

Material Morphology and Electrical Resistivity Differences in EPDM Rubbers

Linda A. Domeier, Nancy Yang

Sandia National Laboratories, Physical and Engineering Sciences Center, Livermore, California 94550

Received 10 April 2008; accepted 7 July 2008

DOI 10.1002/app.28984

Published online 19 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electrical resistance anomalies noted in EPDM gaskets have been attributed to zinc-enriched surface sublayers, about 10- μm thick, in the sulfur cured rubber material. Gasket over-compression provided the necessary connector pin contact and was also found to cause surprising morphological changes on the gasket surfaces. These included distributions of zinc oxide whiskers in high pressure gasket areas and cone-shaped features rich in zinc, oxygen, and sulfur primarily in low

pressure protruding gasket areas. Such whiskers and cones were only found on the pin side of the gaskets in contact with a molded plastic surface and not on the back side in contact with an aluminum surface. The mechanisms by which such features are formed have not yet been defined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3973–3984, 2008

Key words: rubber; surface; sublayer; zinc; sulfur; blooming

INTRODUCTION

Ethylene Propylene Diene Monomer (EPDM) rubber formulations are widely used in sealing applications such as o-rings and gaskets and are generally considered nonconducting. Multiple pin connectors with EPDM rubber gaskets in a protecting cover (Fig. 1), however, were sporadically reported to show reduced electrical resistance values during testing. These covers and gaskets were paired with the connector face shown in Figure 2. Pin contact due to over-compression of the gaskets was evident in the problem units and rapidly evaporating liquid films, later identified as carbon disulfide, were noted when the connectors were opened. The carbon disulfide films did not explain the low resistance values but did suggest that a sulfur cured material might be involved. A subsequent gasket replacement program required the use of a peroxide cured EPDM material.

Sheet materials used in the connector gaskets had been supplied by two vendors using proprietary formulations. Assembly records did not note the material used in particular gaskets. The two sheet materials are referred to here as EPDM-C and EPDM-S. (As discussed later, C refers to a cumyl peroxide cured EPDM and S refers to a sulfur cured EPDM.) The EPDM used in the replacement gaskets (EPDM-R) was a peroxide cured formulation con-

trolled by a government specification and was provided by one of the original vendors.

As gaskets were replaced they were retrieved and made available for a study to understand the cause of the unexpected resistance anomalies. Electrical resistance tests were not carried out during the gasket replacement program and the performance of the gaskets at that time is unknown.

EXPERIMENTAL

During the gasket replacement program, retrieved gaskets and covers were placed in screw cap SPME (Solid Phase MicroExtraction) vials to minimize the loss of any volatile species (40 ml clear vials from EPScientific, Miami, OK). Twenty of the retrieved samples (G-1 to G-20), selected to represent a range of compression patterns and age, were analyzed by SPME and then sectioned for further analysis, both chemical and by scanning electron microscopy (SEM). Other retrieved gaskets were used for initial SEM evaluations (S-1 and S-2) and electrical resistance tests (E-1 to E-6). Four gaskets, retrieved earlier because of their anomalous electrical resistance tests, were also evaluated chemically and two (A-1 and A-2) were available for SEM examination. Test slab and sheet samples of a range of EPDM and butyl rubbers were used as comparisons in the chemical analyses. Table I lists the gaskets and EPDM materials evaluated in the study and their designations.

Thermal desorption and ion chromatography analyses were carried out at Sandia National Laboratories in Albuquerque, NM and SPME analyses were carried out at both Lawrence Livermore National

Correspondence to: L. A. Domeier (ladomei@sandia.gov).

Contract grant sponsor: United States Department of Energy; contract grant number: DE-AC04-94AL85000.

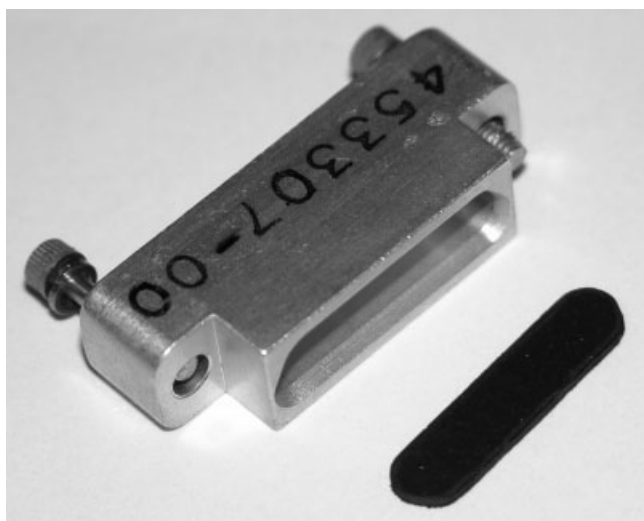


Figure 1 Connector protective cover with EPDM gasket.

Laboratory and at Sandia National Laboratories in Livermore, CA. Thermal desorption samples were heated up to 200°C and the outgassed organics were analyzed by GC/MS (gas chromatography-mass spectrometry). Most of the SPME analyses were carried out on samples stored at ambient temperature and were again coupled with GC/MS. A limited number of SPME analyses on samples heated overnight at 60°C provided higher levels of outgassed species.

SEM with energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS) as well as X-ray diffraction (XRD) were used to evaluate the rubber microstructure and feature compositions. These analyses and the electrical resistivity measurements were carried out at Sandia, CA.

EPDM FORMULATION BACKGROUND

EPDM elastomers are formed by the polymerization of ethylene, propylene, and one of three diene monomers (1,4-hexadiene, 5-ethylidene norbornene, dicyclopentadiene). One or more elastomers are blended with additional ingredients to provide either a free radical or sulfur crosslinking reaction.

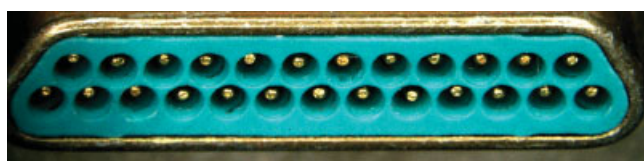


Figure 2 Connector face with beveled pin cavities and DAP (diallyl phthalate) molding in aluminum frame. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Gasket and Rubber Sheet Designations

Gaskets	Description
A-1 and A-2	Two of four retrieved gaskets with low electrical resistance examined by SEM.
S-1 and S-2	Two retrieved gaskets used for initial SEM evaluations.
G-1 to G-20	Twenty retrieved gaskets used for chemical and SEM evaluations.
E-1 to E-6	Six retrieved gaskets used for electrical measurements.
EPDM-C	One of two proprietary EPDM materials used to make the retrieved gaskets. Peroxide cured.
EPDM-S	One of two proprietary EPDM materials used to make the retrieved gaskets. Sulfur cured.
EPDM-R	Specification controlled formulation used to make replacement gaskets. Peroxide cured.

