

**New insights into the role played by ZnO in sulfur crosslinking by  
ways of a sulfur donor**

*Gina Butuc<sup>1,3\*</sup>, Arne Janssen<sup>2</sup>, Kees van Leerdam<sup>2</sup>, Auke Talma<sup>2</sup>, Anke Blume<sup>3</sup>*

1. Nouryon, 525 W Van Buren, Chicago, IL, 60607, USA; [gina.butuc@nouryon.com](mailto:gina.butuc@nouryon.com)
2. Nouryon, Zutphenseweg 10, 7418 AJ Deventer, The Netherlands
3. University of Twente, Faculty of Engineering Technology Department of Elastomer - Technology and Engineering, Enschede, The Netherlands

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\* Speaker

## **Abstract**

*Sulfur crosslinking was discovered by Goodyear and Hancock more than 150 years ago and led to the development of a new material science application – rubber. Since the first discovery of ways of vulcanizing rubber for improved dimensional stability, mechanical properties and chemical resistance, sulfur continued to be analyzed to elucidate its role in the crosslinking process. Early after the discovery was made, it was determined that vulcanization by ways of elemental sulfur alone is too slow for commercial purposes and ways to expedite the crosslinking reaction were studied. Zinc oxide (ZnO) in combination with stearic acid were discovered as best ways for improved sulfur reactivity in the vulcanization process. Zinc ions combine with stearic acid and a cyclic tetrasulfide which acts as a sulfur accelerator to form an active complex which catalyzes the vulcanization process. Since the mechanism of reaction is complex, analyzing the structure at the nano level could yield an insight into the process. This paper is focusing on transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy (EDX) for an in-depth analysis of the process with an emphasis on ZnO crystallography/surface chemistry and its influence on sulfur crosslink process.*

## **Introduction**

Either naturally derived or synthetically produced elastomers need to be subject to further chemical processing to achieve the dimensional stability required by rubber applications and this process is known as vulcanization. Sulfur crosslinking or vulcanization is the most common way of achieving the mechanical strength and required in rubber applications <sup>1-4</sup>. It is seldomly occurring that elemental sulfur is used as the sole crosslinking agent, usually there are other sulfur compounds called accelerators that are helping in the vulcanization process. Although the process of vulcanization has been known for more than 100 years, the mechanism of reactions is still yet to be fully understood. The main reason of this knowledge gap is the complexity of rubber compounds which often contain more than 5 components involved in the vulcanization itself, therefore the full mechanism of crosslinking is not fully understood. The mechanism of sulfur crosslinking has been elucidated in the case of elemental sulfur, both radical or ionic initiated process <sup>5-6</sup>. However, a large number of sulfur crosslinking applications involve crosslinking by ways of sulfur accelerators and for these reactions it is generally understood that the mechanism is specific to each type of accelerator <sup>7,8</sup>. In recent years, special attention is given to polymeric sulfur either as is or sulfur organic copolymers as vulcanization agents since that presents the advantage of improved solubility of sulfur species in the polymeric matrix <sup>9</sup>.

It is already known that ZnO is playing an important role in rubber compounds, particularly in the sulfur related vulcanization. Interestingly, in the early years of rubber vulcanization ZnO

was only used as an inorganic reinforcing filler. It was not until the 1920s that it was proven that sulfur vulcanization process can expedite using ZnO in combination with stearic acid <sup>10,11</sup>. The role of ZnO and stearic acid was not fully understood and it is only in recent years that scientists started studying the chemical process by using both small-angle neutron scattering and X-ray techniques suggesting that an intermediate structure of ZnO/stearic acid is formed <sup>12,13</sup>.

Besides participating in the crosslinking process, ZnO plays an important role in reducing the rubber hardening as an undesired side effect of oxidative aging occurring in sulfur cured compounds, particularly in styrene butadiene rubber (SBR). In this type of system, the main role of ZnO is to activate the sulfur cure and a by-product of this cure reaction is ZnS <sup>14, 15</sup>. Free sulfur present in an aged elastomer compound is resulted from polysulfidic bonds cleavage into disulfide or even monosulfide bridges.

