APPLICATION NOTE

Characterization of tire fillers with Axia ChemiSEM

A new and more efficient approach to failure analysis

Abstract

Tires are often considered as low-tech commodities. However, contrary to popular perception, tires are actually highly engineered structural composites. Tires contain many rubber compounds (up to 20, with several types of microstructures) that provide different levels of grip and traction. Fillers are added to the main polymer matrix to facilitate rubber reinforcement.

Tire failures often occur due to a lower or decreased material quality, and an optimal and homogenous dispersion of all the different fillers is a key factor for a higher material quality. Analytical techniques like SEM-EDS are required to understand the root cause of a failure but the material contrast obtained from a backscattered electron image is not enough to distinguish between the large variety of materials employed.

This application note demonstrates that the live quantitative elemental analysis of Axia ChemiSEM provides an efficient and easy way to characterize the different fillers, despite their similar compositional contrast.

Introduction

Tires are designed to perform for thousands of kilometers, while maintaining the same performance and safety properties under a wide range of conditions.

In failure analysis, tread (part of the tire in contact with the road) detachment and tire aging are listed among the most common tire failures. The possible causes for these failures are usually directly or indirectly related to material or manufacturing defects. Reduced elasticity of the rubber parts due to aging takes place even if tires are not in use (rubber mixtures tend to harden over time naturally).

Natural and synthetic rubbers are the main raw materials used to manufacture a tire. In order to develop proper characteristics of strength, resilience, and wear-resistance, rubber products are modified by adding fillers, as a reinforcement, to each of the different rubber compounds.

The original purpose of fillers was to lower the final cost of the product. Nowadays however, rubber manufacturing technology has seen an increasing amount of research in selective fillers for their abilities to enhance different composite characteristics, depending on their chemical composition (Brewer HK, 2006).

Specific fillers can improve durability of the product, the cost, and the processability during the manufacturing process. Reinforcing fillers are often more than 40 percent of the whole tire compound, and play a key role in the elastic efficiency and tire aging leading to subsequent possible failure.

Filler dispersion in the rubber matrix is the parameter that controls performance. Improving the filler dispersion leads to an improved polymer-filler interaction, which will subsequently improve the elastic behavior of the material and the rolling resistance of the tire.

Methods

Scanning electron microscopy (SEM) with backscattered electron imaging (BSE) and energy dispersive X-ray spectroscopy (EDS) are the go-to solutions for characterizing different additives and their dispersion within the polymer matrix. BSE images are commonly considered the easiest way to obtain compositional information. This is because the contrast seen with BSE images is due to the variation in atomic number. This helps to easily differentiate the rubber matrix (low atomic number) from inorganic particles (high atomic number) that are generally used as fillers. However, the large variety of materials employed nowadays in the tire industry makes it necessary to use EDS analysis to discriminate between the different elements. However, conventional EDS characterization is expensive, slow and complicated. The need to set up the parameters (which requires extensive knowledge and experience) and the system for data acquisition, has made it inefficient and impractical.

In this application note we present a characterization of the different fillers in a tire cross section obtained using the Axia ChemiSEM, a completely new platform that's designed to provide the most efficient SEM-EDS user experience possible. Axia's main feature - the live quantitative elemental mapping - resolves the above-mentioned limitations of conventional EDS.

Analysis

A conventional failure analysis workflow makes use of microscopic analysis to discover the root cause of a failure. It does this by first using low magnification analysis to characterize the specimen and identify possible regions of interest. For this purpose, a large field-of-view SEM image using Axia ChemiSEM's navigation montage of the prepared cross section has been acquired. Navigation montage is a built-in function of the SEM, which allows easy navigation on large samples. It automatically collects multiple neighboring images, creating a large-scale overview of the sample in a short period of time.[1]

