Technical

Role of zinc oxide in sulfur crosslinking

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Executive summary

Sulfur crosslinking was discovered by Charles Goodyear and Thomas 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.

Although the discovery of sulfur crosslinking was in itself a game changer, it was determined that vulcanization was too slow for commercial purposes and as such methods to expedite the crosslinking reaction were studied. Zinc oxide in combination with stearic acid were discovered as the best ways for improved sulfur reactivity in the vulcanization process. Zinc ions combine with stearic acid and cyclic tetrasulfide (acting as a sulfur accelerator) to form an active complex which catalyzes the vulcanization process.

Because 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.

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 required in rubber applications.[1-4]

It is seldom that elemental sulfur is used as the sole crosslinking agent. Usually there are other sulfur compounds

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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 for this knowledge gap is the complexity of rubber compounds, which often contain more than five ingredients 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.[5-6] However, a large number of sulfur crosslinking applications involve crosslinking through sulfur accelerators, and for these reactions it is generally understood that the mechanism is specific to each type of accelerator.[7,8]

In recent years, special attention is given to polymeric sulfur either as is or in the form of sulfur organic copolymers acting as vulcanization agents because they present the advantage of improved solubility of sulfur species in the polymeric matrix.[9]

It already is known that zinc oxide is playing an important role in rubber compounds, particularly in the sulfur related vulcanization. Interestingly, in the early years of rubber vulcanization, ZnO only was used as an inorganic reinforcing filler. It was not until the 1920s that it was proven that sulfur vulcanization process can be expedited using ZnO in combination with stearic acid.[10,11]

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.[12,13]

Aging of elastomer compounds is caused mainly by free sulfur resulted from polysulfic bonds cleavage into disulfide or even monosulfide bridges. 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 SBR. In this type of system, the main role of ZnO is to activate the sulfur cure having ZnS as a by-product of the cure reaction.[14,15]

In this research, the role played by the ZnO as crosslinking facilitator was investigated in a novel polymeric material blend with increased resistance to non-polar hydrocarbon solvents. The novelty polymer-oligomer mixture for rubber applications is based primarily on EPDM.

The curative system for the blend is dual organic peroxide and sulfur, and the focus of this investigation is on the role ZnO plays in the polysulfides cure. Dual cure is getting an increased attention recently because it has the advantage of imparting best properties derived from each type of curative.[16] 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) is produced by Nouryon Functional Chemicals and commercialized under the trade name of Thioplast CPS200; and is a low molecular weight oligomer, with a Mw ~5,000 and a high sulfur content of 50 percent.[17] The physical appearance of this product is of a viscous liquid.

The EPDM is produced by Arlanxeo and commercialized under the trade name of Keltan 2450. This elastomer has a low Mooney viscosity ML (1+4) @ 125ºC of 28, and a relatively high ethylene content of 48 percent, while the ethylene norbornene content is of 4.1 percent.

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; and
- 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 load cell of 5kN. Stress strain tests were performed according to ASTM D1708 at a crosshead speed of 50 cm/min.

The 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 45 percent normal paraffin, 50 percent iso paraffin, and 5 percent aromatic hydrocarbon.

For imaging a scanning electron microscope, (SEM) Zeiss CrossBeam 540 was used, equipped with an Oxford Instruments X-Max^N 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

Fig. 1: CTS molecular structure.

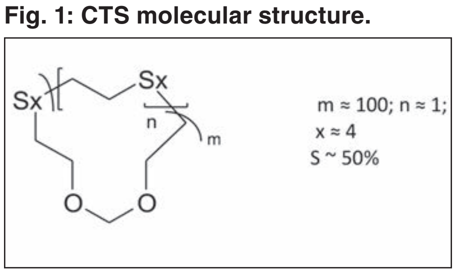


Fig. 2: EPDM molecular structure.[16]