In this research, the role played by the ZnO as crosslinking facilitator was investigated in a novel elastomer blend with increased resistance to non-polar hydrocarbon solvents. The novelty polymer-oligomer blend for rubber applications elastomer blend is based primarily on ethylene propylene diene terpolymer (EPDM). The curative system for the blend is dual organic peroxide and sulfur, the focus of this investigation is on ZnO role plays in the polysulfides cure. Dual cure is getting an increased attention recently since it has the advantage of imparting best properties derived from each type of curative <sup>16</sup>. For EPDM, this kind of dual cure system could lead to improved scorch time during curing, improved mechanical properties, such as higher elongation at break and increased tear strength, as well as better heat stability of the resulting compound and improved compression set. In this complex system the role of ZnO is unclear, but with the help of analytical techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), both coupled with energy dispersive X-ray spectroscopy (EDX) the role of ZnO and stearic acid in facilitating sulfur cure of a non-polar elastomer, using a sulfur donor type system could be explained.

## **Materials and experimental description**

**Cyclic tetrasulfide (CTS)** produced by Nouryon Functional Chemicals and commercialized under the tradename of Thioplast CPS200 is a low molecular weight oligomer, Mw ~5000 and a high sulfur content – 50% <sup>17</sup>. The physical appearance of this product is of a viscous liquid.

**Ethylene propylene diene terpolymer (EPDM)** produced by Arlanxeo and commercialized under the tradename of Keltan 2450. This elastomer has a low Mooney viscosity ML (1+4) @ 125 °C of 28 and a relatively high ethylene content of 48% while the ethylene norbornene content is of 4.1%.

**Crosslinking agents** are as follows:

- Dicumyl peroxide (40 wt.%) on clay produced by Nouryon and commercialized under the trade name of Perkadox BC-40K-pd, in powder form.
- ZnO technical grade by Spectrum Chemicals
- Stearic acid technical grade by Spectrum Chemicals

Compound mixing equipment was performed in a Brabender internal mixer with a capacity of 0.5L and intermesh rotors.

Mechanical properties were measured using a tensile tester by Instron, model 4500 series with a loadcell of 5kN. Stress strain tests were performed according to ASTM D1708 at a crosshead speed of 50 cm/min.

Fluid immersion test was performed according to ASTM D471 at room temperature and atmospheric pressure. The hydrocarbon fluid used for immersion is IRM 903 which comprises of 45% normal paraffin, 50% iso paraffin, 5% aromatic hydrocarbon.

For imaging a scanning electron microscope (SEM) Zeiss CrossBeam 540 was used, equipped with an Oxford Instruments X-Max<sup>N</sup> 150 silicon drift detector (SDD) for EDX (using Aztec software), and ATLAS 5, a correlative workflow software for large area imaging and slice-and-view experiments for tomography. SEM-EDX Spectrum Images (SI) and large area SEM maps were acquired at a primary electron beam energy of 6 keV at a beam current of 300 pA.

Cross-sections of the rubber samples for SEM were prepared either by cutting with a razor blade perpendicular to the surface or by using a Leica EM UC7 ultramicrotome under cryogenic conditions. The cross-sections were attached with Silver DAG (provided by agar scientific) onto Al based stubs. A Leica EM ACE600 high vacuum sputter/coater was used to coat the samples with 12 nm amorphous C to increase the electron conductivity.

Imaging at higher magnifications was performed on a Thermo Scientific Talos F200X S/TEM Transmission Electron Microscope. This microscope is equipped with a high brightness X-FEG electron source and Super-X energy dispersive silicon drift detectors (SDD's). The

instrument was mainly operated in STEM mode at an accelerating voltage of 200 keV with a beam current of 500 pA. Imaging was commonly done using a high angle annular dark field (HAADF) detector.

EDX spectrum images (SI) were acquired and processed in the Thermo Scientific Velox Software. Typical acquisition conditions were image sizes of 1024x1024 pixels at a dwell time of 25  $\mu$ s/pixel.

Electron transparent films for the STEM-EDX investigations were prepared with a Leica UC7 Ultramicrotome under cryogenic conditions (-120° C). The thin sections were collected dry on holey carbon filmed Cu grids.

## Results and discussion

This paper is focused around the role of ZnO as crosslinking facilitator for sulfur cure. The curative system used is a dual system organic peroxide and sulfur generated in situ by the CTS in a blend of EPDM and CTS (Fig. 1). The dual cure system is used for improved scorch time during curing, improved mechanical properties and better compression set. While the peroxide cure mechanism is understood, the sulfur cure is more complex in this system and it is facilitated by the presence of ZnO and stearic acid.