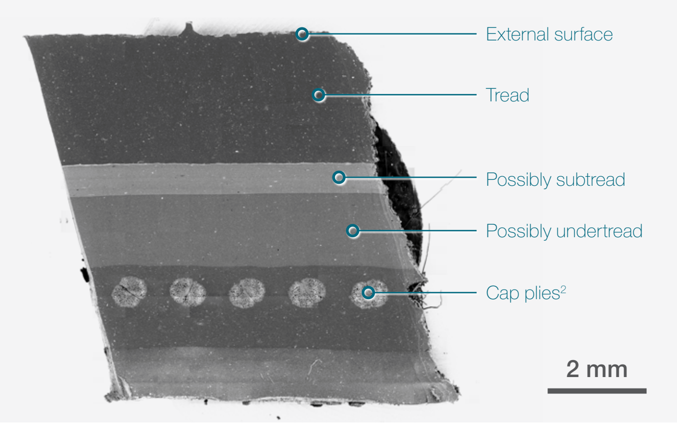

Figure 1. 19x19 tiles montage. Tot acquisition time ≈ 15 mins. Acc voltage 20 keV, beam current 0.94 nA, Low vacuum (30 Pa).

Higher levels of magnification are needed to evaluate microfeatures like the dispersion of the different fillers and their distribution over various layers.

The conventional fillers, in rubber technology, are carbon black and zinc oxide. Carbon black is probably the oldest and most commonly used reinforcing filler. However, the application of carbon black is not the preferred solution anymore as it creates environmental problems. In addition, carbon black has the tendency to agglomerate within the rubber matrix.

The second most abundant material in the tread rubber matrix is zinc oxide, which has many advantages when used as an additive in rubber compounds. Along with sulfur, it is a crucial ingredient, as it promotes the process of vulcanization (the tire curing shortens the time and impacts the length and number of crosslinks in the rubber matrix). In addition, its good conductivity improves the removal of heat generated during the tire motion.

A first characterization of the fillers and additives has been performed by screening some of them in the upper layer of the tire (Figure 2).

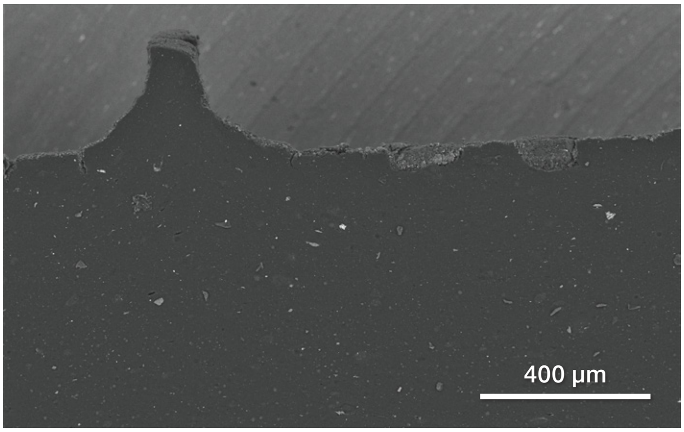

Figure 2. Upper surface (tread). Acc voltage 20 keV, beam current 0.48 nA.

Further analyses of some of the visible objects have been acquired. Axia ChemiSEM, while working in a conventional SEM imaging session, provides a fast and full understanding of their composition. It also seamlessly provides all the needed chemical information, without changing the methodology or acquisition conditions.

Figure 3 presents a cluster of zinc oxide particles. Axia ChemiSEM's graphical user interface allows the operator to acquire different signals simultaneously in order to increase the amount of information. The left image is a secondary electron image and provides topographical information (shows that the particles are embedded). The right image is a backscattered electron image that shows the particles have a higher atomic number than the rubber compound surrounding them.

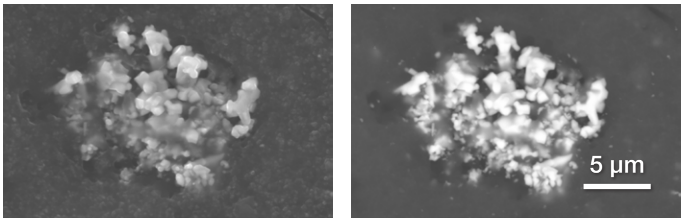

Figure 3. Secondary electrons and backscattered electrons image of a Zn oxide particles cluster. Acc voltage 20 keV, beam current 0.48 nA, acquisition time 40 s.

