MATERIALS

A STUDY OF THE EFFECT OF ELASTOMERIC SEALS EXPOSED TO OZONE

When considering an elastomeric seal, there is a list of process capability parameters surrounding the proper selection. Included are composition, sizing, expansion/contraction under use, elongation, chemical and thermal resistance, Shore Hardness and compression set, just to name a few. However, when looking at the big picture of a liquid distribution system, the elastomeric seal as a single point of failure or contamination is often overlooked for its importance.

Focusing on one of the most common elastomeric seals, the invention and perfection of the O-ring is relatively new to the industrial world. Niels Christensen patented the O-ring in the late 1930s but it was not until World War II that its unique usage was fully understood by aircraft manufacturers (1). Even though this simple piece of sealing material has kept a low profile in importance, it remains a vital part of everyday industry and commerce.

So it is that within the vast wet world of fluid transfer elastomeric seals that O-rings or gaskets are common place in mechanical joining. Unions and flanges are good examples. Perhaps the lack of understanding of O-rings and their important job in the microelectronics sector can be traced to the fact that tool makers design wet benches or chambers and the O-ring is along for the ride (2). Another reason certainly resides in the lack of standards. However, as the microelectronics industry continues to pursue faster throughput via more aggressive conditions, the physical and mechanical properties of elastomeric seals will be challenged to the point of failure unless a wider perception of strengths and weakness is developed and conveyed. Ozonation is one topic need this broader understanding.

And, it should not be overlooked that a menagerie of other industries, such as water treatment and municipal potable water providers as well as the food industry, begins to rely more and more on ozonation as a disinfection media. The reasons for this are some advantages of ozonation over other disinfection methods; for example, ozone being a very strong oxidant, the reduction of taste and odor of water and the removal of iron and manganese by ozone is well known (3, 4). Within the microelectronics sector specifically, technical articles do address the use of ozone (5) in high-purity water where some advantages of its use are mentioned.

In spite of this trend and the strong oxidation of organic substances by ozone, very little is being published on the influence of ozone dissolved in water on elastomeric seals. In contrast, the resistance of rubber to ozonated atmospheres, its testing and the mechanisms involved have been an issue for decades (6-10). The reason for this was that unsaturated elastomers, as natural rubber, are readily attacked by ozone in the atmosphere, causing failures. Car windshield wipers are a good example.

For transport of ozonated water, long years of experience shows that the conveyance of water containing typical amounts of ozone as used in microelectronics, around 200 parts per billion (ppb), does not lead to failures or specifics problems. Nevertheless, more severe use conditions leave the enduser to consider the ramifications of elastomeric seal selection. To help fill this knowledge gap, we set out to subject various elastomeric materials to increasing levels of ozone concentration and exposure time.

Experimental – Ozone Exposure

The experimental procedure for ozone exposure was designed to determine the usefulness of the test materials in applications with aqueous ozone concentrations of less than or equal to 1 parts per million (ppm). The critical variables that were identified included: ozone concentration, water temperature, pH, system line pressure, and test water impurities. These variables were controlled and/or logged over the course of the exposure, with the intent to retrospectively evaluate their impact on the test results.

The test bench was a closed loop system constructed from unplasticized polyvinyl chloride (U PVC). Water was pumped from a holding tank through a venturi where gaseous ozone was injected to ozonate the water. After the water passed through a static mixer, any unabsorbed gas was removed from the line using a degas chamber. An ozone analyzer then measured the concentration upstream of the test materials before the water returned to the holding tank. The holding tank was used to increase the total volume of water, thus decreasing the concentration variability throughout the system. This simple loop allowed for continuously circulating ozonated water to react with the test materials at a steady concentration, but even this simple system was not without its complications.

Since aqueous ozone will oxidize organic and inorganic compounds, a variety of byproducts can contaminate a closed loop test bench during use. If biodegrad-

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able organic matter does form, the system will be susceptible to biological growth, which can lead to unwanted degradation of the test materials (4). This presented some unique challenges in the determination of the test procedure because the test bench was not constructed from high-purity materials. Non-high-purity piping systems will always have some level of contamination, and as the ozone reacted with the test materials, test bench, and any contaminants, by products were formed that would remain in the closed loop system until they were removed.