Polysulfides are known to have a high resistance against swelling in hydrocarbon solvents<sup>18,19</sup>. CTS was chosen for this experiment due to its sulfur donor properties in such a manner that it has the right scorch time (other types of polysulfides, such as polysulfides containing thiol end groups exhibit high scorch<sup>18</sup>). CTS as a blend with EPDM with the resulting EPDM-CTS blend targeted to have an improved resistance against swelling in hydrocarbon solvents. The CTS is undergoing a ring opening reaction from which it is releasing sulfur species in the form of mono and disulfide which can further participate in crosslinking reactions. The ring opening reaction should be facilitated by ZnO, but the mechanism of the reaction is not understood.

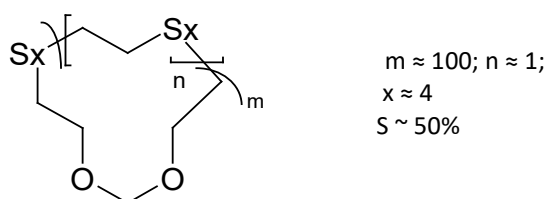


Fig. 1. CTS molecular structure

EPDM has a fully saturated backbone and unsaturation is added in the small side chains as crosslinking sites. Its structure is indicated in Fig. 2.

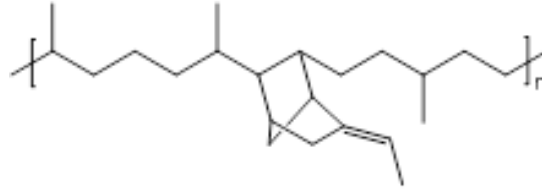


Fig. 2. EPDM molecular structure <sup>16</sup>

Since rubber compounds are having a complex composition, the formulations presented in this paper are scaled back to basic contributors to the elastomer network to facilitate the investigation on sulfur crosslinking and the role played by ZnO and stearic acid. Presented in this paper, there are three compounds having the compositions listed in Table 1 were mixed using an internal mixer followed by shaping on a two-roll mill and cured at 177 °C. The fillers used for these applications were selected to have a comparable surface area for easy of comparison, which is 60 (m<sup>2</sup>/g) for the silica particles and 83 (m<sup>2</sup>/g) for the carbon black.

Compound	EPDM-CTS (phr)	EPDM-CTS-SiO <sub>2</sub> (phr)	EPDM-CTS-CB (phr)
Ingredients			
EPDM	75	75	75
CTS	25	25	25
Carbon black (CB)	-	-	30
Silica (SiO <sub>2</sub> ) non-surface treated	-	30	-
Dicumyl peroxide 40% on clay	6	6	6
ZnO	5	5	5
Stearic acid	5	5	5

Table 1. EPDM-CTS elastomer composition

Testing at the macro structure level, Shore A hardness has an expected lower value for the non-filled compound (45) as compared to the filled rubbers (54 for silica filled material and 56 for CB filled material). Mechanical properties are presented in Fig. 3. The unfilled compound shows as expected lower moduli, tensile strength and elongation at break. Interestingly, the compound containing carbon black has much improved mechanical properties when compared against the compound containing silica. This could be explained by carbon black's affinity to the EPDM elastomer therefore presenting a good reinforcing behavior. By comparison, silica - being a polar material - has a greater affinity towards the CTS part of the network which is firstly less abundant, and secondly is the weaker of the two main phases due to its low molecular weight. Also, the silica filler used in this experiment does not contain a coupling agent which is known to enhance the reinforcing silica properties. Future studies of compounds containing silica fillers are incorporating coupling agents, which has the potential to improve the filler reinforcement behavior.