Carbon black fillers are added to modify the final mechanical properties such as hardness and tensile performance. Other ingredients modify the mixing uniformity, flow characteristics, oxidative stability, or other properties. General discussions of EPDM and rubber technology can be found in numerous reviews.¹⁻³

Table II lists typical ingredients in peroxide and sulfur cured EPDM formulations. Peroxide cured formulations use dicumyl peroxide or other initiators and also often contain polyfunctional monomers such as trimethylolpropane trimethacrylate to improve crosslink density. Sulfur cured formulations contain sulfur as well as a range of additives such as benzothiazoles and similar compounds to control the cure rate and the number of sulfur atoms in the crosslinking sulfur chain. The mechanism of sulfur vulcanization has been studied for years and remains both complex and incompletely understood. The EPDM-C and EPDM-S materials were proprietary formulations and their exact compositions are not known. The peroxide cured formulation shown in Table II is the EPDM-R used in the replacement

TABLE II
Typical Ingredients in Peroxide and Sulfur Cured EPDM Seal Formulations

Ingredient	Peroxide cured	Sulfur cured
EPDM rubber(s)	100	100
Zinc oxide stick (85%)	5	4
Carbon black(s)	65	50
Stearic acid	–	1
Antioxidant	2	0.5
Trimethacrylate	10	–
Peroxide (dicumyl, etc.)	12	–
Sulfur	–	1.5
Mercaptobenzothiazole	–	0.5

gaskets and was developed under a government contract.

A common ingredient in both peroxide and sulfur cured formulations is zinc oxide. In sulfur cured materials, zinc oxide takes part in the cure chemistry and is partially converted to zinc sulfide. In peroxide cured materials, zinc oxide is often retained due to its beneficial effects on blend uniformity and mechanical properties. Dispersion of powdered zinc oxide is sometimes problematic and it can be preblended with, for example, naphthenic oils in an 85/15 oxide/oil ratio to form a soft stick product. The sticks are easily handled and provide a more uniform dispersion.⁴

RESULTS AND DISCUSSION

Thermal desorption, SPME, and ion chromatography analyses

None of the organic or ion analyses suggested any unusual species in the anomalous gaskets or a cause for the observed electrical resistance anomalies. Both the thermal desorption and SPME results provided indicators of the cure chemistry in many but not all of the samples. Other commonly observed organics included antioxidants, plasticizers, carboxylic acids, amines, cleaning solvents, and others.

A commonly observed volatile organic was carbon disulfide (boiling point 46°C) and it is believed that this was the rapidly evaporating film noted in anomalous gaskets opened in the field. It was surprising that enough carbon disulfide was present to provide a visible film and this heavy surface concentration is probably related to the distinct gasket over compression noted in these samples. Carbon disulfide may be a trace impurity in the benzothiazoles used in sulfur cured rubbers and is also sometimes used to modify the surface characteristics of carbon black fillers.⁵⁻⁷ There are also reports on the evolution of carbon disulfide during sulfur vulcanization in which thiocarbamates are used as accelerators⁸⁻¹¹ although such curatives did not appear to have been used in any of these formulations.

The presence of carbon disulfide in thermal desorption or SPME analyses was not found to conclusively indicate a sulfur cured material. Trace amounts were sometimes observed where not expected, possibly due to system retention or to non-curative sources such as the carbon blacks used in the formulation. The presence of mercaptobenzothiazole (MBT) or similar species was definitive for a sulfur cured rubber, however, and was generally coupled with the presence of carbon disulfide.

Many peroxide cured rubbers use dicumyl peroxide. A common byproduct of this curing agent is cumyl alcohol, often accompanied by acetophenone,

and both provided indicators of dicumyl peroxide cured EPDMs.

Two gaskets which had shown anomalous resistivity were analyzed by thermal desorption and showed prominent mercaptobenzothiazole and hydroxybenzothiazole peaks, as well as carbon disulfide, indicating a sulfur cured rubber. SPME analyses on twenty of the retrieved gaskets (G1-G20) were carried out on samples stored at ambient temperature and did not provide definitive curative information. Ten of these same twenty samples were also analyzed by thermal desorption and six showed benzothiazoles indicative of a sulfur cured EPDM. Five of these six also showed carbon disulfide. The other four did not show peaks clearly indicative of either a sulfur or peroxide cure chemistry.

Control rubber samples were also analyzed by thermal desorption and SPME, including a series of SPME samples which had been stored at ambient temperature for 7 months. This prolonged storage allowed for further outgassing from the rubber. Three different sheets of EPDM-C were sampled and all showed cumyl alcohol peaks in the thermal desorption and in the aged SPME samples. The replacement EPDM-R, as expected, and two other EPDM materials also showed cumyl alcohol peaks. Only one material, EPDM-S, showed no peaks clearly indicative of a peroxide or sulfur cure. It did show carbon disulfide in the SPME analyses, however.

EPDM-S was the only material used to fabricate gaskets not clearly shown to be peroxide cured and it was deduced that this was a sulfur cured material. Sulfur cured gaskets retrieved from stockpile, including at least two and probably all of the anomalous gaskets, were apparently made from EPDM-S. This formulation is proprietary but based on a sulfur curing system providing mercaptobenzothiazole residues. Retrieved gaskets not made from EPDM-S would have been made from EPDM-C.

Ion chromatography for negative ionic species was carried out on two of the anomalous gaskets, the rubber controls, and on partial samples of half of the twenty retrieved gaskets selected for study. All showed similar ions and ion concentrations with only minor variations which did not suggest a cause for the observed low electrical resistivity measurements. Commonly observed anions included chloride (usually the dominant species), nitrate, carbonate and sulfate. Lower concentrations of formate, oxalate (a common ingredient in metal cleaning formulations), acetate, and others were noted. Such anions might be trace materials or contaminants in the rubber formulations and/or picked up in handling of the rubber performs, sheets, or gaskets.



Figure 3 Compression patterns of retrieved gaskets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Initial gasket examinations

Retrieved gaskets showed visual compression patterns as shown in Figure 3 ranging from “none” (~ 5% of the gaskets examined) to slight (~ 15%) to distinct (~ 75%) to severe (~ 5%). The extent of pin contact varied significantly along with gasket compression. Simple pin penetration was common in the distinctly compressed gaskets while extensive surface damage was noted in the severely compressed gaskets. The connector face causing this compression pattern is shown above in Figure 2 and consists of a DAP (diallyl phthalate, a highly crosslinked thermoset) plastic connector with beveled cavities in which the connector pins are housed. Both the enclosing connector case and connector cover are fabricated from aluminum 6061-T6 with a chromate coating and were procured from ITT Canon. The protective EPDM gaskets are added later.

The retrieved gaskets had been in the connectors for 4–8 years. No correlation of compression severity and time was noted and the degree of compression was attributed to tolerance variations within the gasket and the connector. EPDM is generally known for its excellent aging behavior and resistance to compression set.

