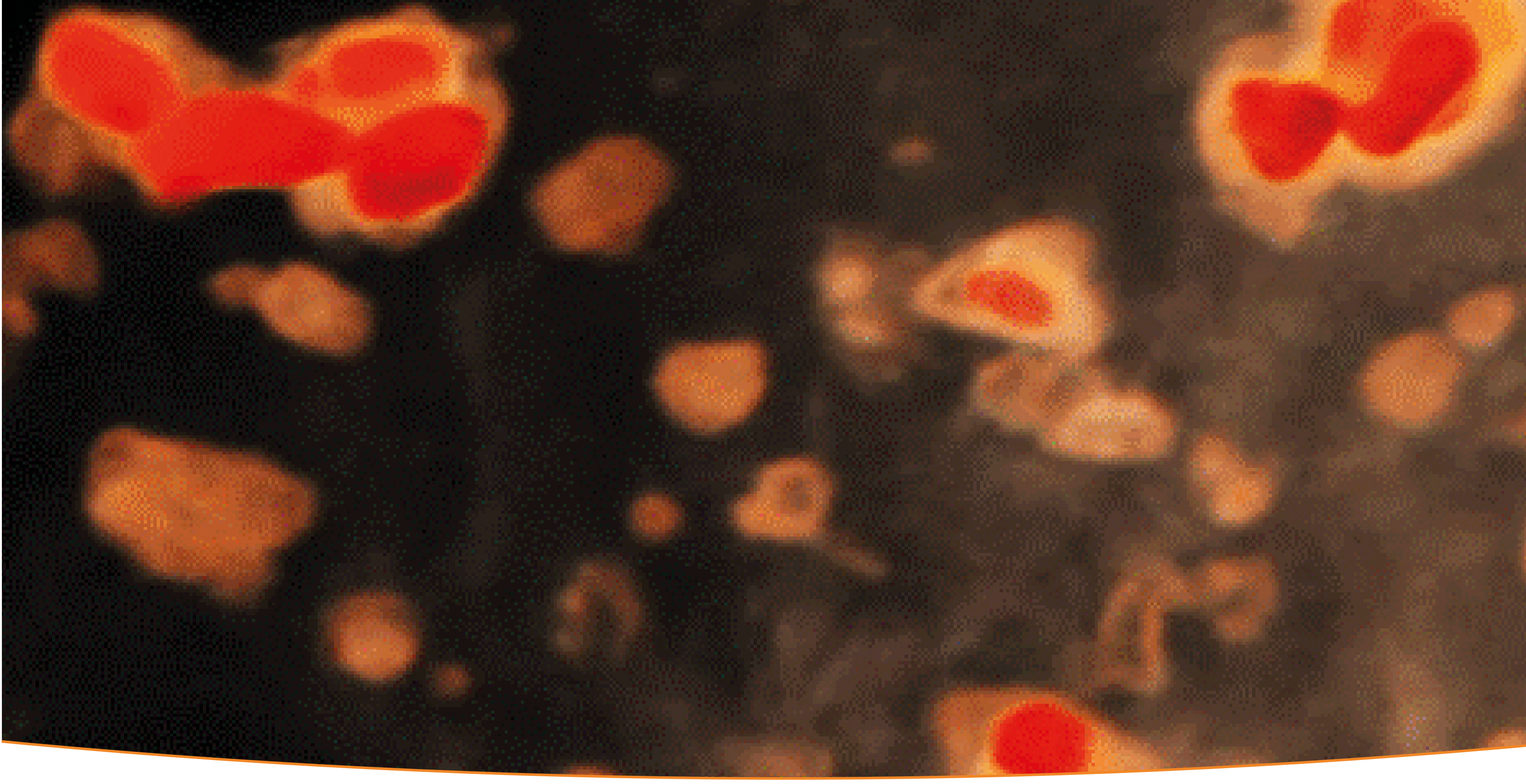

Optimizing rubber performance guided by microscopy

Visualizing the distribution and role of rubber components using microscopic techniques

Executive Summary

To ensure the optimal performance of composite materials it is critical that mixing results in the desired distribution of chemicals (or particles) and that the right chemistry is taking place. Microscopic examinations of composites can be a key enabler in delivering structure – property relationships, greatly accelerating new product development activities.
This White Paper demonstrates how, for rubber processing, the visualization of the ingredient distributions has contributed to improved mixing and with that to improved performance. Local chemical identification at the nanoscale yielded valuable mechanistic insights in the crosslinking process.