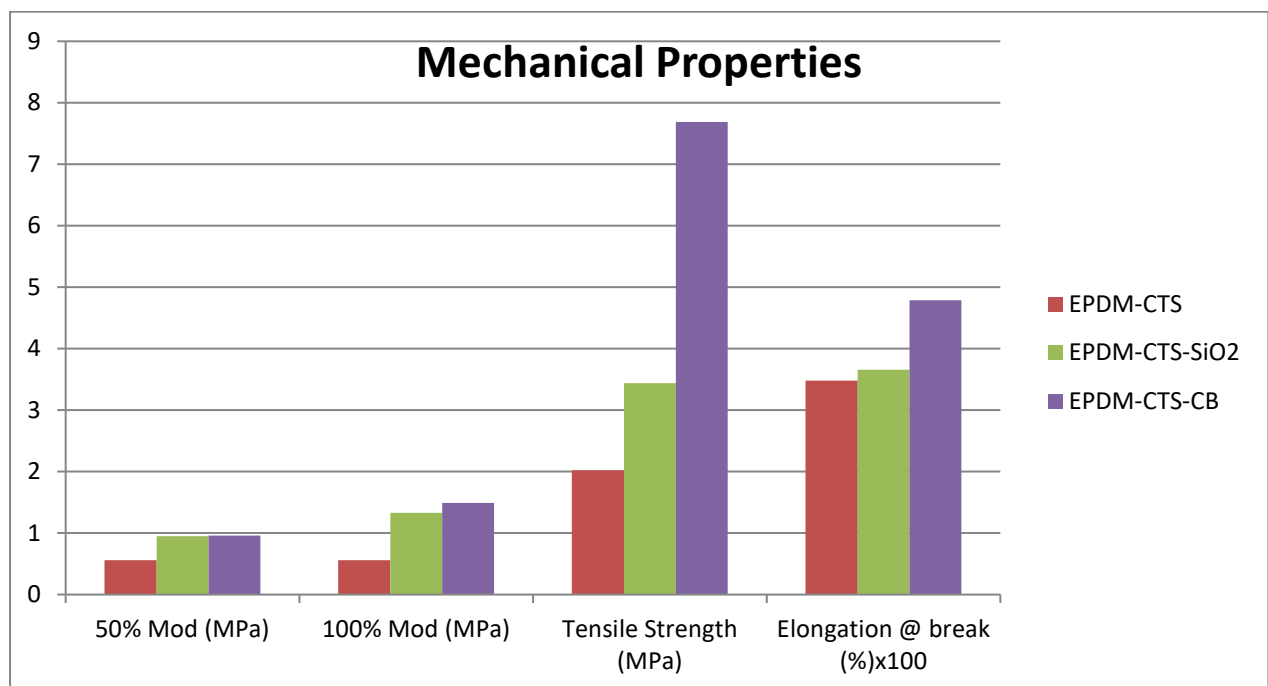


Fig. 3. Mechanical properties of EPDM-CTS compounds

A fluid immersion test was performed according to ASTM D471. Materials were immersed in the test fluid and removed periodically for measuring of fluid absorption/adsorption until equilibrium. Fluid absorption measurements were performed by weighing of the test specimens. The test results are presented in Fig. 4.