SEM and related analyses of gasket surfaces

No specific findings were expected from the initial SEM analyses. One of the two gaskets first analyzed by SEM showed a distinct compression pattern (S-1) while the other was only slightly compressed (S-2). The gaskets were halved and mounted showing both the front and back sides.

The compressed side of gasket S-1 showed a remarkable distribution of high aspect ratio whiskers, cone shaped features, and rubber surface damage as shown in Figure 4. The whiskers were long hexagonal shapes and were distributed primarily on the compressed flat surfaces between rubber protrusions

corresponding to the pin holes in the connector. The cone features in this and subsequent samples were more often grouped on the rubber protrusions. The back side of this gasket and both sides of the less compressed S-2 gasket were all generally feature free except for variations in the rubber surface.

EDS and element mapping analyses indicated a zinc oxide composition for the whiskers, consistent with the known hexagonal shape of zinc oxide crystals. The cones were rich in zinc, oxygen, and sulfur. Limited further analysis of these features has not identified a specific cone composition as yet and searches for Zn/O/S found no properties or references. The consistent shape of these features suggests a fixed composition.

Zinc oxide has a range of measured conductivities depending on the material preparation process, temperature, and measurement technique. Although the possibility of such whiskers forming a low resistance

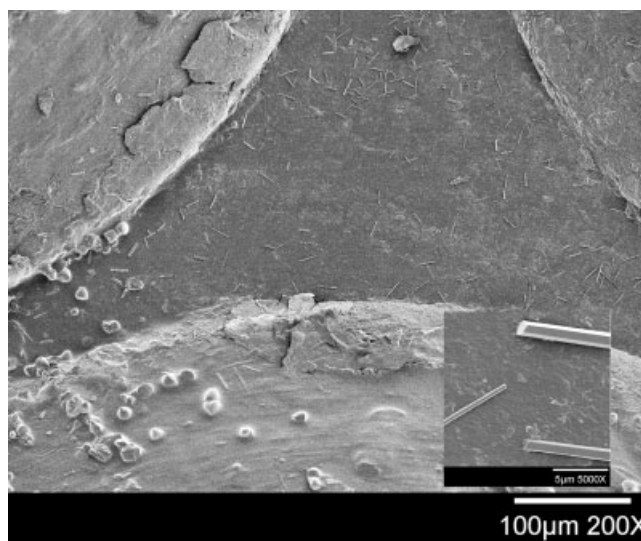


Figure 4 Whisker and cone features noted on compressed side of gasket S-1.

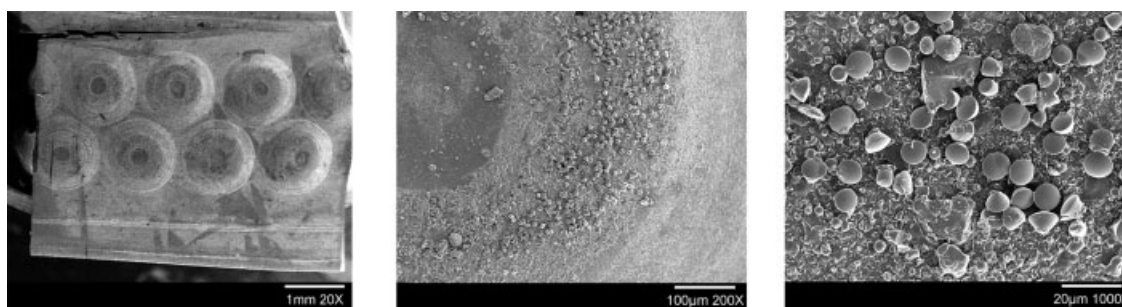


Figure 5 Gasket surface showing concentration of cone features on protruding rims (Gasket A-2).

path was considered, such conductance would clearly require a significant number of randomly arrayed whiskers with overlapping contacts.

Two gaskets which had demonstrated low electrical resistance before retrieval (A-1 and A-2) were available for SEM evaluation and had distinct compression patterns similar to that seen in gasket S-1. Punctures from the connector pins were evident. Whiskers were most notable in gasket A-1 while cones were most notable in gasket A-2. The zinc oxide whiskers again appeared most prevalent in the compressed flat areas while the cone features were primarily distributed around the rim of punctured rubber protrusions as shown in Figure 5. Features denoted as platelets were also noted in the area just around a punctured rim and may be precursors to the better defined cones. These were also observed in other gaskets, but their composition has not been established.

Figure 6 shows pictures of the three major feature types (whiskers, cones, and platelets) noted on these and other gaskets examined. The zinc oxide whiskers showed a wide range of lengths and diameters. The cone shaped features appeared anchored in the rubber surface and several appeared to have been mechanically dislodged. There was again a range of sizes although all of these features maintained the same well-defined shape. As will be noted later, neither whisker nor cone features have been found on control sheet materials although platelets were found in one EPDM. It is probable that both the zinc oxide whiskers and the cone shaped fea-

tures are formed on the surface of the compressed rubber gaskets and grow in size there.

SEM overviews of all twenty samples G-1 to G-20 selected from the retrieved gaskets (on the center section after cutting into thirds) were obtained as well as higher magnification pictures looking at the general level of zinc oxide whiskers present. Those nine gaskets clearly showing zinc oxide whiskers are shown in Figure 7. Where the punctured gasket protrusions were also shown, distributions of cone features were commonly observed.

These overviews indicated a strong correlation of whisker and cone feature formation with the level of gasket compression. Gaskets with no compression pattern were feature free. Gaskets with slight compression patterns were sometimes feature free or sometimes showed low concentrations of features. Gaskets with distinct compression patterns showed varying distributions of zinc oxide whiskers as well as the cone features previously noted in gaskets S-1, A-1, and A-2. An exception to this trend was the absence of whisker and cone features in two gaskets with severe compression and pin damage to the gasket surface. Cracks in the surface of one of these gaskets suggested stress relief at the surface and these two gaskets remain under study.

The anomalous gaskets A-1 and A-2 had shown whisker and cone features primarily on the front, pin side with a very few, perhaps dislodged, features on the back sides. The twenty retrieved gaskets selected for study had been sectioned and mounted for SEM evaluation with only the front side visible.

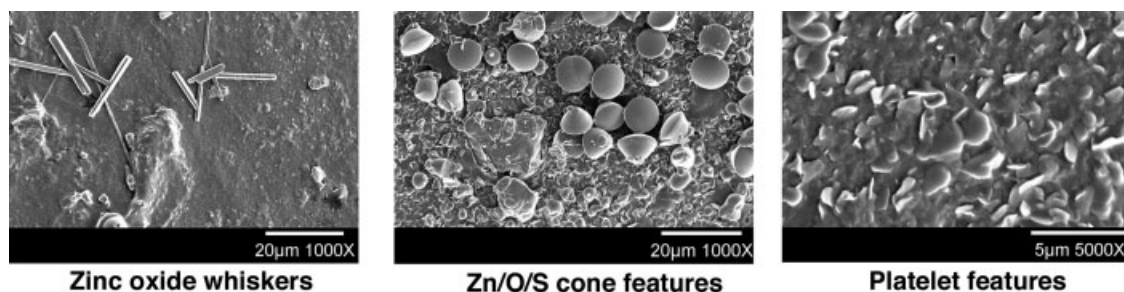


Figure 6 Surface feature types on EPDM rubber.