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1. A navigation montage can also be used as a map to navigate the sample surface or center a feature of interest by automatically driving to the stage position in one click.
2. Cap plies are an extra layer of polyester fabric (or nylon) to provide strength and stability. Cap plies are not found on all tires but are mostly used on tires with higher speed ratings.

One of the key features of the live quantitative mapping provided by Axia ChemiSEM is its full integration within the SEM user interface. As a result, X-rays are continuously acquired and processed, even during live imaging or the acquisition of the previously shown image. For this reason, a simple click is all that's needed to show the quantitative elemental maps (Figure 4).

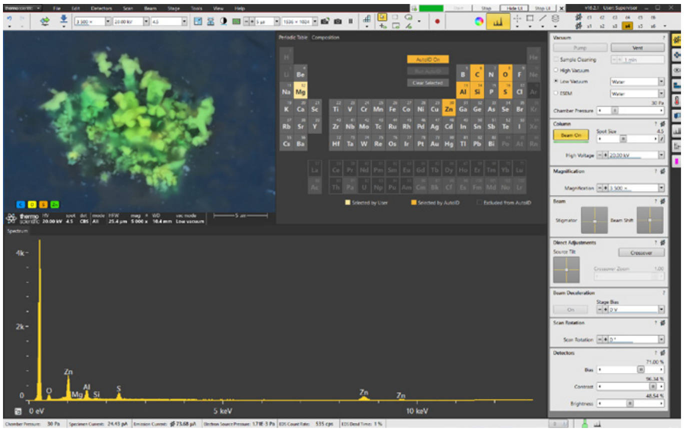


Figure 4. Axia ChemiSEM user interface with integrated live quantitative elemental mapping. It shows the quantitative elemental image during its acquisition, the spectrum of the area acquired, and the periodic table to select/unselect elements of interest.

Within the same acquisition (40 s for this region of interest), different elements can be selected or deselected to highlight their distribution (Figure 5). This makes locating different filler compositions much easier and faster to target where more detailed analyses are required.

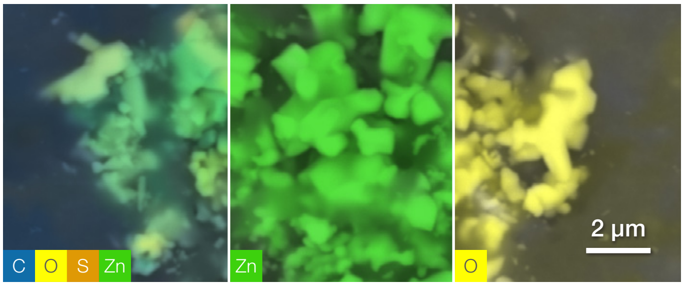


Figure 5. Quantitative elemental images, showing from left to right respectively all elements shown, zinc distribution and oxygen distribution. Some disuniformities in the distribution may be due to shadowing.

Figure 6 below reveals another abundant filler in the tread (upper part of the tire cross section). From the image, it's clear that this filler is very near the external surface of the tire.

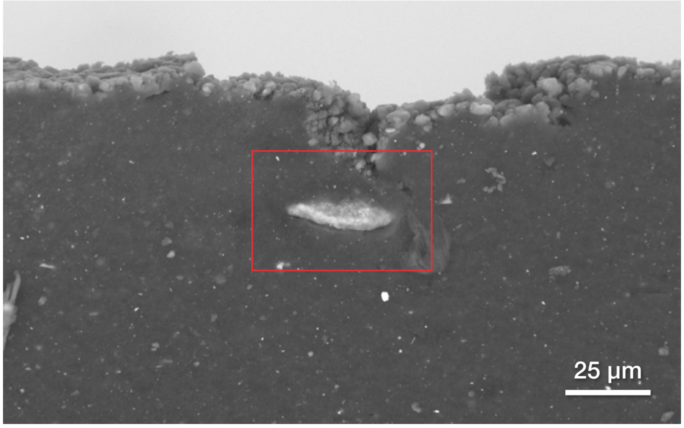


Figure 6. Backscattered electron image showing the position of another type of filler.

Elemental distributions and quantitative information are obtained by acquiring quantitative elemental images, followed by a point analysis on the particle.