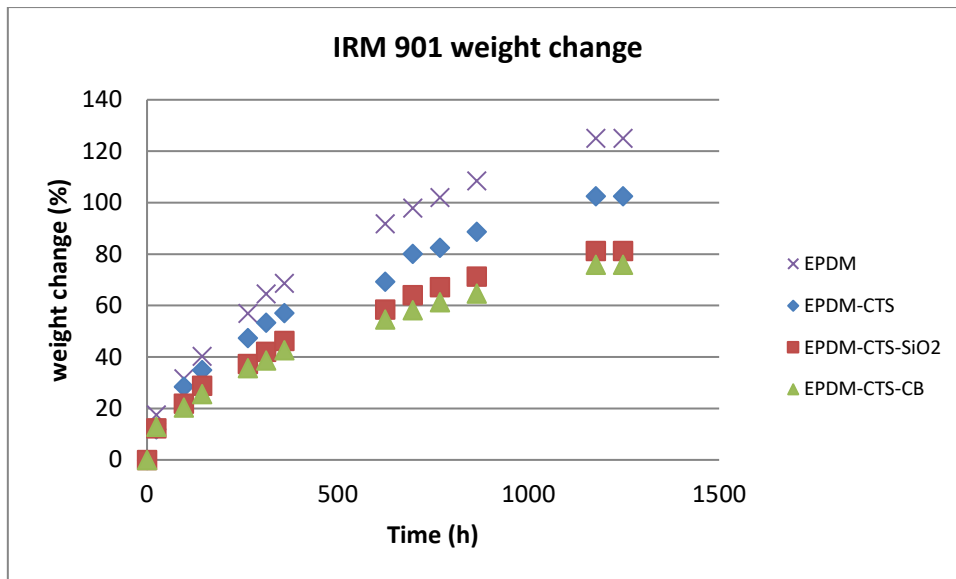


Fig. 4 Hydrocarbon absorption of EPDM based compounds

EPDM peroxide cured was used without CTS as a reference material, also containing 5 phr of ZnO and stearic acid, respectively. It is known that EPDM performs poorly when exposed to hydrocarbon solvent<sup>20</sup>. Therefore, it is no surprise that the reference material is the worst performer in the fluid exposure test performed by an increase of 131% of its original weight. By comparison, a compound containing 25% CTS is showing a reduction of fluid absorption of approximately 28%. The EPDM-CTS compounds also containing silica and carbon black, respectively showed an even higher resistance to swell in hydrocarbon solvent, but this superior result is a filler effect.

Looking at the micro level and analyzing the structure of the compounds by SEM (Fig. 5), the homogeneity of the compounds can be compared. In the non-filled compound (EPDM-CTS), the continuous phase is EPDM while the discrete phase is the CTS. It is expected and proved in this experiment that the dispersion is greatly improved when filler is added, as indicated in Fig. 5 for the carbon black filled compound (EPDM-CTS-CB).



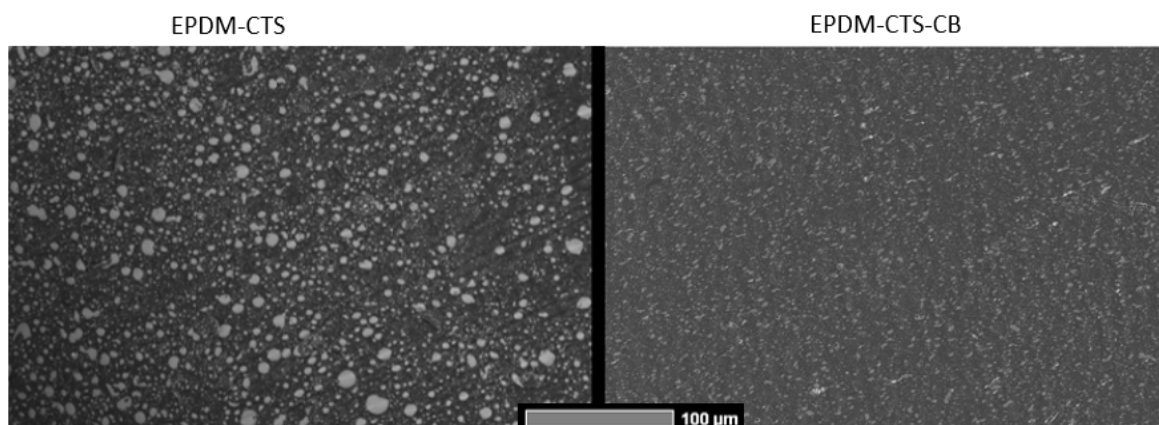


Fig. 5. SEM images of unfilled and CB filled compounds

A side by side comparison of CB filled compound (EPDM-CTS-CB) versus silica filled compound (EPDM-CTS-SiO<sub>2</sub>) at smaller scale of 20 μm appears to have a more homogeneous CB filled compound than the silica filled compound. The homogeneity of the two materials is similar, but the contrast given by silica and CTS makes appear as slightly less homogeneous. SEM pictures of CB and silica filled compounds, respectively are shown in Fig. 6.