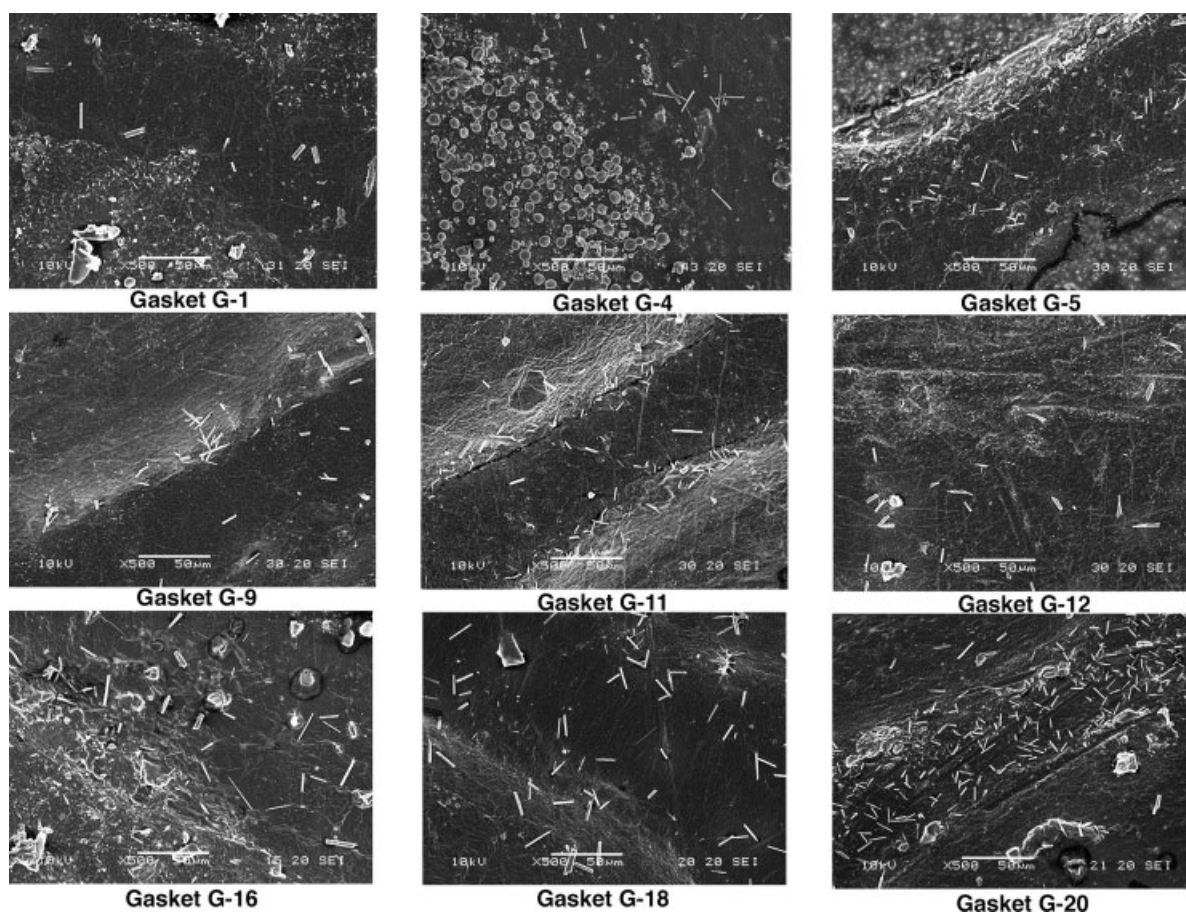


Figure 7 EPDM gaskets showing distributions of zinc oxide whiskers and other features.

An additional four gaskets with distinct compression patterns were halved and mounted with both sides visible. Three of these gaskets again displayed whisker and cone features on the front, pin side of the gaskets. None showed such features on the back side. The fourth gasket showed extreme pin penetration damage, similar to gaskets noted earlier, and had no distinct features on either side of the gasket.

The front or pin side of the gaskets, when mounted in the connector, was pressed against a diallyl phthalate (DAP) connector face with pin cavities as shown in Figure 2. The back side was pressed against an aluminum 6061-T6 cover, shown in Figure 1, with a chromate coating. The effects of different compressing surfaces, plastic versus metal, on the surface growth of zinc oxide whiskers and cone shaped features remain to be investigated, but this is believed to be an important parameter in the formation processes.

SEM and related analyses of gasket cross sections

In addition to the gasket surface evaluations, cross sections of gaskets A-1 and A-2 were encapsulated in epoxy and planarized for SEM examination. Both

cross sections showed distinct 5- to 10- μm -thick subsurface layers on both the front (pin side) and back sides of the gaskets. Gasket A-1 is shown in Figure 8. The layer thickness was relatively uniform and was not thicker in either the compressed flat areas or protruding areas of the top side. The thickness uniformity suggested that these layers were not formed by compression of the gaskets in the connector, a nonuniform pattern, and were instead formed during molding and curing of the original sheet material. The dark bands in these cross sections are gaps between the gasket surface and the encapsulating epoxy.

Element mapping by SEM/EDS and WDS of the areas shown in Figure 8 clearly indicated enrichment of the subsurface layers in oxygen, sulfur and zinc. Many of the bright particles observed in the gasket bulk were enriched in oxygen and zinc and appear to be small zinc oxide crystals or other oxides. EDS measurements of the oxygen/carbon, zinc/carbon, and sulfur/carbon ratios in the sublayer and in the gasket bulk allowed estimation of the degree of sublayer enrichment. The sublayers in both gaskets appear to have roughly sixfold enrichment in zinc, fourfold enrichment in sulfur and threefold enrichment in oxygen.

