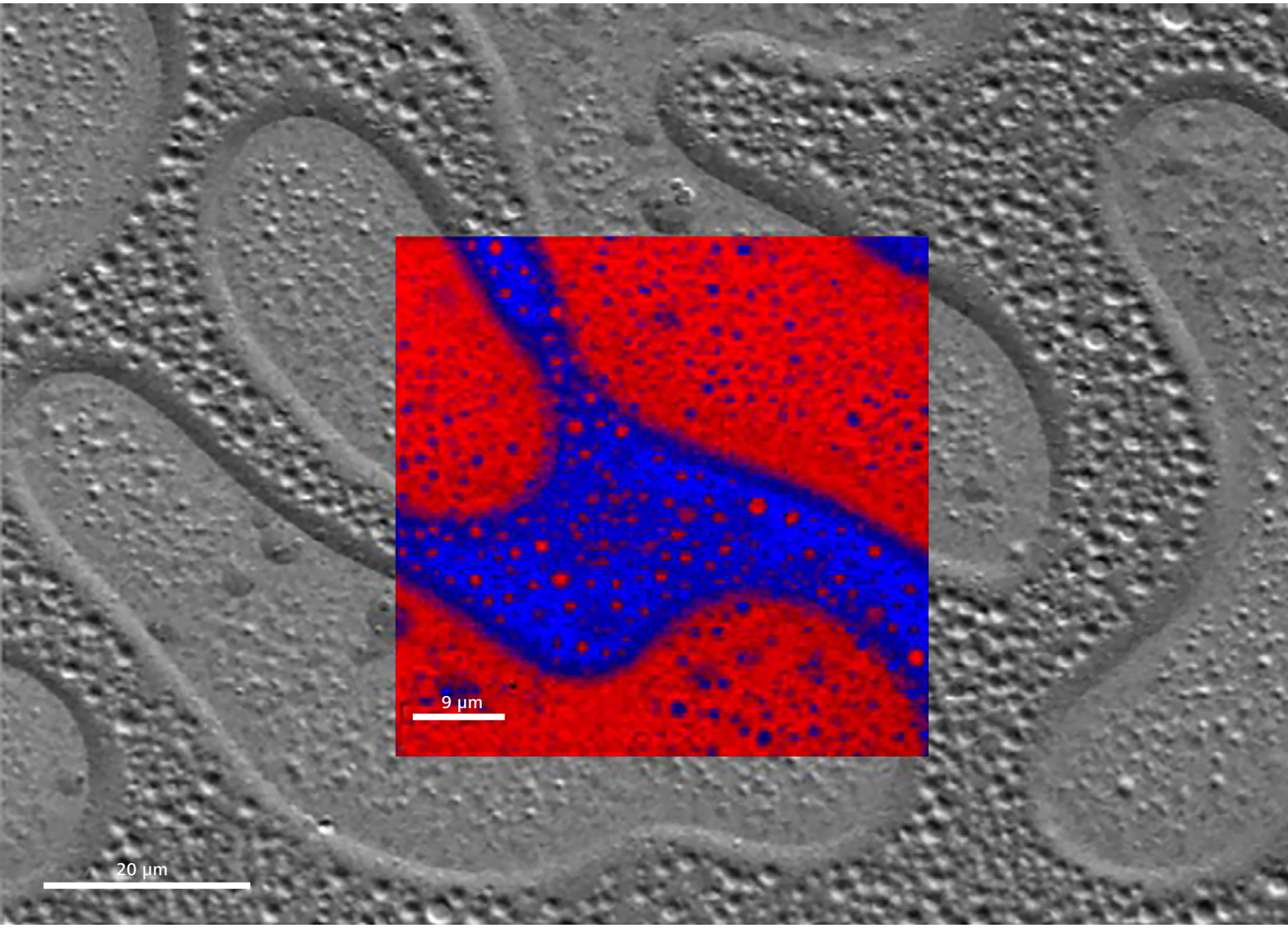
Application Note



Characterizing Polymers Using Correlative Raman Imaging Scanning Electron Microscopy (RISE Microscopy)

ZEISS FE-SEM with WITec Confocal Raman Imaging

Seeing beyond

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ZEISS FE-SEM with WITec Confocal Raman Imaging

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Introduction

Thanks to their role as functional, protective and non-conductive materials, polymers have a broad range of applications in industries like energy, packaging, paper, pharmaceuticals, membranes and filters, smart textiles and medical applications. The development of polymers requires a better understanding of material structure and failure mechanisms, as well as of the manufacturing processes and performance of these materials. Despite being used for many years, many polymers are still challenging to understand because of their complex structures.