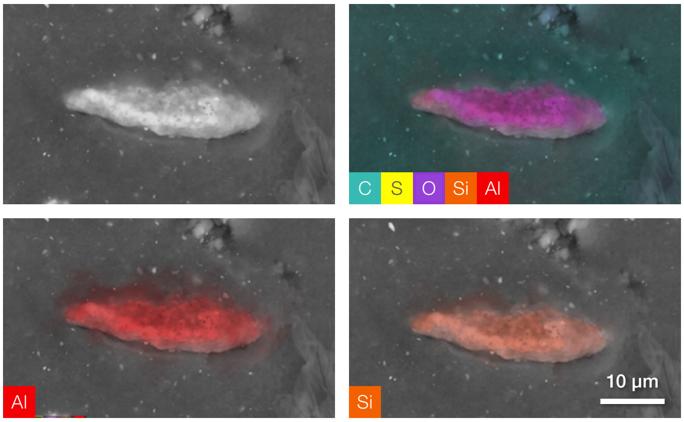


Figure 7. Backscattered electron image and a complete set of quantitative elemental images showing, in the upper right image, all the elements present in the ROI (including C, O and S). The last two images show Al and Si distribution on the particle. Acc voltage 20 keV, beam current 0.94 nA, acquisition time ≈ 100 s. To be noted, the elemental distribution and the related set of images have been obtained using only one image acquisition.

Element	Atomic %	Atomic % error
C	28.6	0.2
O	52.0	0.2
Al	12.4	0.0
Si	6.8	0.0
S	0.2	0.0

Figure 8. Point analysis acquired for 60 s. Average count rate ≈ 3000 cps.

Point analysis in Figure 8 highlights that the Al content is double the Si content. When combined with the information provided by the quantitative elemental images, these results suggest this particle is one of the aluminosilicate fillers (Al_2SiO_5). These fillers are synthetic additives commonly employed in the tread to increase the strength of the compound and enhance its mechanical properties. An abundant amount of oxygen and a relatively high percentage of carbon can be assigned to the signal coming from the rubber below the particle.

As previously mentioned, fillers are generally used to reinforce and strengthen the rubber structure. However, some of these fillers are classified as semi-reinforcing or non-reinforcing fillers (Roy K, 2019) as they are not meant to enhance the mechanical properties. A variety of non-black fillers, as they are called, are used in the rubber components. These include calcium carbonate, clay, talc and precipitated silica.

The following characterizations show two examples of calcium carbonate and talc respectively. Their nature and chemical composition have been assigned to these specific materials using Axia's fast and accurate ChemiSEM Technology.

Images below have been collected in the rubber layers below the tread layer. These different compounds shown a clear abundancy of the filler calcium carbonate.

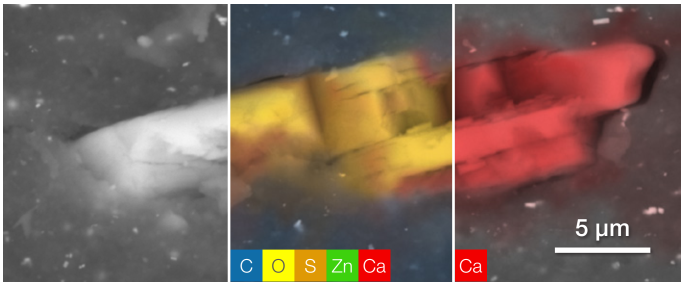
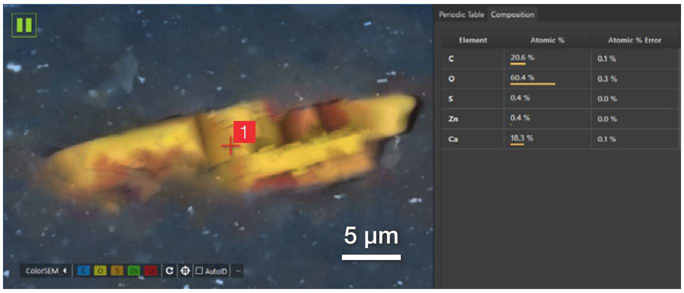


Figure 9. Layered filler. From left, backscattered electron image, ChemiSEM image with all the present elements selected, quantitative elemental image showing Ca distribution over the particle. Acc voltage 20 keV, beam current 0.48 nA, acquisition time 40 s.