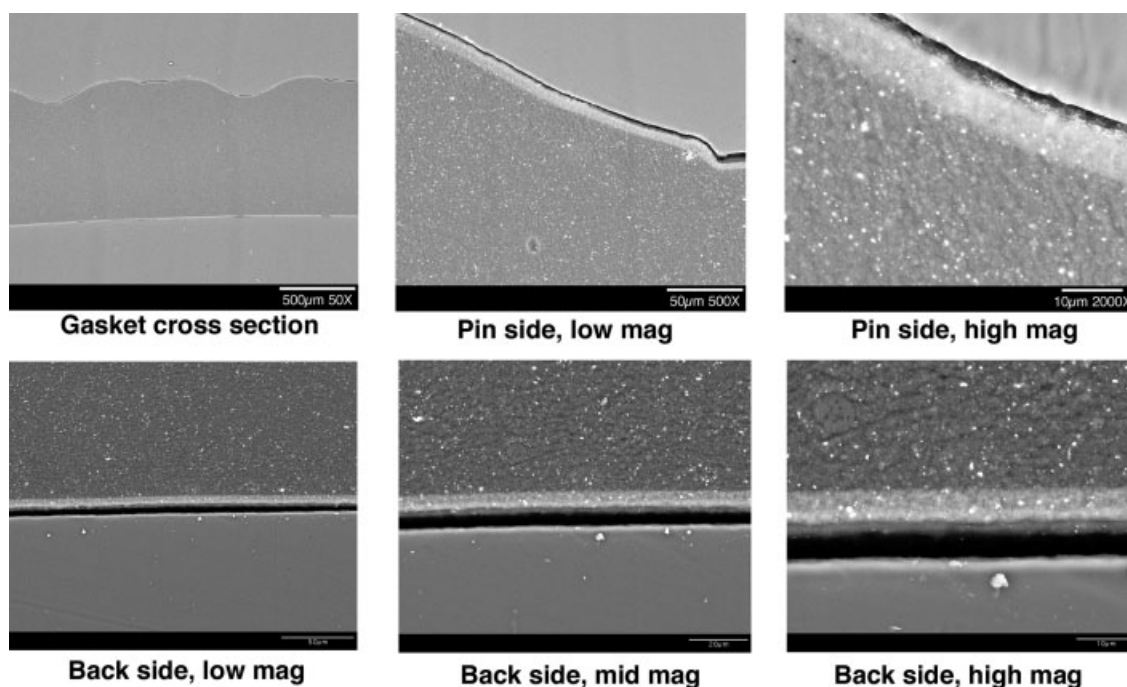


Figure 8 Gasket A-1 cross sections.

The presence of sublayers enriched in zinc, oxygen, and sulfur suggests the possibility that such layers are only formed in rubber formulations containing sulfur. As discussed later, these sublayers are also consistent with the well known “blooming” of various rubber ingredients on the surface during cure, particularly in sulfur cured formulations.

SEM and related analyses of EPDM sheet material surfaces and cross sections

SEM examination of the three EPDM sheet samples and a new, unused gasket found no evidence of surface whisker or cone features. The EPDM-S sample showed areas with platelet features similar to those seen in gaskets A-2 and others.

In cross section SEMs, shown in Figure 9, distinct surface sublayers, top, and bottom, like those observed in the anomalous gaskets A-1 and A-2 were seen in one sample, the sulfur cured EPDM-S. No sublayers were noted in EPDM-C. Both the EPDM-R sheet and the new gasket made from this material showed a less distinct subsurface band but did not show the bright sublayer seen in EPDM-S. Both element mapping and EDS again confirmed enrichment of zinc, oxygen and sulfur content in the EPDM-S sublayer. No sublayer enrichment was seen in the other three samples and the cause of the visual bands in EPDM-R and the new gasket is unknown. High Z bright particles in the SEMs were

shown by EDS to be variously enriched in aluminum, silicon or zinc.

Sublayers, surface features, and rubber blooming

Cross section evaluations of the anomalous gaskets and the EPDM sheet materials support the idea that sulfur is required, beyond the levels present as impurities in carbon black, to enable the formation of sublayers rich in zinc, oxygen, and sulfur during rubber processing. It is likely that such an enriched layer provides a precursor to the observed zinc oxide whiskers and the Zn/O/S containing cones. The results to date further suggest that compression is required to transform these sublayers into the observed whiskers and cones. It is speculated that a transparent zinc oxide film may be formed at the surface and serve as an intermediate precursor to actual whisker formation.

In comparing the nine of twenty study gaskets which exhibited whisker formation with the SPME and thermal desorption results, four of these gaskets were demonstrated to be sulfur cured by the presence of benzothiazole species. All nine gaskets showed peaks for carbon disulfide in either the SPME or thermal desorption or both. None showed cumyl alcohol peaks and it is believed that all these gaskets were fabricated from the sulfur cured EPDM-S. Two gaskets which exhibited benzothiazole peaks in thermal desorption analyses did not show