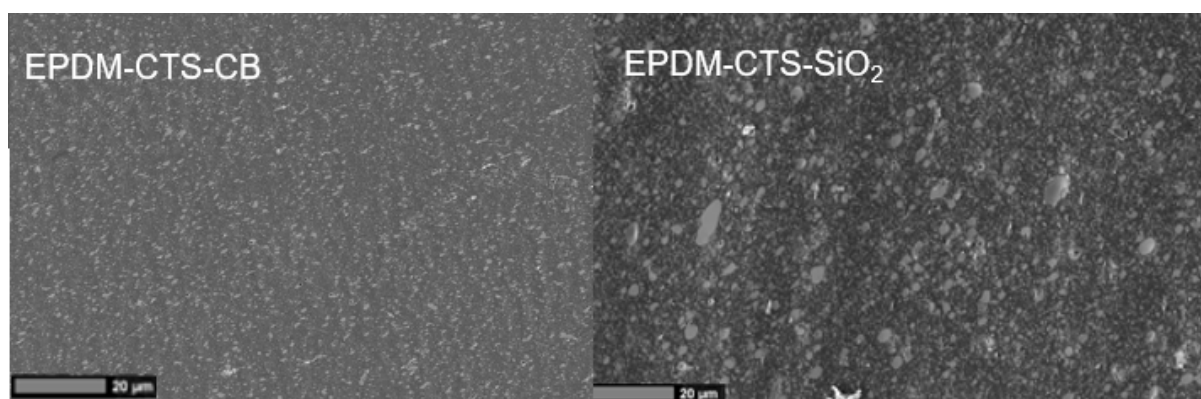


Fig. 6. SEM image of CB and silica filled compounds

Further research is focused on improved dispersion of the two phases EPDM and CTS using a compatibilizer.

At even higher magnifications (nm scale) by using STEM/EDX the role of ZnO can be analyzed in depth in generating the sulfur in-situ. Fig. 7 a) identifies a small agglomerate of ZnO in the EPDM compound. Using EDX imaging it can also be identified the presence of two other Zn species, the first one is ZnS present as small (3 nm) nanoparticles in abundance particularly surrounding the ZnO agglomerate. The presence of ZnS is identified by superimposing the two images identifying Zn presence and S presence. The second Zn compound is a faint,

featherlike structure which is considered to be zinc stearate. Although the ZnO and ZnS are found in a close neighborhood of each other, with ZnS being more scattered and surrounding the ZnO clusters, the zinc stearate compound is generally found at a bit larger distance from ZnO, suggesting a higher mobility. It seems to be that both ZnO and ZnS being inorganic materials do not solubilize in EPDM, but zinc stearate has a relatively higher solubility in the polymer matrix. Zinc stearate appears at a distance further away from the ZnO crystals cluster supporting the idea of a higher solubility of this chemical compound in EPDM.

CB particles are also playing a support role, facilitating the sulfur generating reaction, as seen in Fig. 7 b-c) where sulfur as clusters of ZnS are seen on the surface of CB particles. Fig. 7 d) is a close look at clusters of ZnO and ZnS.

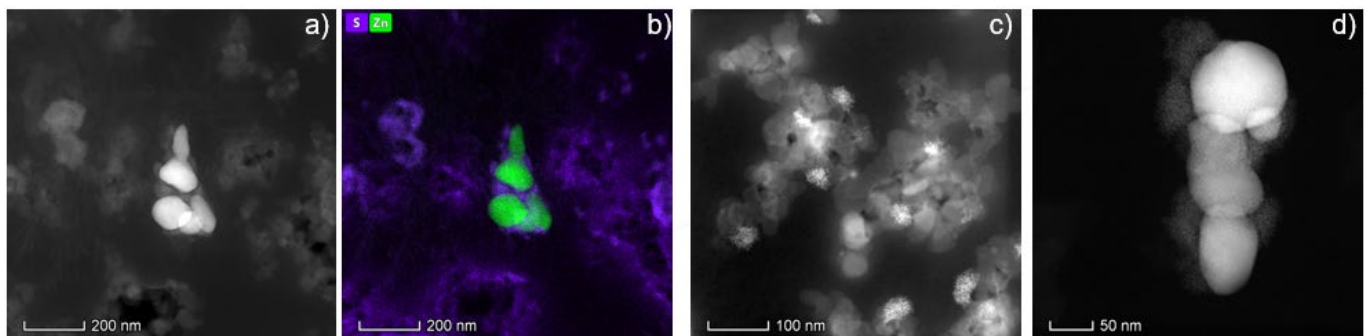


Fig. 7. STEM/EDX images of CB filled compound

Similar features are seen in the case of silica filled compound in Fig. 8, the same three types of Zn species are present. Once again ZnO and ZnS are clustered together while zinc stearate gets diffused within the EPDM network. One noticeable difference at least qualitatively is in the relative amount of ZnS present at the surface of silica, which is significantly lower than CB.