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Optimizing rubber performance guided by microscopy

Rubber needs to be crosslinked to achieve dimensional stability, good mechanical properties and chemical resistance. Since the discovery of sulfur as crosslinking agent more than 150 years ago, many initiatives optimized the reaction process, generated improved rubber properties and elucidated the crosslinking mechanism. Recently, a novel sulfur organic copolymer (Thioplast CPS200, a cyclic tetrasulfide (CTS)) was explored as a vulcanization agent for ethylene propylene diene monomer (EPDM) rubber to increase its resistance to non-polar hydrocarbon solvents.

How to visualize the distribution of rubber components?

To optimize the polymer mixing process and to determine the effect of additives on polymer dispersions (e.g. carbon black CB, silica SiO2) ECCD was asked whether it was possible to visualize the distribution of these ingredients. Under industrial curing conditions zinc oxide and stearic acid are used as activators for the crosslinking process and microscopy techniques were used to study the dispersion and mechanistic role of these agents.

Technique selection

The dispersion and/or size of the rubber additives was expected to range from micrometer to nanometer scale. Therefore, it was decided to use both Scanning Electron Microscopy (SEM) and Scanning Transmission Electron Microscopy (STEM) for visualization. This combination covers the expected magnification range needed and has the advantage that imaging can be combined with local chemical analysis using Energy Dispersive X-ray analysis (EDX). Additionally, these techniques can generate 3-dimensional information on the relative location of the rubber components. The irradiation dose must be carefully controlled as the polymers are susceptible to damage by the electron beam.

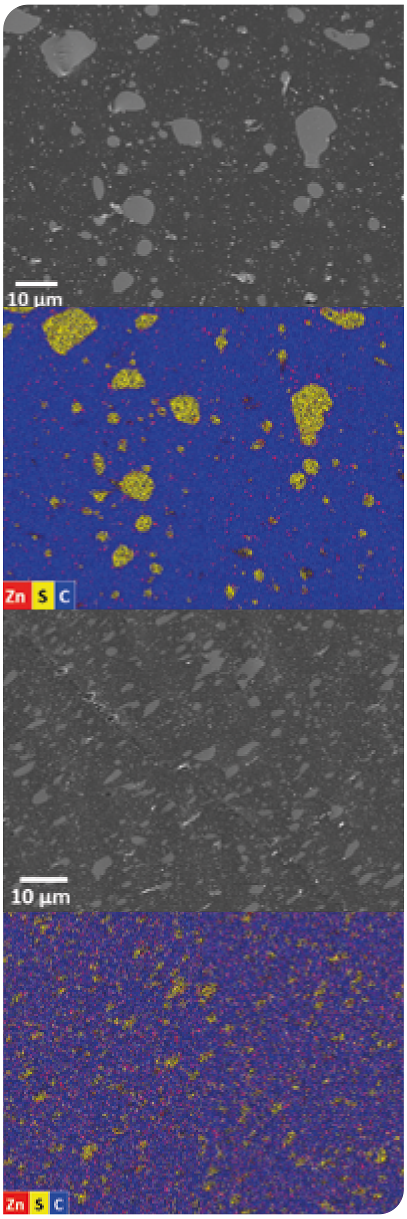

Figure 1. SEM images and overlays of EDX element maps of EPDM-CTS polymer mixtures without (upper set) and with (lower set) carbon black, showing the improved CTS dispersion after carbon black addition

