APPLICATION NOTE

Characterization of glass fiber-reinforced polymers with ChemiSEM Technology

The performance of glass-fiber reinforced polymers strongly depends on contaminations in the material. In this application note we present a new method to efficiently characterize the composition of this polymer composite.

Polymers are materials frequently used in many types of modern industries, ranging from electronics to automotive and marine. These applications often require that the mechanical properties be exceeded; therefore, polymer properties alone are not sufficient, and so reinforcing materials are taken into consideration.

Glass fiber-reinforced polymers (GFRPs) are composite materials made by mixing different types of polymer matrices with one or more types of glass fiber. GFRPs are shown to grow at an impressive rate over time and have become established in relatively new markets due to their unique properties. They combine the strength and stiffness of the glass fibers with the elasticity, light weight, and high durability of the polymer matrix. Each type of glass fiber possesses unique properties, and the specific type is selected based on the application of interest.

For applications requiring excellent electrical insulation, thermal resistance, chemical resistance, and tensile strength at relatively low cost, calcium alumino-borosilicate fibers are used (E-glass). However, these favorable material properties can be affected by contaminations introduced in different stages of the GFRP manufacturing process or when the composite is used in environments for which they were not designed. The contaminations ultimately lead to degraded product performance, such as compromised electrical insulation, mechanical failure, or reduced chemical resistance. Proper assessment of the contaminant's distribution over the GFRP surface or cross section can help prevent such undesired consequences. For this reason, extensive characterization of the material is required in a failure analysis process to identify the possible source of contaminants, subsequently adjusting the manufacturing and handling processes to avoid them.

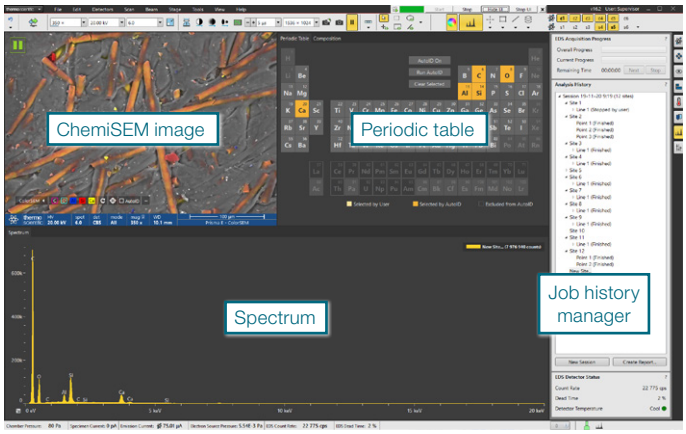

Figure 1. User interface of the integrated SEM-EDS system (ChemiSEM Technology).

Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) is a commonly used technique for characterization of GFRPs. While SEM provides grayscale topographic images, the EDS detection system maps the elemental composition over the area. However, conventional EDS mapping is not always fast; it usually requires users to switch between SEM and EDS systems in a somewhat inefficient process, and it requires a second control PC and operation window for the EDS acquisition software. Moreover, it requires knowledge of the technique to set up the acquisition parameters and interpret the results. In this application note, we present an efficient approach to the contaminant and defect analysis provided by Thermo Scientific™ ChemiSEM Technology, a state-of-the-art, fully SEM-integrated EDS implementation that resolves the limitations of conventional EDS. The EDS detector used for this investigation is a 30 mm^2 Thermo Scientific UltraDry EDS Detector.

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GFRPs and polymers are generally non-conductive materials. Conventionally, to undertake SEM imaging, the samples would need a surface coating, which results in an even more complex interpretation of results.

This Thermo Scientific SEM-EDS system allows data acquisition of any sample in low-vacuum mode and, when needed, in ESEM mode. Low-vacuum mode (variable pressure ranges up to 200 Pa) waives the need for a coating by injecting gas (typically water vapor) into the microscope chamber for charge neutralization, whereas ESEM mode provides a quick way to image outgassing or wet samples by simply adjusting the chamber pressure up to 2,600 Pa by introducing more gas.

Furthermore, the system offers the possibility to mount a pressure-limiting aperture (PLA) that prevents beam spreading (skirting). In this way, the PLA prevents spurious peaks from showing up in the spectrum, making the results more reliable. The PLA also creates differential vacuum regions that not only maintain high vacuum in the electron column but also prevent contaminants from striking the objective apertures. Different PLAs are available, though one is specifically designed for EDS analysis (X-ray cone): an 8 mm long cone that keeps the electron beam in higher vacuum until it is 2 mm above the sample surface. The X-ray cone effectively decreases the electron beam scattering and maintains the primary beam that reaches the sample to generate enough X-rays for EDS analysis.