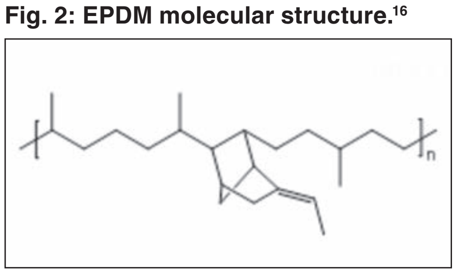
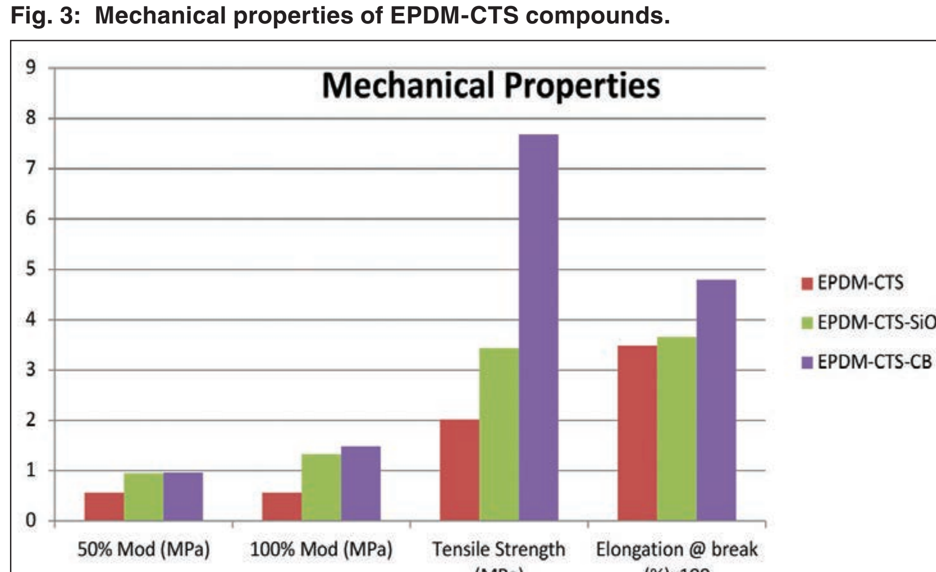


Table 1: EPDM-CTS elastomer composition.

Ingredients \ Compound	EPDM-CTS (phr)	EPDM-CTS-SiO2 (phr)	EPDM-CTS-CB (phr)
EPDM	75	75	75
CTS	25	25	25
Carbon black (CB)	-	-	30
Silica (SiO2) non-surface treated	-	30	-
Dicumyl peroxide 40% on clay	6	6	6
ZnO	5	5	5
Stearic acid	5	5	5

Fig. 3: Mechanical properties of EPDM-CTS compounds.



The authors

Gina Butuc is a doctoral candidate at the University of Twente, faculty of Engineering Technology, Department of Elastomer Technology and Engineering, and a technical development manager for crosslinking peroxides and polymer additives at Nouryon Functional Chemicals.

Butuc

She has more than 20 years of experience in the polymer field, either polymer synthesis or application development and polymer testing, ranging from bench chemist to business management.

Butuc is the inventor or co-inventor of six U.S. and international patents and the author of four technical articles and two book chapters. She holds a master's degree in organic chemistry from the University of Bucharest and a bachelor's in physical chemistry from the same university.

Arne Janssen currently is working for Zeiss Microscopy as product manager for electron microscopy. Janssen holds a doctorate in geological and earth sciences/geosciences from Westfalische Wilhelms—Universitat Muenster.

Kees van Leerdam is an analytical scientist, specializing in microscopy and surface analysis. Van Leerdam has worked in different science-related roles in the chemical industry for almost 30 years, serving many different markets such as catalysis, fibers, pharmacy, mining, paper, coatings and polymers. Van Leerdam holds a doctorate in applied physics on surface analysis from the Eindhoven University of Technology, and a master's degree in chemistry on catalysis from Utrecht University.

Auke Talma has been working for AkzoNobel/Nouryon for the past 35 years, in various functions ranging from scientist to research and development director for basic and applied research of additives for the rubber industry, radical polymerization, thermoset and sulfur chemistry. He is the inventor of Perkalink 900, an antireversion agent for elastomer compounds. Talma holds a doctorate in organic chemistry, from Groningen State University and a post-doctorate from the University of Twente.

Anke Blume studied chemistry at the university of Hanover Germany from October 1988 until July 1993. In the last year of her study, she came in the first contact with rubber during her master thesis. Consequently, she carried out her doctoral thesis at the German Institute for Rubber Technology, which she finished November 1995.