A 30-second point analysis was run in the center of the particle. It revealed an equal amount of Ca and C and three times the amount of oxygen, confirming that it can be assigned to calcium carbonate ($CaCO_3$).



Element	Atomic %	Atomic % Error
C	20.6 %	0.1 %
O	60.4 %	0.3 %
S	0.4 %	0.0 %
Zn	0.4 %	0.0 %
Ca	18.3 %	0.1 %

Figure 10. Partial view of the user interface showing the point where the point analysis has been acquired and the related quantification. Acc voltage 20 keV, beam current 0.48 nA, 5000 cps, acquisition time 30 s.

$CaCO_3$ is an inorganic compound which is classified as a semi-reinforcing filler, as it has little ability to enhance the mechanical properties of the whole rubber compound. Being a low-cost material, it has a long history of use in plastics and rubber; the addition of $CaCO_3$ increases the product's volume (hence reducing the needed amount of natural rubber, which is more expensive). It also improves other characteristics like the hardness of the final material, abrasion and heat resistance.

Other particles with similar composition, but different shapes, have been investigated. Another example is presented in Figure 11.

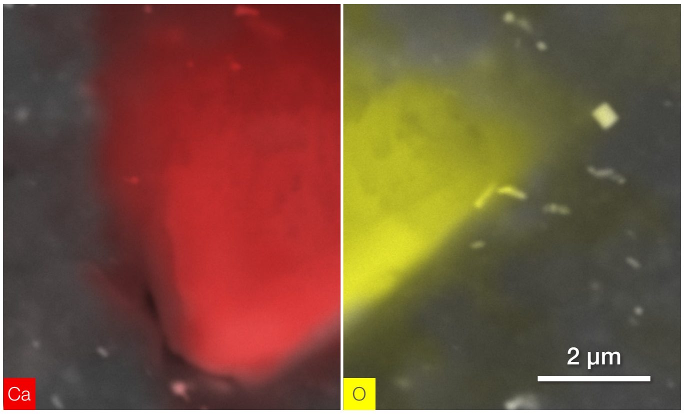


Figure 11 $CaCO_3$ particle. Ca distribution (left) and O distribution (right). Acquisition time 40 s.

Hydrous magnesium silicate, commonly known as talc ($Mg_3Si_4O_{10}(OH)_2$), is another type of filler, that has been employed in the rubber industry for over 40 years. Talc is a naturally occurring mineral; it is not used in tread rubber compounds, but instead is used in the inner layers where it provides higher tear resistance. Consequently, talc is crucial for increasing the tire's toughness and durability.

Figure 12 shows a complete set of quantitative elemental maps of one of the many clustered additives that are found in the subtread and undertread.