In this regard, GFRP investigation has been conducted in low-vacuum mode with a chamber pressure of 80 Pa while using the X-ray cone.

When investigating GFRPs in SEM, backscattered electron (BSE) images, as the one presented in Figure 2, provide the materials contrast needed to distinguish the polymer matrix from the glass reinforcement. In addition, particles are visible, which are suspected to be potentially related to contaminations.

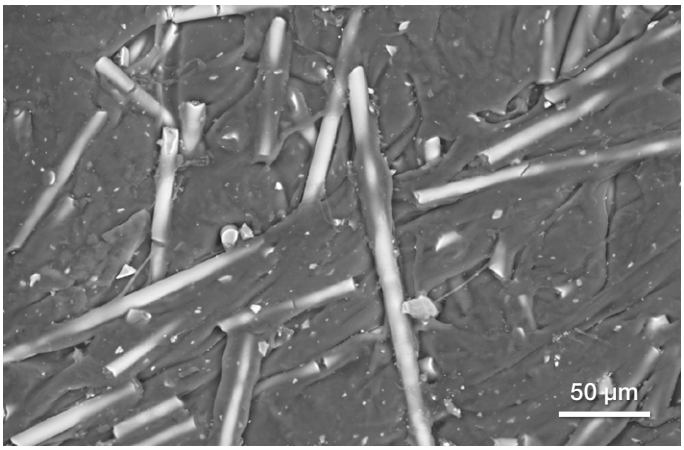


Figure 2. Glass fibers in a polymer matrix: an example of GFRP.

However, to quickly characterize the corresponding compositions, we need fast elemental information from EDS, and so this is when ChemiSEM Technology comes into play. ChemiSEM Technology, while acquiring the BSE image, displays chemical information on the imaging area (Figure 3). A set of elemental maps can be acquired during a single-frame image acquisition.

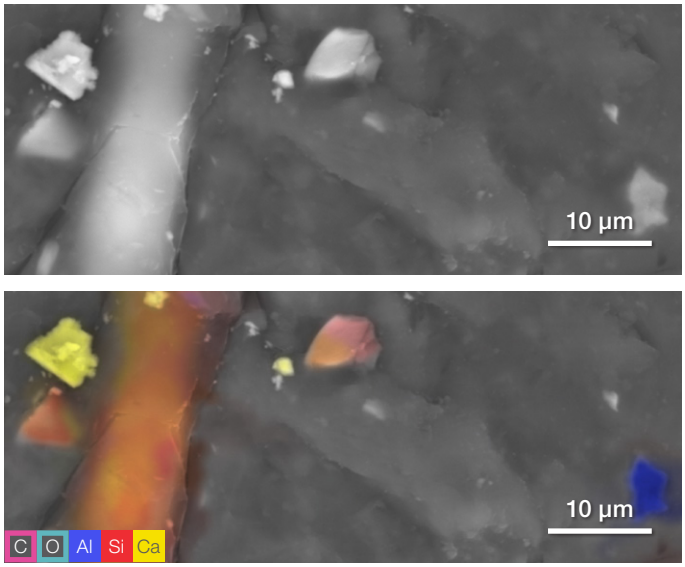


Figure 3. Top: high-mag view of the area presented above in grayscale. Bottom: ChemiSEM image. Only the elements of interest have been selected to highlight features of interest. Dwell time 1 us, total acquisition time 40s.

To make a direct comparison, a gross counts EDS map of the same view in Figure 3 has been collected with the same acquisition parameters (acceleration voltage, beam current, and acquisition time) used for the ChemiSEM image, as shown in Figure 4.

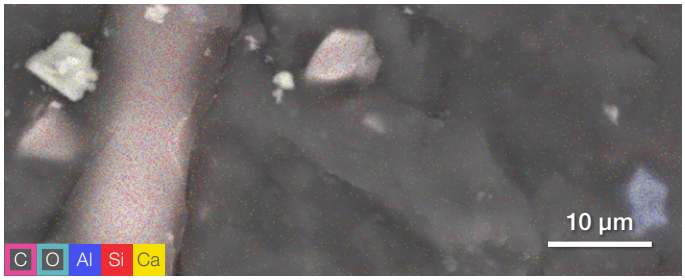


Figure 4. Traditional gross counts map of the area shown above , acquired in the same amount of time. Total acquisition time 40s. Average count rate 40,000 cps. Average total counts ≈ 350,000.