Traditional characterization methods often imply time-consuming sample preparation and are limited in terms of revealing the fine details of their structure. Scanning electron microscopy can be challenging as these materials are in most cases beam-sensitive and non-conductive; high resolution imaging is often a challenge. Modern microscopy addresses all the challenges mentioned above and allows researchers to image non-conductive samples without sputter coating to perform multi-modal analysis and investigate regions of interest in a complete and integrated workflow.

This paper presents an optimal solution set to characterize polymers and illustrates how correlative Raman imaging scanning electron microscopy (RISE) can be used to analyze aging of battery separators, identify polymers in blends, and improve the quality of paper.

Correlative Raman Imaging and Scanning Electron Microscopy (RISE Microscopy)

A field emission scanning electron microscope (FE-SEM) is equipped with a high-quality electron source based on field emission that allows researchers to image polymers and beam-sensitive materials at low accelerating voltages. ZEISS FE-SEM is based on the ZEISS Gemini design and has best-in-class low kV imaging performance with highest sample flexibility, i.e., no stage bias is required, and low vacuum imaging mode is available optionally. Furthermore, FE-SEM is used to image and characterize surfaces from the centimeter range down to sub-nanometer resolution, allowing overview images of the sample and nanometer scale investigations of regions of interest. This technique enables researchers to image samples at the highest resolution. Low accelerating voltages or the use of low vacuum mitigates or eliminates beam charging effects thus removing the need to sputter coat samples with a conductive film. Hence, it is possible to analyze polymers without any sample preparation even though they are non-conductive, beam-sensitive materials.

Confocal Raman imaging is an established spectroscopic imaging method used for optically characterizing the chemical and molecular components of a sample with diffraction-limited resolution. RISE microscopy is the combination of confocal Raman imaging and scanning electron microscopy in one

instrument. It incorporates the chemical sensitivity of the non-destructive, spectroscopic Raman technique with the high resolution imaging capabilities of the electron microscope and allows researchers to expand and combine analyses beyond elemental data from energy-dispersive X-ray spectroscopy (EDS). Additionally, RISE microscopy allows the characterization of sensitive materials inside the vacuum chamber without exposure to air. In contrast to existing combinations in which single Raman spectra are typically collected from areas several micrometers in size, the RISE combination allows for diffraction-limited confocal Raman imaging of the exact same sample position from which the SEM image was taken. It can also generate 3D images and depth profiles to visualize the distribution of the molecular compounds within a sample volume. Both analytical methods are fully integrated in the RISE microscope. A precise translation stage automatically transfers the sample inside the microscope's vacuum chamber and re-positions it between measurements (Figure 1). The integrated RISE software carries out the required parameter adjustment and component alignment. The acquired results can then be correlated and the Raman and SEM images overlaid to provide a complete understanding.

In the case of polymers, Raman analysis provides insights into the chemical fingerprint, differentiates polymorphs with the same chemical compounds and different crystal structures and determines the stress or strain in the sample. None of these analyses can be performed using EDS alone, so the integration of the RISE system in combination with EDS takes the analysis of these materials one step further and provides a complete solution to investigate polymers and illuminate more research insights to fully understand the nature of the samples.