After nine months of post-doctoral study at the DIK, Blume started in September 1996 as a member of the product development group silica in the Applied Technology Department of Degussa A.G. She worked there in different positions, always related to the development of silica and silane for use in rubber.

Degussa changed owners several times and now is known as Evonik Resource Efficiency GmbH. Since August 2011, Blume has been an IP manager for silica and silane for rubber applications. In October 2013, she reduced her working time at Evonik and started at the University of Twente as chair of Elastomer Technology and Engineering.

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 1,024 by 1,024 pixels at a dwell time of 25 µs/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.[18,19] CTS was chosen for this experiment because of its sulfur donor properties in such a manner that it has the right scorch time (other types of poly-

See **Crosslinking**, *page 18*

Technical

Crosslinking

Continued from page 17

sulfides, such as polysulfides containing thiol end groups, exhibit high scorch).[18]

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.

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**.

Because 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** that 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 ease of comparison, which is 60 (m^2/g) for the silica particles and 83 (m^2/g) for the carbon black.

Fig. 4: Hydrocarbon absorption of EPDM-based compounds.

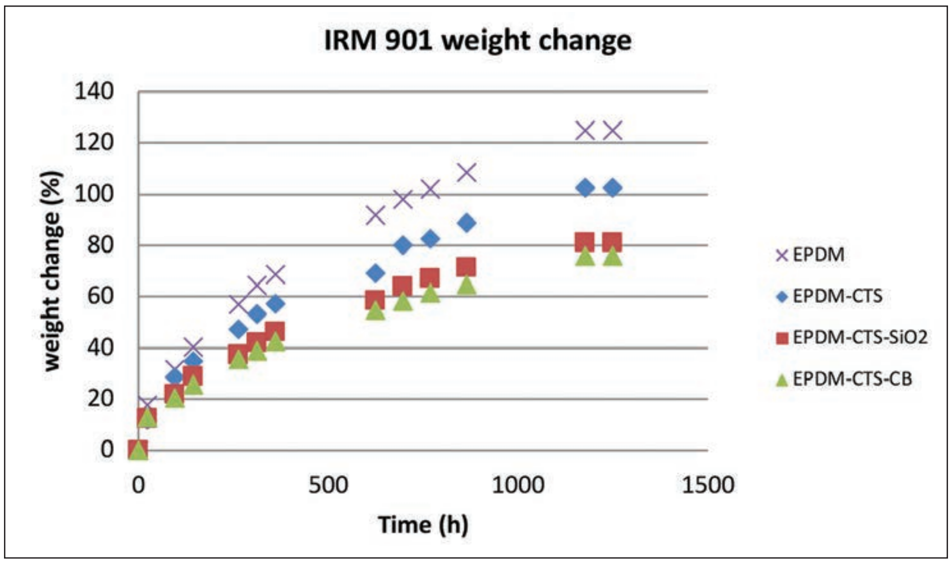


Fig. 5: SEM images of unfilled and CB-filled compounds.