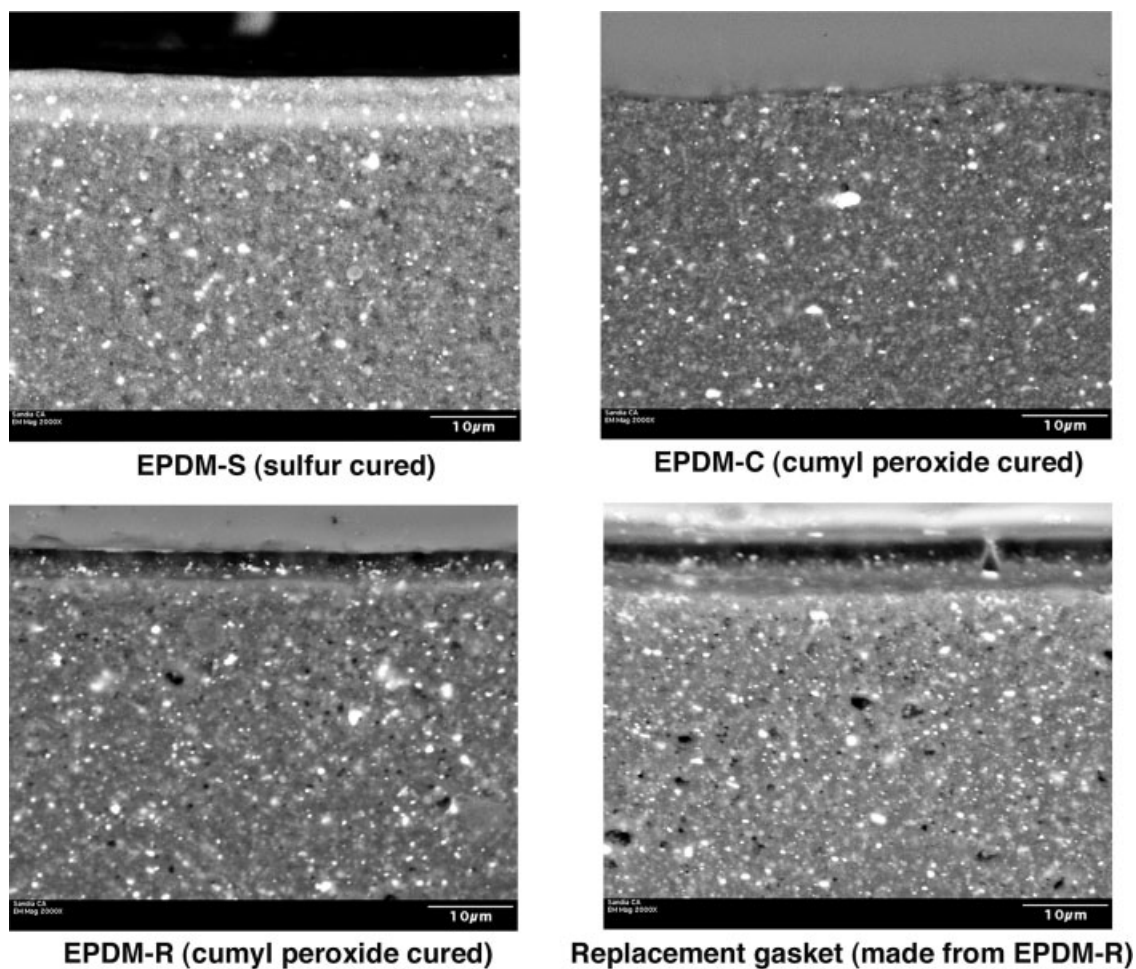


Figure 9 SEM cross sections of EPDM sheet materials and a replacement gasket.

whisker formation and had only slight compression patterns. Other gaskets, shown in Figure 7, with similar compression patterns did show whisker and cone features and the exact combination of cure chemistry and compression required to cause whisker and cone formation remains to be defined.

Although sublayers, whiskers, and cones have not previously been reported, a related and widely reported behavior is the “blooming” of various ingredients at rubber surfaces during cure and under compression. Blooming of many species can result in surface films, which are sometimes desirable, and surface imperfections which are undesirable.¹² Blooming during cure can also leave accumulated residues on the mold surface which in turn can contaminate subsequent moldings or damage the mold surface.^{13,14} Suppliers of chemicals to the rubber industry commonly advertise the improved solubility and reduced blooming seen with some of their additives.

A species often identified in rubber blooming is zinc sulfide which is formed from zinc oxide during sulfur vulcanization.^{15,16} Migration of sulfur itself can also occur and blooming, in general, appears to be more prominent in sulfur cured formulations

than in peroxide cured formulations.^{1,17} Ingredients such as waxes and similar low molecular weight species readily migrate to the surface and this blooming has been related to concentration, temperature and also pressure.¹⁸ In some cases, such migration is expected and beneficial as it provides a wax film on the rubber surface which protects against ozone damage or enhances appearance.¹

The specific migration of zinc oxide itself has not been studied although poor dispersion during mixing is known to leave residues on the surface, and cause less efficient curing. These issues have led to the use of zinc sticks to improve dispersion. Studies of zinc oxide dispersion have used various methodologies.^{19–21}

The presence of enriched sublayers as seen here is consistent with the migration and blooming of various species in molded rubber articles. Blooming was also observed in the retrieved gaskets where surface patterns on the back side of the gaskets and deposited contaminants on the cover surface matched the compression patterns imposed by the connector. Some obvious examples of this behavior are shown in Figure 10. The bloomed and deposited materials

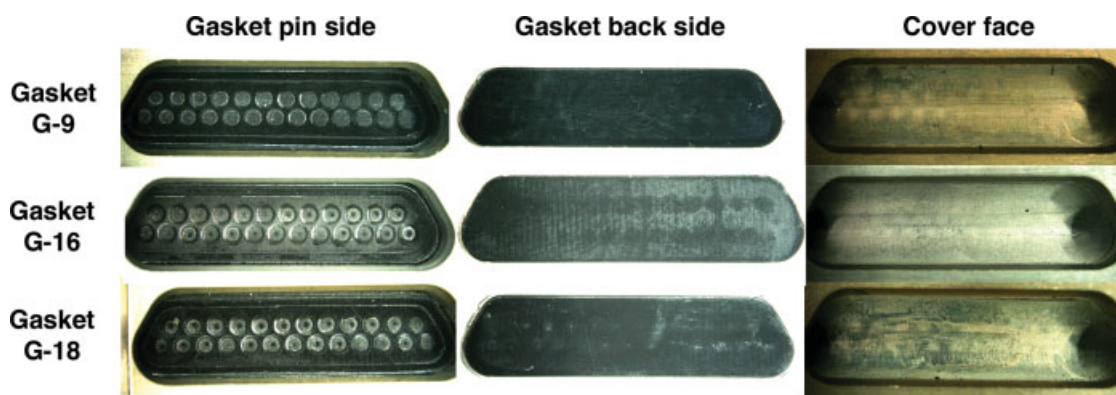


Figure 10 Examples of surface blooming in compressed gaskets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

have not been identified as yet, but clearly suggest the influence of compression on migration behavior. The cure chemistry of these and other gaskets with evident blooming has not been clearly established in most cases, but most did show carbon disulfide in the organic analyses and some, including the G-18 shown, were clearly sulfur cured as shown by the presence of benzothiazoles.

It has been suggested¹¹ that earlier work on wax migration¹⁷ can be generalized to other species and would be consistent with such pressure sensitive patterns. In that study, species which were more soluble at higher pressures were postulated to become less soluble as the species migrated to areas of reduced pressure. The areas of least pressure in the gaskets would be those matching the pin holes in the connector face. This reduced pressure is also felt on the opposite side of the gaskets, causing the observed patterns. Such compression effects may indicate that the unidentified cone features noted in the anomalous and other gaskets arise from migration of specific components within the Zn/O/S enriched sublayer to the low pressure protruding, and often punctured gasket areas.

The zinc oxide whiskers have been generally concentrated in the flat, compressed areas on the front side only of the gaskets. This might suggest a differ-

ent or additional process beyond migration leading to their formation. The absence of whiskers on the back of the gaskets also suggests a role for the contacting surface which was DAP on the front and chromated aluminum on the back. The high concentrations of zinc oxide needed to support crystal growth may be supplied by the enriched sublayers but might also require an intermediate zinc oxide film with even greater enrichment. No direct evidence for such a thin, perhaps submicron, transparent film has been found as yet.

Zinc oxide morphologies

The nature of zinc oxide added to rubber formulations was of interest and three samples were submitted for SEM characterization. One was a zinc oxide stick (AkroZinc Bar 85, an 85/15 zinc oxide/naphthenic oil blend) and the other two were powders, one recently purchased from Aldrich Chemical and one obtained from an old, undated (perhaps decades old) can of zinc oxide powder from St. Joseph Lead Co.