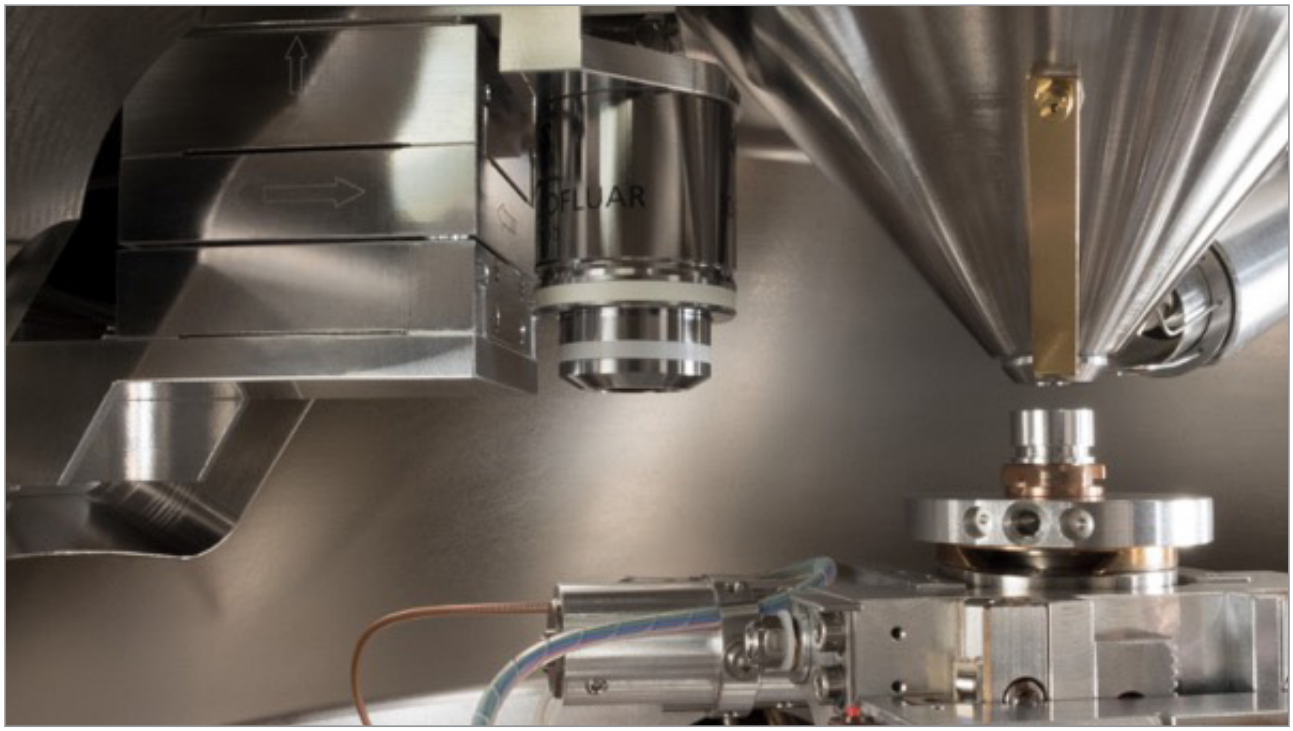

Figure 1 *Integrated RISE system showing the stage that automatically transfers the sample.*

Battery Separator Characterization Using Integrated Scanning Electron Microscopy and Raman (RISE)

The battery separator isolates the two electrodes of the lithium-ion battery, playing a very important role in determining the working temperature of the battery. This parameter is essential for battery safety. The performance of the separator (e.g., aging) is usually determined by its composition. The separator is polymeric and often comprised of polyethylene (PE) and polypropylene (PP). While the SEM and EDS analyses are very useful for the analysis of the electrodes [1], characterization of the battery separator requires Raman analysis. To be able to fully characterize the performance of the batteries, an integrated *in situ* system that combines imaging capabilities with analytical capabilities (EDS and Raman) is required.

Figure 2 shows an example of the analysis of a commercial 18650 battery that was cross-sectioned and imaged using RISE. Fig. 2a reveals an EDS map of the cross section. This technique is very sensitive to elemental distribution and reveals the composition of the Li-Cathode and the metallic conductors. However, EDS is blind to low k materials such as an anode consisting of graphite and polymers. Raman on the other side is sensitive to chemical bonds, thus it reveals the various allotropes of carbon in the anode and the composition of the polymeric separator (Fig. 2b, c). The Raman analysis of the battery separator reveals three polymeric layers as shown in Figure 2c: two PP layers depicted in yellow and a middle PE layer in green. The presence of the three different layers was impossible to identify using EDS analysis.