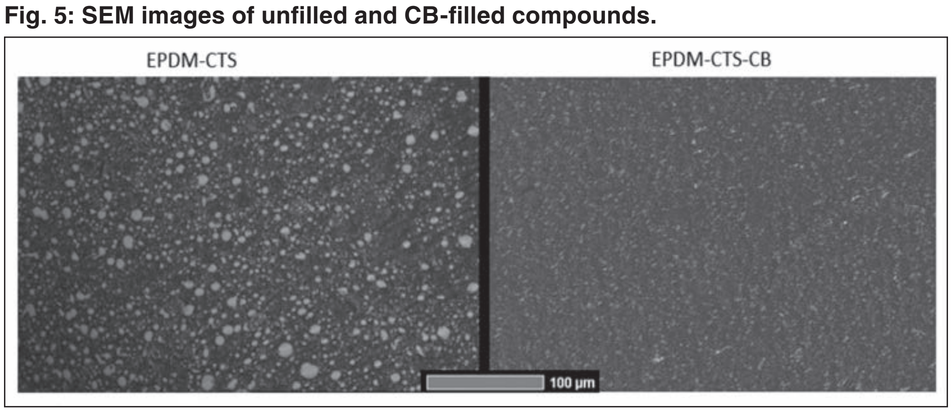
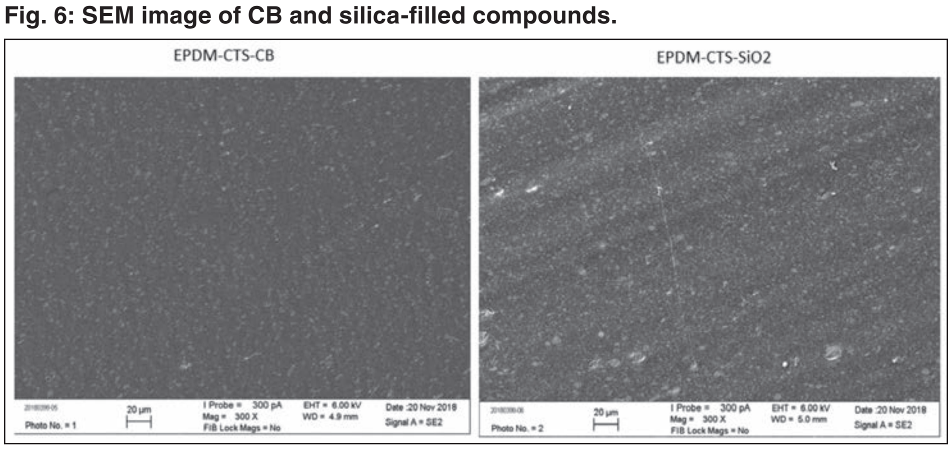


Fig. 6: SEM image of CB and silica-filled compounds.



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 toward the CTS part of the network, which is first less abundant, and second is the weaker of the two main phases because of 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 have the potential to improve the filler reinforcement behavior.

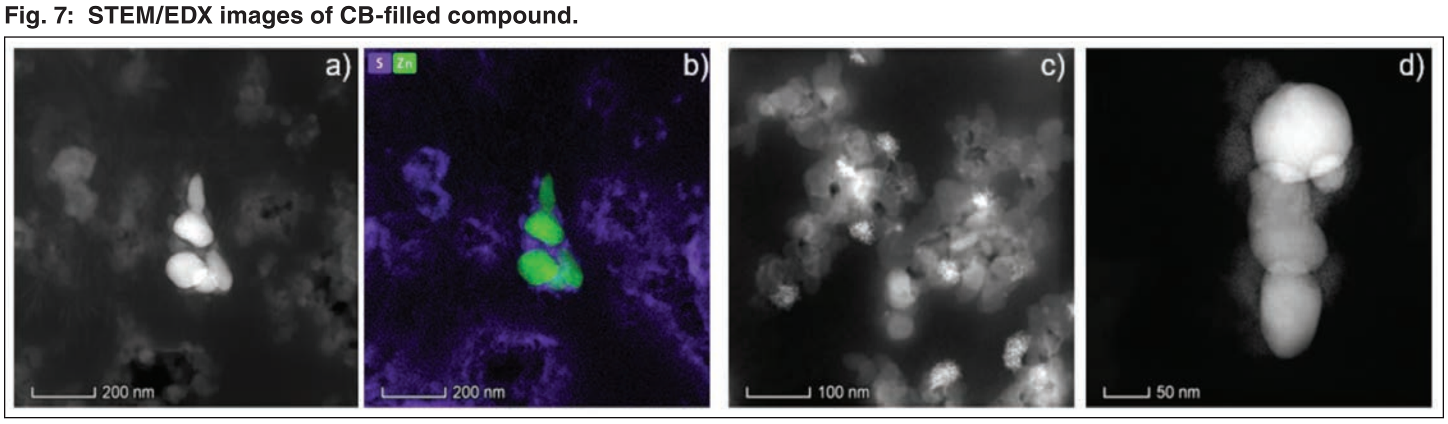
A fluid immersion test was performed according to ASTM D471. Materials were immersed in the test fluid and removed periodically for measuring of fluid absorption/adsorption until equilibrium. Fluid absorption measurements were performed by weighing of the test specimens. The test results are presented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

EPDM peroxide cured was used without CTS as a reference material, also containing five phr of ZnO and stearic acid, respectively. It is known that EPDM performs poorly when exposed to hydrocarbon solvent.[20] Therefore, it is no surprise that the reference material is the worst performer in the fluid exposure test performed by an increase of 131 percent of its original weight. By comparison, a compound containing 25 percent CTS is showing a reduction of fluid absorption of approximately 28 percent. 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 discreet 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).