As shown in Figure 11, neither the zinc stick nor Aldrich powder showed noticeable zinc oxide whiskers. The older powder did appear to have random high aspect ratio whiskers growing out of the

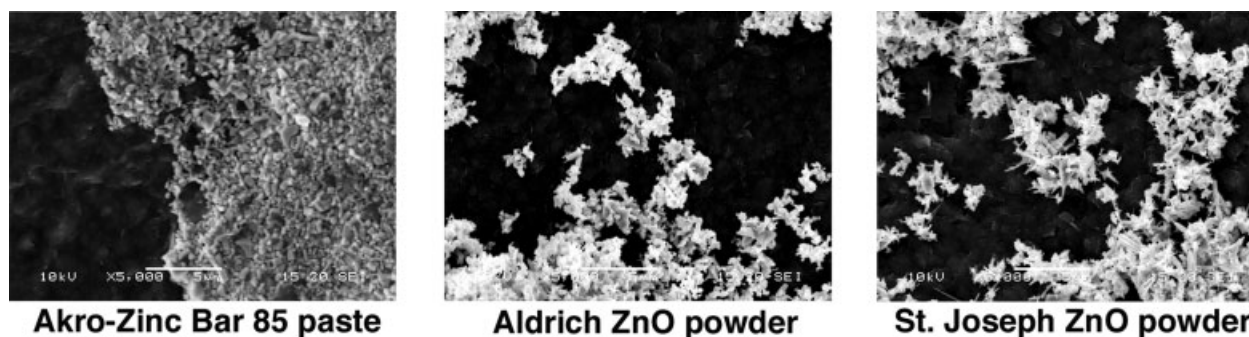


Figure 11 SEM pictures of zinc oxide materials.

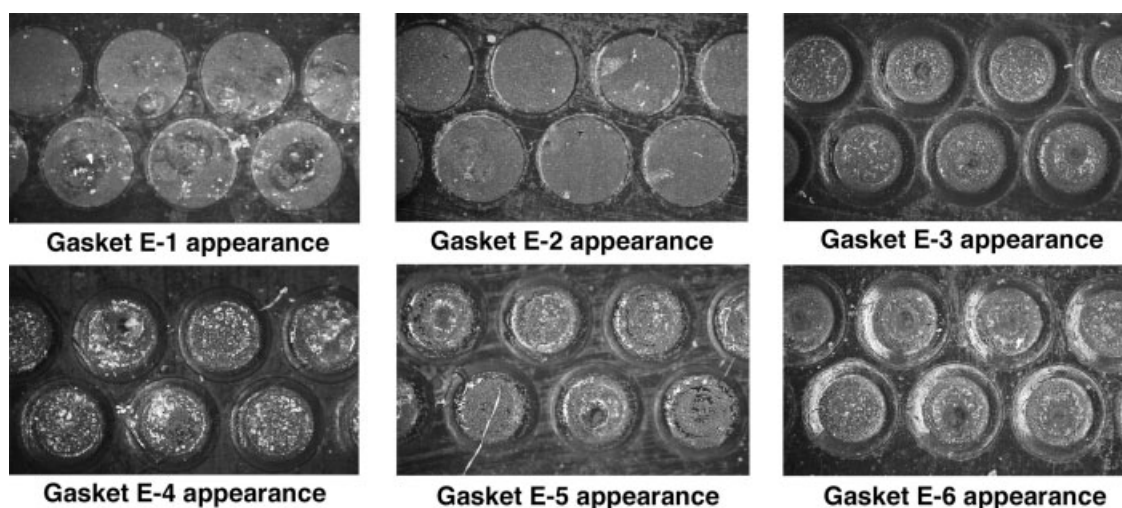


Figure 12 Compression patterns of gaskets showing reduced electrical resistivity.

highly faceted particles. It is unlikely that inventory control in commercial blenders would allow the use of extremely old samples of zinc oxide in their rubber formulations. It is also questionable whether high aspect ratio zinc oxide whiskers would survive the blending and molding operations and find their way to the rubber surface.

The zinc oxide whiskers are presumably formed on the surface of the compressed gaskets by mechanisms which have not been elucidated. Their surprising length, around 20 μm in some cases, and wide range in thickness, however, suggests a robust growth process.

Electrical resistivity measurements on gaskets

Electrical resistance measurements were carried out on retrieved gaskets which covered a range of compression patterns as shown in Figure 12. These were not part of the G-1 to G-20 group examined by SEM. Measurements were also carried out on two unused replacement gaskets. A Keithley 2002 Multimeter with fine tip probes was used along with an adjustable stand to help provide uniform contact pressure. The actual depth and location of the probe tips on the gaskets was difficult to know or control with this simple equipment, but consistent measurements were still obtained. Measurements were carried out on both the front and back sides of the gaskets.

The two new gaskets, made from peroxide cured EPDM-R, showed no measurable conductivity. The retrieved gaskets (E-1 to E-6) showed erratic and continuously decreasing resistivity values which leveled off after several minutes. The resistance was very sensitive to local vibrations and any movement in the counter surface or adjustable stand. Perhaps most surprising, similar resistance behavior was found on both sides of the gaskets and the resistivity

on the back side was in fact lower than on the front. Although erratic, the values leveled off at about 5–60 $\text{M}\Omega$ on the front side of the gaskets and at about 1–3 $\text{M}\Omega$ on the back side. Some values were still declining when the measurements were stopped.

The compression patterns in the six gaskets showing conductivity were similar to patterns in those gaskets which had generally shown zinc oxide whisker and cone distributions. Although the electrical measurement samples have not been examined by SEM, it is expected that they would also show whisker and cone features. As in the earlier samples, these features would be expected only on the pin side of the gaskets and not on the back side and only in gaskets made from the sulfur cured EPDM-S.

The decreased resistance seen on the back side of these gaskets would suggest that the probes were contacting a zinc-enriched sublayer on both sides of the gasket or perhaps a transparent and continuous film of zinc oxide. The disruption of the surface on the pin side of the gaskets would reduce the conducting area of either the sublayer or a zinc oxide film and might therefore account for the lower resistivity seen on the smooth back side. The absence of zinc oxide whisker and cone features on the back side of similar gaskets clearly indicates that they are not a major source of reduced electrical resistance.

Electrical resistivity measurements on sheet materials

Similar electrical measurements were made on the three EPDM sheet materials. No measurable conductivity was observed in either the EPDM-C or EPDM-R samples, both cured with cumyl peroxide. The EPDM-S sample, the only sulfur cured material and the only material shown to have a zinc-enriched

sublayer, did show decreased and erratic resistivity in the sub-M Ω range which was again very pressure sensitive.

The EPDM sheet results suggest that the zinc-enriched sublayer in the EPDM-S material is responsible for the low resistance values noted in the connector application. Such an enriched sublayer would be expected in all the gaskets made from this material. The absence of more anomalous reports probably reflects the variance noted in gasket compression and pin contact as well as the unknown percentage of gaskets made from EPDM-S and EPDM-C. These results also suggest that all the retrieved gaskets showing decreased electrical resistivity (E1–E6) were made from this sulfur cured EPDM-S. Thermal analyses have not yet been carried out on those gaskets.