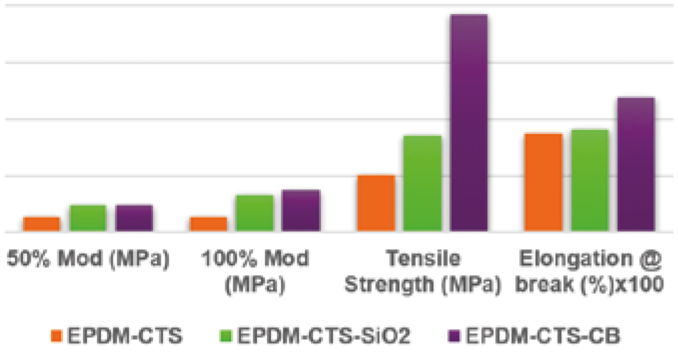

Figure 2. Mechanical properties of rubber formulations.

Sample preparation

High quality SEM and (S)TEM analyses require that cross-sections and thin slices (50-100 nm) of the rubber sheets are available. This cutting process is typically done by an ultramicrotome using a diamond knife under cryogenic conditions, the latter to deal with the flexibility of rubber.

Results

Based on the SEM-EDX images the impact of the rubber mixing process and the addition of additives on polymer dispersion could be determined (e.g. Figure 1). By adding carbon black an improved dispersion of CTS could be reached. The observations were in good agreement with the mechanical properties (Figure 2), showing a.o. a higher tensile strength for rubber formulations including CB. As a result, clear guidelines for further development could be derived.

From a mechanistic point of view the role of ZnO and stearic acid in the crosslinking process could also be determined (e.g. Figure 3). The original ZnO particles (50-200 nm) react to form both aggregates of ZnS nanocrystals (3 nm) and featherlike structures of Zn stearate. Apparently zinc ions combine with stearic acid and the cyclic tetrasulfide (Thioplast) to form an active complex that catalyzes the vulcanization process.

Conclusion

The ECCD successfully developed an analytical approach to visualize the different components in a novel cured rubber mixture. New insights on location, dispersion and reactivity of the ingredients were obtained. This has contributed to a faster and more focused product development process for the customer.

More reading
Butuc et al., Role of zinc oxide in sulfur crosslinking, Technical Notebook in Rubber & Plastic News, February 10th (2020) p. 16.

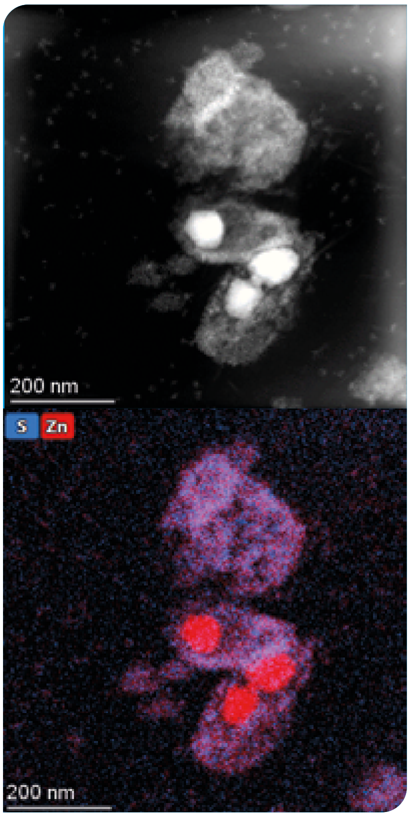

Figure 3. STEM image (top) and overlay of EDX element maps (bottom), showing that ZnO nanoparticles (bright, 50 nm) are converted to agglomerates of finely dispersed zinc sulfide (3 nm) during curing of the polymeric mixture.

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Delivering Expertise to your Business

Nouryon, ECCD
Zutphenseweg 10
7418 AJ Deventer
The Netherlands

T +31 (0)570 679108
E ECCD@nouryon.com

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