The distinctive comparison between the ChemiSEM view in Figure 3 and the corresponding traditional gross counts EDS map in Figure 4 clearly demonstrates that the ChemiSEM image provides much more sufficient chemical information due to its vivid colors, compared to the sparse data points obtained by conventional EDS collection.

Furthermore, for more comprehensive chemical information, ChemiSEM Technology can provide a clearer view of element distribution within the same image by the selection of specific elements (Figure 3, lower image) to eliminate irrelevant information and highlight the elements of interests. Only aluminum, silicon, and calcium are shown to better illustrate their distribution in the glass fibers, while carbon and oxygen, which are primarily in the polymer matrix, have been deselected.

The views in Figure 3 and Figure 5 both demonstrate the presence of possible contaminations.

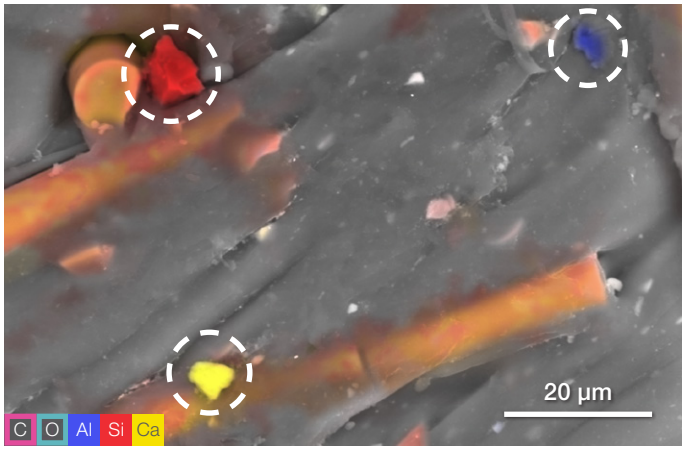


Figure 5. ChemiSEM image of possible features of interest (i.e., materials contaminations). (Image resolution: 1536 x 1094. Acquisition time: ≈20s. Acc. Voltage: 20 keV. Beam current: 4.5 nA)

In fact, these particles, ranging from 5 to 10 µm in size, are composed of chemical elements differing from the primary glass fiber compositions. Figure 6 shows three ChemiSEM images, each with an individual element selected as identified in Figure 5 to highlight the specific predominant element distribution in the entire area.

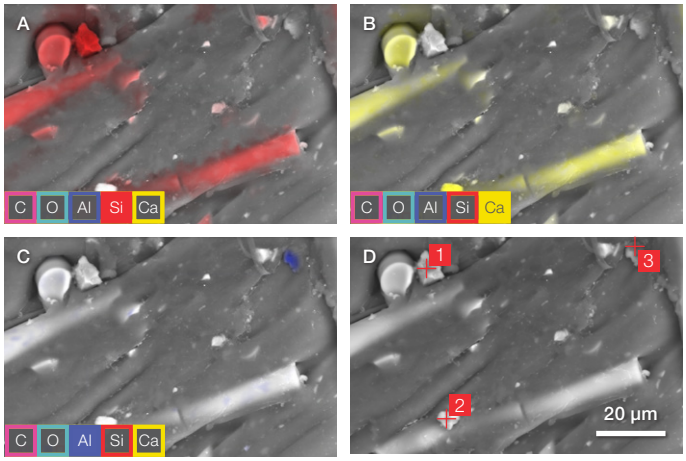
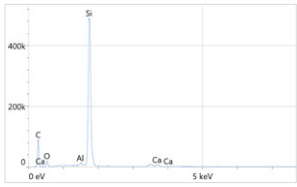


Figure 6. (A) Silicon ChemiSEM image, (B) Aluminum ChemiSEM image, (C) Calcium ChemiSEM image. (D) Points analyzed. (Point acquisition time: 120s. Average count rate: 40,000 cps. Average total counts: ≈ 5 million)

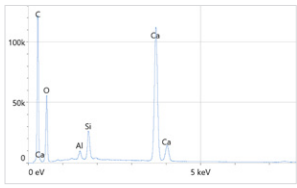
To unravel the source of these identified contaminants, more information on the particles' composition is required, resulting in the further acquisition of a variety of Point & ID analysis.