An additional analysis was performed to characterize the battery separator after cycling to observe how the structure changes. Figure 3 shows a comparison between a fresh separator and a separator from a cycled battery. The Raman analysis reveals a change of the orientation of the PP chain molecules in bulk polypropylene. The direction of the structures is indicated by the arrows. The fresh separator consists of uniaxial PP, while the separator from a cycled battery is of bi-axial polypropylene. This indicates a rupture of the long uni-axially oriented polypropylene chains after cycling and a reorientation of these shorter chains, which can significantly influence the Li transport, impedance and thus the lifetime of the battery.

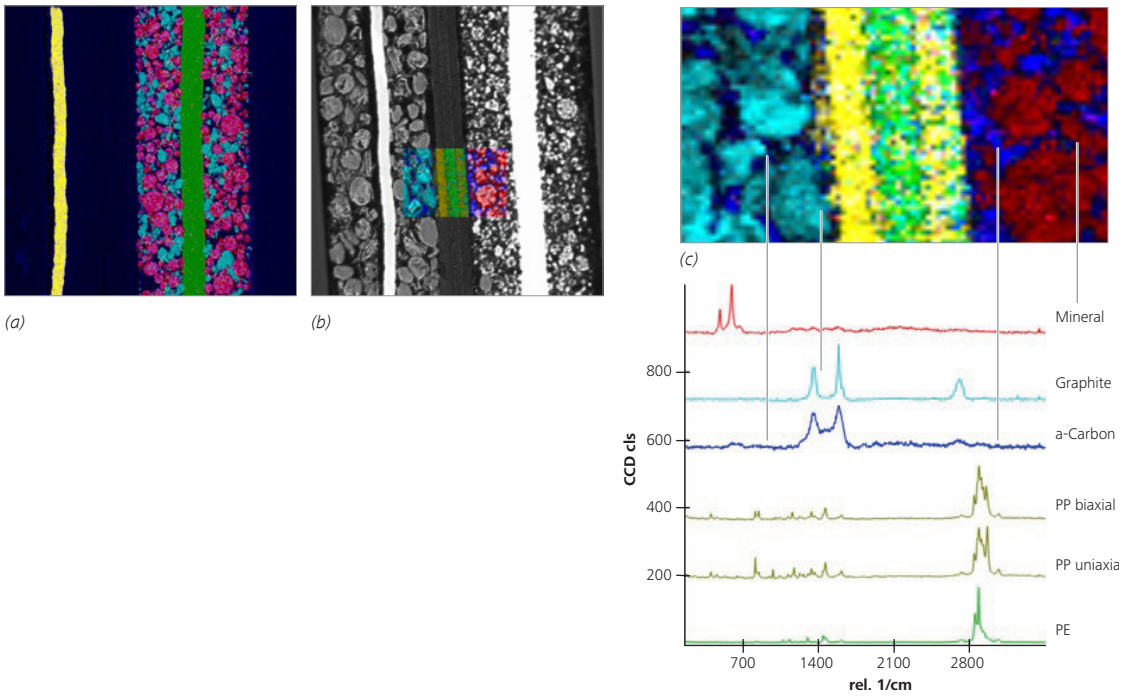

Figure 2 *(a) EDS mapping, (b) SEM imaging and Raman overlay of the same area and (c) Raman imaging of the separator showing two different polymers[1].*

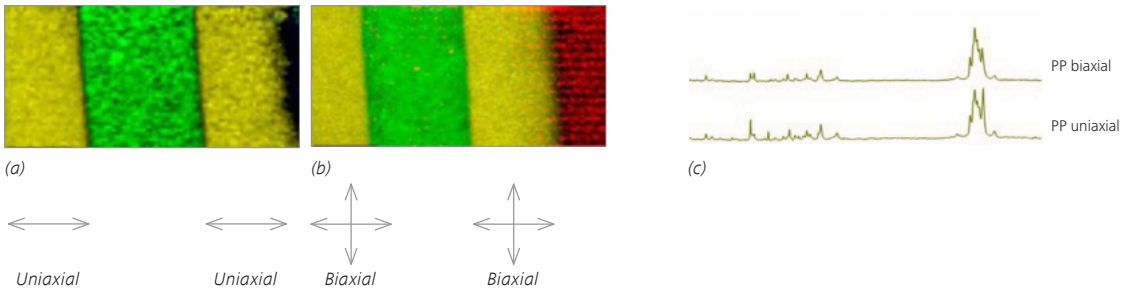

Figure 3 *Raman analysis of the battery separator: (a) before aging, (b) after aging and (c) Raman spectra[1].*