A side by side comparison of CB-filled compound (EPDM-CTS-CB) versus silica-filled compound (EPDM-CTS-SiO_2) 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 it appear as slightly less homogeneous. SEM pictures of CB and silica-filled compounds, respectively, are shown in **Fig. 6**.

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



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. 7a** identifies a small agglomerate of ZnO in the EPDM compound. Using EDX imaging it also can 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, feather-like 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 also are playing a support role, facilitating the sulfur generating reaction, as seeing in **Fig. 7b-c**, where sulfur as clusters of ZnS are seen on the surface of CB particles. **Fig. 7d** is a close look at clusters of ZnO and ZnS.

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.

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 also is indicating the presence of all three Zn species, ZnO, ZnS and zinc stearate. Once again ZnO and ZnS are within close proximity, but zinc stearate is diffusing away from the surface of ZnO and into the EPDM matrix as indicated in **Fig. 9**.

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 also is concluded that zinc stearate is less efficient in sulfur crosslinking because of its solubility in the polymeric matrix.

See **Crosslinking**, *page 19*

Akron rubber workers: It's time to tell your stories

By Sue Walton
Crain's Akron Business

AKRON—The city of Akron is asking rubber workers and their families to share their voices to help preserve the industry's legacy.

In September, the city announced it would commemorate its heritage as the Rubber City by installing a 12-foot bronze statue of a rubber worker in a new roundabout at Main and Mill streets. The design of the work, by sculptor Alan Cottrill and to be installed later this year, was inspired by the image on the cover of the book "Wheels of Fortune" by David Giffels and Steve Love, both formerly writers for the Akron Beacon Journal newspaper.

But the statue isn't the only thing that looks to preserve Akron's rich rubber industry history. As part of the project, an interactive kiosk, with audio and visual storytelling featuring former rubber workers, will be installed in the northeast corner of the intersection.

Akron Stories, a group led by artist and business owner Mac Love, is leading the storytelling project, which is being funded, along with the kiosk, by the sale of commemorative bricks. About 130 bricks already have been sold, according to a recent news release. They're available for purchase online.

The group already has collected dozens of stories for the oral history project but wants more, so it has scheduled recording sessions from March through May across Summit County.

"This is our opportunity to celebrate the people who made Akron the rubber capital of the world," Love said in the release. "We want to help visitors and residents learn about Akron's unique history, how it shapes our identity and how it is driving our future."

Collected stories will be archived with the Akron-Summit County Public Library and be available online, with excerpts featured as part of the interactive kiosk downtown, Akron Stories said.

Akron resident Miriam Ray is founder of the Akron Stories initiative, according to its website, and has worked toward making the storytelling project a reality since 2016.

"From the very beginning, I asked people for their stories and quickly realized they were as important as the rubber worker statue itself," Ray said in a statement. "We are three generations removed from these workers and it is so important that future generations get to know them."

Added Josy Jones, the project's director of storytelling, in a statement: "We are hearing from people who remember their family members coming home coated in black tire remnants. They remember the sounds and energy of Main Street and the brilliance and resilience of their working mothers. … Many (workers) were actively involved in the union, standing up for their rights and shaping a future for their children."

This rendering shows the bronze sculpture of a rubber worker planned for a new roundabout at Main and Mill streets in downtown Akron.

Organizers want to hear from as many rubber workers and their families as they can, and ask contributors to schedule an interview at AkronStories.com or by calling 330-238-8588, the release said.

Auto makers to stop monthly new vehicle sales reports

By Urvaksh Karkaria
Automotive News

For the longstanding auto industry tradition of reporting monthly new-vehicle sales, the dominoes are falling.

In fact, the game now is, more or less, over.

Audi, BMW, Nissan, Porsche and Volkswagen have made back-to-back announcements that they will stop reporting their model-by-model monthly sales results across the U.S., switching instead to quarterly reports. Toyota has joined the rebellion by brands that represent the bulk of U.S. sales, although last week it held out the possibility of at least making its monthly results available on a less formal basis.