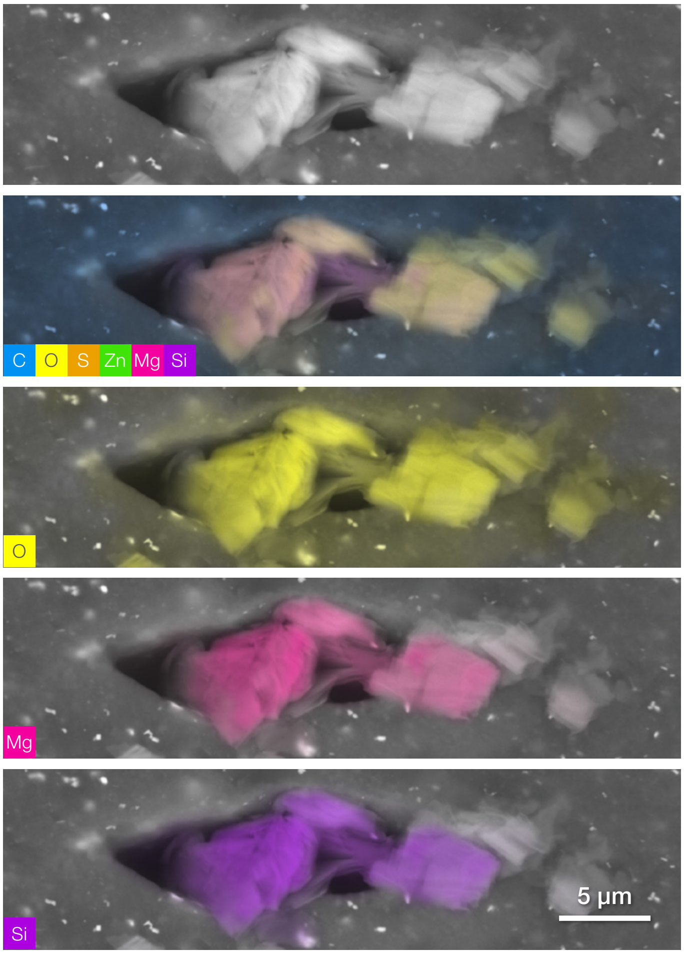
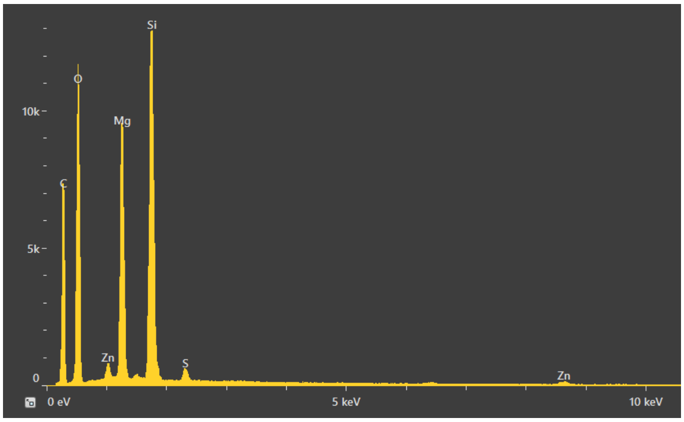


Figure 12. Oxygen, magnesium and silicon rich fillers. The set of images has been acquired in one time by simply saving the conventional greyscale image and then turning on the live quantitative elemental analysis and selecting or unselecting the different elements in order to highlight their distribution.

The morphology of the imaged filler shows that these particles have a plate-like appearance. The crystal habit information coupled with quantitative elemental information provided on-the-fly during the image acquisition, clearly indicates that they can be classified as talc.

In order to have a better understanding of the quantities, a point analysis has been also acquired. The spectrum presented in Figure 13, shows small peaks for Zn and S, which are coming either from the rubber matrix or from the relatively high amount of zinc oxide particles surrounding the ROI. In fact, a high acceleration voltage such as 20 keV generates an interaction volume that includes signal from the area surrounding the point of interest.



Element	Atomic %	Atomic % error
C	38.4	0.2
O	44.5	0.2
S	0.3	0.0
Zn	0.3	0.0
Mg	7.5	0.0
Si	9.0	0.0

Figure 13. Spectrum resulting from the point analysis of the talc particle and related quantification. Acc voltage 20 keV, beam current 0.48 nA, acquisition time 60 s.

Quantification confirms that the Mg:Si ratio is around 3:4, as it is in talc. Oxygen is slightly higher which is probably due to the presence of an oxygen signal coming from the rubber.

Conclusions

Tire failures are often linked to an inhomogeneous dispersion of the different fillers and SEM, with the contribution of EDS, is key to understand the root cause of failure.

In this application note, we have demonstrated how the challenging work of properly identifying both the distribution and identity of filler materials in tires is made more efficient by using live quantitative imaging and analysis provided by the Axia ChemiSEM. Filler materials have been properly identified and their distribution easily observed due to the sample centricity of the Axia ChemiSEM analytical workflow.

References

Brewer HK, C. S. (2006). The Pneumatic Tire. U.S.A: U.S. Department of Transportation, National Highway Traffic Safety Administration.

Roy K, D. S. (2019). A critical review on the utilization of various reinforcement modifiers in filled rubber composites. Journal of Elastomers & Plastics, Vol. 52(2), 167–193. doi:10.1177/0095244319835869

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