Correlative Raman Imaging Scanning Electron Microscopy in the Paper Industry

The paper processing industry faces many challenges in improving the quality of paper in addition to understanding and optimizing the manufacturing process. To obtain a high-quality paper, coatings are usually applied to enhance the properties of the paper or the quality of the printing process. The distribution of binders and pigments in coated paper in both the paper cross-section and on its surface need to be understood with high resolution imaging. RISE provides the capability of imaging paper without sputter coating it as well as the analytical capability of obtaining compositional maps. This information is essential in the industry to reach commercial profitability and productivity targets.

Figure 4 shows an example of the RISE analysis of a paper cross section, emphasizing the advantages of being able to correlate information from the SEM as well as the compositional mapping of the region of interest. In this case, three different layers have been identified: caolin, polymer, calcite and cellulose. This analysis allows the researcher to observe the distribution of calcite and also measure and observe the thickness of the caolin and different polymer coatings to improve the surface of the paper. RISE provides a thorough analysis and understanding of the quality of the paper and can contribute to the improvement of the manufacturing process.

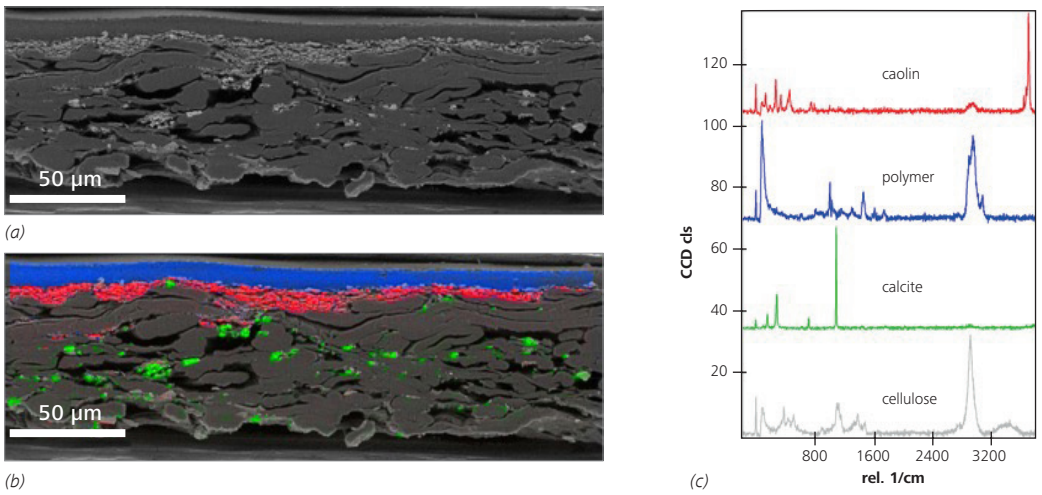

Figure 4 *RISE analysis of paper: (a) FE-SEM image, (b) Raman and FE-SEM overlay and (c) Raman spectra for caolin (red), polymer layer (blue), calcite (green) and cellulose (grey).*

Correlative Raman Imaging Scanning Electron Microscopy of Polymer Blends

In some applications, it is challenging to understand the structure of the samples without using complementary techniques. For example, Figure 5 (a) shows a polymer blend between poly methyl methacrylate (PMMA) and polystyrene (PS). The image was acquired by scanning electron microscopy using a low accelerating voltage and beam energy on an uncoated sample.

The two polymers form a blend that can be imaged using the FE-SEM with the surface and domain structure observed with high contrast. However, since it is not possible to fully differentiate the domain structures and separate the two phases by FE-SEM alone, additional techniques are needed. EDS analysis is limited in this case as it cannot easily distinguish the polymers due to their compositions. The fully integrated RISE technique is an excellent solution to fully understand the structure of the sample.

Using RISE, the domains can be distinguished, as shown in Figure 5 (b,c). PMMA is shown in red and PS in blue. Raman data can be overlaid and correlated with the high resolution SEM image so domain structure can be imaged at the same region of interest.