To lessen the effects of this, deionized (DI) water was used as the test water and roughly one third (125 liters [L]) of the test water was replaced daily over the course of the exposure time. This constant cycling of the test water reduced the effects of any by-products or contaminants in the system and helped maintain a pH of 7, which was periodically verified using litmus paper.

The obviously most important variable, ozone concentration, was logged once every second along with water temperature during testing. With a pH of 7, and a water temperature of 20°C, the half-life of aqueous ozone is roughly 15 minutes, while the residency time over the test materials was roughly 1 minute. It was important to maintain line pressure in the system because it affects the injection system and the ozone sensor. If there are fluctuations in line pressure, the suction at the venturi will not be stable resulting in inconsistent dosing. Pressure variations could also create unstable flow across the ozone sensor or damage it, resulting in inconsistent data collection. A series of pressure gauges were used to monitor line pressure and a pressure reducing valve was used to protect the ozone sensor.

An ATI Q-45H heated metal oxide sensor (HMOS) ozone analyzer measured the concentration of aqueous ozone in the system. This type of sensor measures dissolved ozone by heating a small substrate. The presence of ozone will change its resistance proportionally to the concentration of ozone present. These types of sensors are very sensitive and responsive at low concentrations (<=1ppm) with a high degree of accuracy and reliability.

The ozone generator feed gas was compressed, dried, filtered air or compressed oxygen, depending on the target concentration. The compressed oxygen was created on-site using a Solvay AFT-12 pressure swing absorption oxygen concentrator with the feed gas being dried filtered air. The ozone generator used was a Triogen Lab-2B air cooled corona discharge generator, also called a silent discharge generator, to create ozone from the feed gas. These types of generators create ozone by passing oxygen filled gas through electrodes that are separated by a dielectric and discharge gap (4).

A feedback system was set up between the ozone analyzer and the generator using a programmable logic controller (PLC). This feedback system controlled the amount of ozone being injected by the system by varying the output of the generator proportional to the concentration being relayed by the ozone analyzer. Using this system, the concentration variance was limited to ±10% of the target over the course of the exposure time.

The tested O-ring materials were chosen because they are typically used or under consideration for use in high-purity water. Two grades of black fluoroelastomer (FKM) were compared. One sourced in Europe, which is being used as a standard FKM O-ring within Georg Fischer (GF) Piping System's non-high purity products (marked as FKM black 1), the other one is a commonly used grade sourced in the United States (marked as FKM black 2). Along with this, the GF choice for high-purity water piping systems, a white high-purity FKM O-ring designated as FKM white), was tested as well. Some users prefer fully fluorinated solutions, therefore a perfluoroelastomer (FFKM) and a fluorinated ethylene propylene (FEP) coated FKM O-ring were included in this study. As ethylene propylene diene monomer rubber (EPDM) is a standard material for sealing applications and reported to be resistant to ozone in air, it was also introduced into the test.

Each test round consisted of 5 O-rings per test material with 2 to 5 control samples, depending on the availability of the material. The in-line chamber used for exposing the elastomeric materials was made of U-PVC, which allowed the media to flow over the samples at a flowrate of approximately 2,200 L per hour /hr. The O-rings were torsional stressed, and secured in clusters specific to each material.

Torsional stress was applied to the samples by twisting the O rings into figure eights, then folding them in half to create a circle. They were then secured using ozone-resistant straps, exposing the maximum amount of surface area to the ozonated water. It was vital to stress the O-rings because there would be an applied stress under typical usage in a piping system, thus it would yield a result that would be more industry applicable. Two test rounds were conducted, the first with a target concentration of 0.5 ppm, and the second at 1 ppm. Each test round lasted for 1,000 hr with individual O-ring mass measurements approximately every seven days.

Experimental – Testing/ Analytical

Both reference samples and exposed seals were tested for the influence of the ozone exposure. The first inspection was done optically using a stereo microscope (Leica M205A) to check for visible changes to the surface. Images were taken using a digital camera (Leica DFC 425).

For some samples the surface was further examined using scanning electron microscopy (SEM). The O-rings were cut into short sections, sputtered with gold and visually inspected. The apparatus used was an EVO-MA10 by Zeiss.