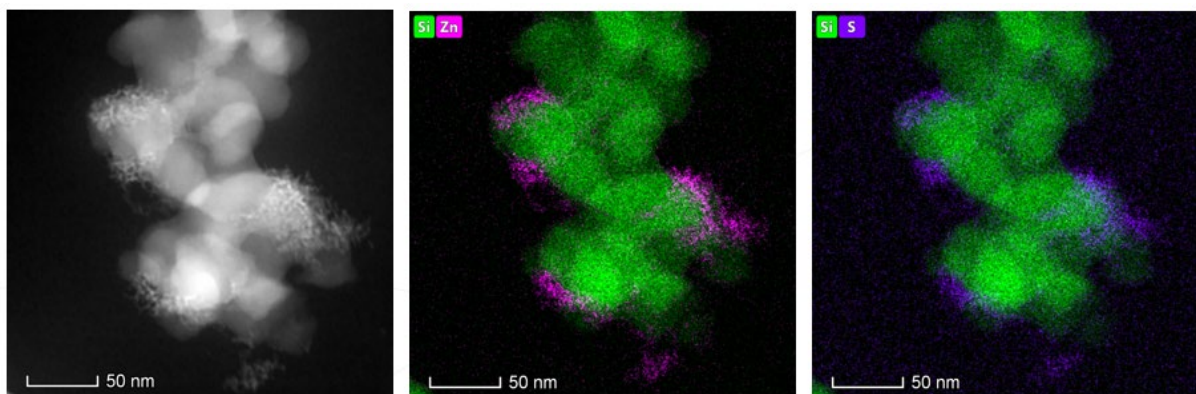


Fig. 8. STEM/EDX images of silica filled compound

These imaging evidences are supporting the hypothesis the sulfur generating reaction being catalyzed by the ZnO crystals in the presence of stearic acid.

Additional supporting STEM images of EPDM-CTS compound filled with silica is also indicating the presence of all three Zn species, ZnO, ZnS and zinc stearate. Once again ZnO and ZnS are within closed proximity, but zinc stearate is diffusing away from the surface of ZnO and into the EPDM matrix as indicated in Fig. 9.

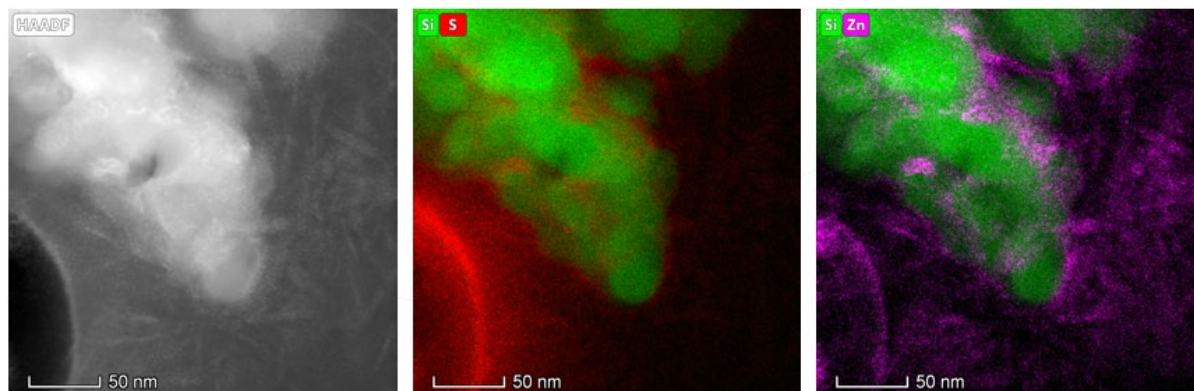


Fig. 9. Additional STEM/EDX images of silica filled compound

## Summary

This research project takes a different approach to investigate the sulfur crosslinking by ways of imaging of ZnO. With the use of STEM/EDX it is demonstrated that the ring opening sulfur generating reaction occur at the surface of ZnO present in the compound and the reaction is facilitated by the presence of stearic acid. Resulting free sulfur is captured by the ZnO which turns into ZnS. It is also concluded that zinc stearate is less efficient in sulfur crosslinking due to its solubility in the polymeric matrix.

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