The stampede away from tradition follows similar decisions by U.S. auto makers.

First, it was the California upstart Tesla refusing to go along with the industry establishment, providing only global quarterly results. In 2018, industry leader General Motors balked, saying it was done with the practice. And last year, GM's two Detroit competitors, Ford Motor Co. and Fiat Chrysler, followed suit.

Many observers lay the disruption at the feet of Tesla.

The closely watched, publicly traded startup chose not to advertise its month-in, month-out achievements as it launched, and Wall Street didn't seem to mind its lack of transparency. Tesla's stock rose to unprecedented heights, making the company worth more on paper than GM and Ford combined.

"The auto industry is asking itself: 'Tesla doesn't do monthly reporting and they are being hugely rewarded, so why do we do it?' " Tyson Jominy, vice president of the Power Information Network at J.D. Power, told *Automotive News.*

Auto makers apparently see an opportunity to take a break from monthly pressures and find a truer picture of their market results, especially now, at a time of falling sales and shifting consumer preferences. Sales of some car models have plummeted in the past two years, but only because customers are driving off dealership lots in new crossovers instead of sedans.

"We think it's a good way for us to provide a clearer picture of the sales performance over a longer period of time," a Nissan spokesman said. "There's a lot of monthly variances in sales—there's spikes and troughs. We think this will just smooth those."

Added Jominy: "There's not a lot of good news to go around. So how many times in a year do you want to give bad news?"

Skewed view?

Measuring quarterly instead of monthly also may paint a picture of a smoother sales year. Year-over-year monthly comparisons can garner big headlines among consumers but are sometimes misleading because of fluctuations in the number of selling days.

This year, an extra calendar weekend will boost sales volumes in February, May, October and December over 2019 tallies; March, June and November each will lose a weekend. And Labor Day weekend, typically the king of selling weekends, moved to August for 2019 but reverts to September this year.

The reporting change also might lead to healthier industry behavior.

The competitive pressure of the monthly "sales race" has fostered dubious practices and creative accounting. Auto makers have been accused of padding their numbers by coaxing retailers to register vehicles as sold when they are still in inventory. BMW is under scrutiny by the Securities and Exchange Commission, accused of engaging in such tactics in the U.S.

Shifting to quarterly reporting will be good for both dealers and manufacturers, said Patrick Womack, general manager of Laurel BMW of Westmont in suburban Chicago. It takes off some of the pressure to hit 30-day sales targets, said Womack, who also is chairman of the BMW National Dealer Forum.

"We won't have to offer loser deals at month end," he said. "Little things disrupt the market month to month. So quarterly is probably the better and healthier way to look at sales performance."

But the impact will be felt by economists, industry analysts and corporate strategists, Jominy said. The monthly data has, for decades, been "a fantastic barometer" of consumer spending strength, he said.

"Economists look to the auto industry for signs of what's truly going on with consumer demand," Jominy said.

Those economists will soon have to find another way to read the tea leaves.

Technical

Crosslinking

Continued from page 18

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

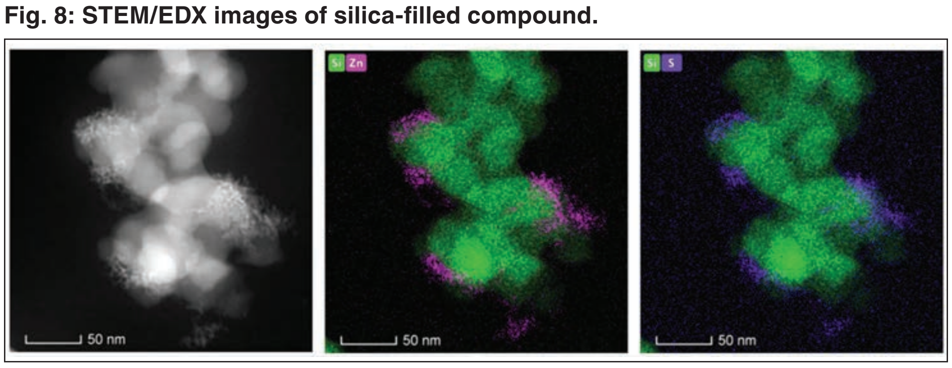

Fig. 9: Additional STEM/EDX images of silica-filled compound.