As a further control, the electrical resistance of the zinc stick paste, containing 85% zinc oxide, was measured and, surprisingly, showed no measurable conductivity. The level of zinc enrichment in the EPDM-S gasket sublayers is estimated to be only about 20–30%. Although not quantitative, this estimate is based on the sixfold zinc enrichment ratio between the rubber bulk and sublayer noted earlier. This may indicate that the carbon black fillers in the rubber matrix also some effect on the sublayer conductivity. The identity and level of these fillers in EPDM-S is not known.

DISCUSSION

The zinc oxide whiskers which were briefly considered a potential conducting pathway now appear to be primarily a symptom of the problem and not a cause. Although gasket over compression leads to both pin contact and feature formation, it appears to be enriched sublayers in the rubber sheet which cause the observed low resistance measurements. The direct formation of zinc oxide whiskers from the enriched sublayer seen in EPDM-S remains questionable, perhaps, in the absence of an even more enriched intermediate zinc oxide film. The presence of such an as yet uncharacterized film on the gasket surfaces, front and back, would also be expected to cause changes in gasket resistivity.

The specific distribution of zinc oxide whiskers in high pressure areas of the retrieved gaskets and contrasting distribution of unidentified Zn/O/S cone features primarily in lower pressure protruding areas suggests dissimilar processes for their formation. Both feature types are presumed to arise from enriched sublayers in the rubber, and platelet surface features seen in the sulfur cured sheet may also be involved as precursors. The absence of whisker and cone features on the back side of the gaskets

clearly suggests a role for the differing (DAP versus chromated aluminum) contact surfaces.

Ongoing studies with simulated compression environments are evaluating the kinetics of feature growth as well as the effects of conducting and non-conducting surfaces including both chromated and bare aluminum. The absence of whisker and cone feature formation in severely compressed and damaged gaskets is also under study.

CONCLUSIONS

Electrical resistance anomalies noted in connector gaskets have been attributed to zinc, oxygen, and sulfur-enriched surface sublayers in the sulfur cured rubber material. Gasket compression is required to provide connector pin contact and has also been found to cause surprising morphological changes in the gaskets. Distributions of zinc oxide whiskers were found in high pressure areas of the gaskets. Cone shaped features rich in zinc, oxygen, and sulfur were noted primarily in the low pressure protruding areas of the gaskets. These features were only found on the pin side of the gaskets facing a plastic connector face and not on the back side facing an aluminum connector cover. Sheet materials and uncompressed gaskets did not exhibit whisker or cone feature formation.

Distinct 5–10- μ m thick sublayers (rich in zinc, oxygen, and sulfur) were noted in cross sections of problem gaskets and also in the sulfur cured EPDM sheet material from which they were apparently fabricated. Similar sublayers were not found in peroxide cured EPDM sheets or in replacement gaskets fabricated from such sheets. Electrical resistivity tests found no measurable conductivity in peroxide cured EPDM sheets or gaskets while a sulfur cured EPDM sheet and retrieved gaskets made from that material did show reduced electrical resistance.

The observed sublayers, zinc oxide whiskers, and cone features have not previously been reported. The sublayers are believed to be formed via migratory processes similar to those which cause surface blooming in many rubber products. The processes by which zinc oxide whiskers and the as yet unidentified Zn/O/S cone features are formed on the surface are clearly related to pressure and contacting surface (plastic versus metal), may involve an intermediate zinc oxide film, but remain unknown.

The generality of these observations in other rubber types has not been explored. The use of peroxide cured rubbers is clearly recommended, however, in applications where decreased electrical resistivity would be problematic.

The authors gratefully acknowledge the assistance of Jeff Chames, Miles Clift, Andy Gardea, and Ryan Nishimoto in

carrying out the ESC, XRD, and related analyses. Ted Borek (Sandia, NM) provided the thermal desorption analyses and Chris Harvey (LLNL) and Andrew Vance (Sandia, CA) provided the SPME analyses. Derek Koida (Sandia National Laboratories, CA) carried out the electrical resistivity tests. Ron Sauls, Quenton McKinnis, Richard Behrens, and Sean Maharrey (Sandia National Laboratories, CA) also contributed in numerous ways.

References

1. Hofmann, W. *Rubber Technology Handbook*; Hanser: Munich, Vienna, New York, 1989.
2. Mark, J. E.; Erman, B.; Eirich, F. R. *Science and Technology of Rubber*; Academic Press: New York, 1994.
3. Rodgers, B.; Waddell, W. H.; Solis, S.; Klingensmith, W. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons: New York 2001; Vol. 21, pp 758–815.
4. Akro-ZincBar 85 data sheet. Available at www.akrochem.com.
5. Gajewski, M.; Janowska, H.; Swiatkowski, A. *Proc Int Rubber Conf* 1979, 101.
6. Goworek, J.; Swiatkowski, A.; Zietek, S. *Mater Chem Phys* 1989, 21, 357.
7. Puri, B. R.; Kaistha, B. C.; Mahajan, O. P. *J Indian Chem Soc* 1973, 50, 473.
8. Ashness, K. G.; Lawson, G. *RubberCon 1981: The International Rubber Conference*, Harrogate, England, E6.1.
9. Helmick, J. S.; Fiddler, W. *J Agric Food Chem* 1994, 42, 2541.
10. Leskovsek, H.; Gregorac, J.; Kralj, B.; Urlep, V. *Vestnik Slovenskega Kemijskega Drustva* 1981, 28, 237.
11. Nieuwenhuizen, P. J.; Ehlers, A. W.; Haasnoot, J. G.; Janse, S. R.; Reedijk, J.; Baerends, E. J. *J Am Chem Soc* 1999, 121, 163.
12. Loadman, M. J. R. *Analysis of Rubber and Rubber-like Polymers*, 4th ed.; Kluwer Academic Publishers: Boston, 1998, Chapter 13.
13. van Baarle, B. *Rubber World* 2001, 225, 34.
14. van Baarle, B. *Rubber World* 2004, 231, 38.
15. Dohi, H.; Horiuchi, S. *Polymer* 2007, 48, 2526.
16. Krejsa, M. R.; Koenig, J. L. In *Elastomer Technology Handbook*, Cheremisinoff, N. P., Ed.; CRC Press: Boca Raton, 1993, Chapter 11.
17. Koczorowska, E.; Jurkowska, B.; Jurowski, B. *J Appl Polym Sci* 1998, 69, 1531.
18. Nah, S. H.; Thomas, A. G. *J Polym Sci* 1980, 18, 511.
19. Laning, S. H.; Wagner, M. P.; Sellers, J. W. *J Appl Polym Sci* 1959, 2, 225.
20. Jurkowski, B.; Koczorowska, E.; Goraczko, W.; Manuszak, J. *J Appl Polym Sci* 1995, 56, 1367.
21. Ulbrich, K. H.; Backhaus, W. *Nederlandse Rubberindustrie* 1977, 38, 4.