Element	Atomic %	Atomic % error
C	63.6	0.2
O	11.2	0.3
Al	0.3	0.7
Si	24.6	0.2
Ca	0.3	0.4



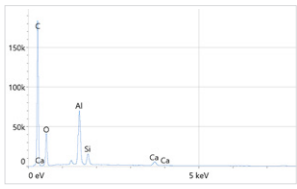
Point 1 quantification and spectrum.

Element	Atomic %	Atomic % error
C	37.0	0.2
O	48.6	0.3
Al	0.6	0.6
Si	1.9	0.3
Ca	11.9	0.2



Point 2 quantification and spectrum.

Element	Atomic %	Atomic % error
C	63.0	0.2
O	30.5	0.3
Al	4.9	0.2
Si	1.1	0.3
Ca	0.5	0.5



Point 3 quantification and spectrum.

The tables above show the quantifications obtained from Points 1, 2, and 3, respectively. For each point analyzed, the most abundant element has been highlighted; should be considered that part of the C and O signal may be due to the polymer matrix. A 20 keV acceleration voltage results in micron-scale interaction volume inside the sample; therefore, we cannot eliminate the possibility that the EDS signal partially comes from the surrounding area. The results demonstrate clearly that the majority of the signal from point 1 has to be assigned to silicon, whereas for point 2, small peaks of silicon and aluminum can both be noticed, possibly coming from the neighboring glass fiber.

Point 3 shows that of the three elements of interest (Al, Si, Ca), Si is the most abundant, confirming a different nature than the two points previously analyzed. Also, in this case, C and O are the most abundant detected elements, as the particle is smaller than the other two, and, as mentioned above, part of the signal has a high chance of coming from the surrounding area or the polymer matrix below the particle.

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As part of the characterization process, different areas have been analyzed using ChemiSEM Technology during a conventional SEM inspection. In this perspective, ChemiSEM Technology has been proven to successfully detect the contaminants' presence even below the polymer matrix surface (as shown in Figure 11 (B)), subsequently providing information on the sample that otherwise would not been acknowledged with a traditional EDS system. The very presence of these contaminants beneath the matrix surface strongly suggests that they are unlikely to have originated from the last stages of the entire manufacturing process.

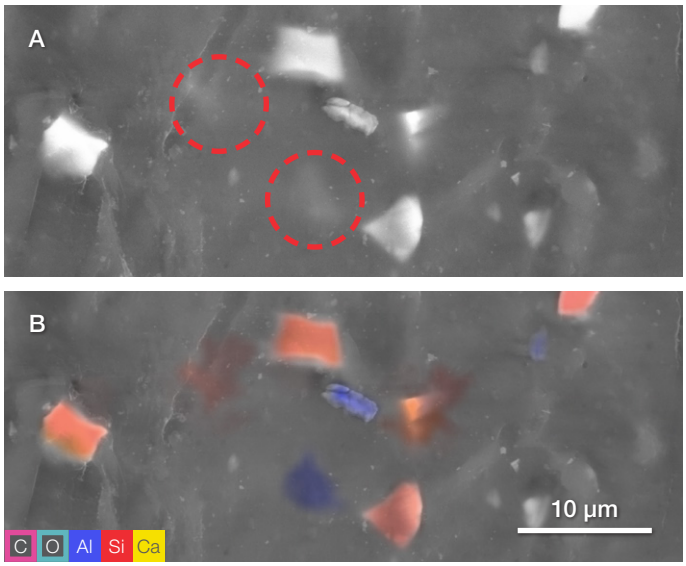

Figure 7. (A) Backscattered electron image of the same detail, (B) ChemiSEM image of a detail.

Particles in the red circles, as marked in Figure 7A, are not evident or noticed purely from BSE imaging without ChemiSEM Technology (Figure 7B).

Conclusion

To assess the quality of polymeric products and their future durability, it is crucial to evaluate the homogeneity of the fiber dispersion within the polymer matrix and identify the presence of possible contamination. Furthermore, a proper, fast, and efficient characterization of the contaminants' nature can benefit the manufacturing process, leading to improvements.

Here, we have demonstrated that such characterization benefits from the always-on nature of ChemiSEM Technology. Defects and external matters are directly visible despite the absence of compositional contrast in the grayscale SEM image. Moreover, the elemental information is displayed directly with the SEM image, which significantly reduces the time to results, thereby eliminating the need to switch between user interfaces.

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