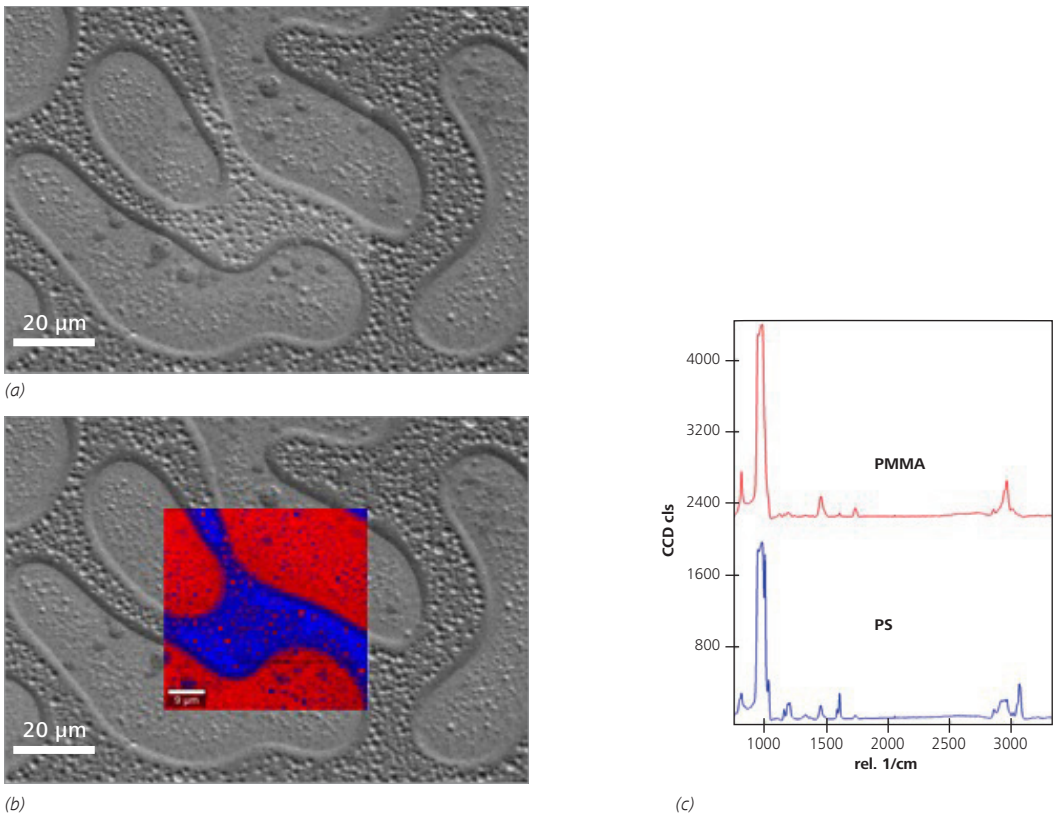

Figure 5 RISE analysis of a PMMA-PS polymer blend: (a) FE-SEM image of the surface of the polymer showing its morphology, (b) overlay of Raman mapping on the FE-SEM images showing the distribution of the two polymers in the blend, and (c) Raman spectra for PMMA (red) and PS (blue).

Conclusion

Polymers are complex materials that require advanced microscopic characterization techniques. A complete evaluation of these materials implies high resolution imaging of beam-sensitive and non-conductive samples and a thorough chemical analysis. The RISE integrated system provides a user-friendly correlative workflow and offers the capability to do analysis beyond EDS via vibrational spectroscopy, while being fully integrated into an SEM.

RISE gives researchers the capabilities to determine the chemical and structural fingerprint of the sample, i.e., recognize molecular and crystallographic information and perform 3D analysis of the sample. Raman mapping can easily be correlated with SEM imaging (using multiple different detectors) or EDS data for a complete analysis of the sample. Any region of interest is automatically transferred from one objective to the other, in an integrated workflow. With numerous applications in different industries such as pharmaceuticals, paper manufacturing, energy materials or packaging, RISE is a powerful tool that helps researchers improve the quality of their material, better understand processes and optimize productivity and profitability.

References:

[1] Stefanie Freitag, Christina Berger, Christian Weisenberger, Andreas Kopp, Timo Bernthaler, Ute Schmidt and Philippe Ayasse, Integrated SEM and Raman Imaging of Lithium Ion Batteries, October 2015.

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