The sealing properties were determined by compression set measurements according to ISO 815/ ASTM D395 Method B. These were determined using a triple measurement on O-ring sections or complete O-rings, depending on the amount of available samples under a compression of 25% for 24 hours at 70°C, and a recovery at standard conditions for 30 minutes. The lower the value the more elastic is the sample, leading to better sealing properties.

To better understand these results, infrared spectroscopy was used to evaluate changes in the chemical composition of the elastomeric surfaces. The measurements were performed using a Bruker Hyperion 2000 IR microscope with a Bruker FT-IR spectrometer (Model Tensor 27) in ATR mode.

Results and Discussion

The first observations regarding resistance of the samples to ozone were made during weighing. It was observed that the surface of the black FKM O-rings developed both discoloration and stickiness during testing time. The O-rings both stuck to the other rings as well as to the gloves during weighing leaving residues thereon. In contrast, the white FKM only developed a minor surface tack. EPDM had formed a liquid- like surface already when weighed for the first time after 7 days of ozone exposure and left black stains on gloves and holder. In contrast, the fully fluorinated materials did not exhibit any recognizable surface change.

Looking at Figure 1, weighing results were not clearly interpretable for FKM black as the data scatters with the weight first increasing and then going down again. We assume that this could be caused by water uptake followed by weight loss because of the surface change.

Both FFKM gained weight during testing, which is probably caused by water uptake of the elastomer. The weight of the FEP encapsulated FKM stayed fairly constant.

The results of the weighing of the EPDM and FKM white O-rings are shown in Figure 2.

The white FPM exhibited the most constant weighing results of all materials tested. In contrast, EPDM showed a constant weight loss over testing time. This is caused by the low water uptake of the EPDM, thus the weight did not increase upon water exposure- and the material loss as observed visually.

These observations during testing led to the assumption that the observed effects would also be seen optically, mechanically, and by chemical analysis.

Results on EPDM

Although the EPDM lost material and displayed a different surface touch when exposed to ozone, the samples did not show any optical change of the surface when they arrived in the lab. Inspection with the light microscope also did not show a change after 1,000 hours of exposure to 1 ppm ozone. Therefore, the O-ring surfaces were inspected using SEM.

SEM shows a constant attack to the

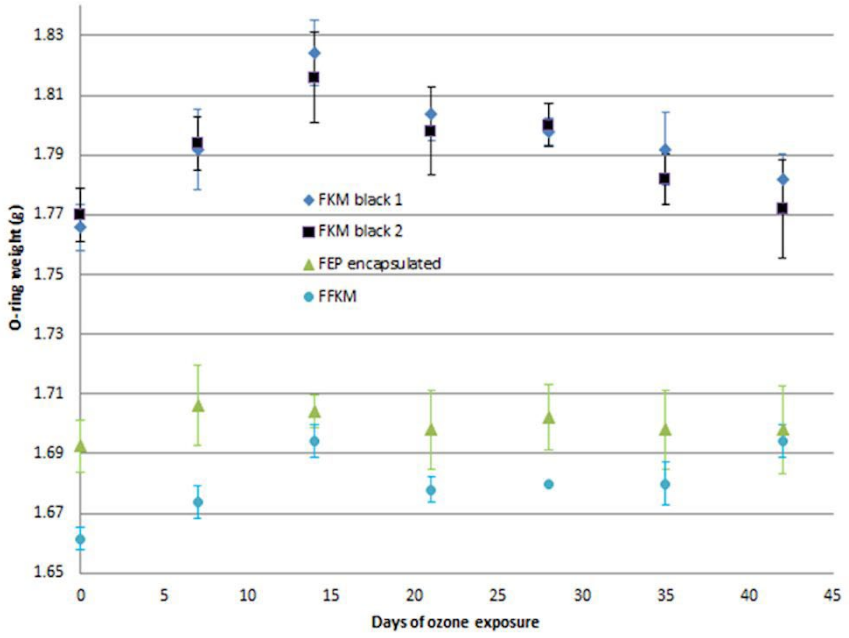

Figure 1. Weight development of FKM black, FEP encapsulated FKM, and FFKM during testing time with 1 ppm ozone.

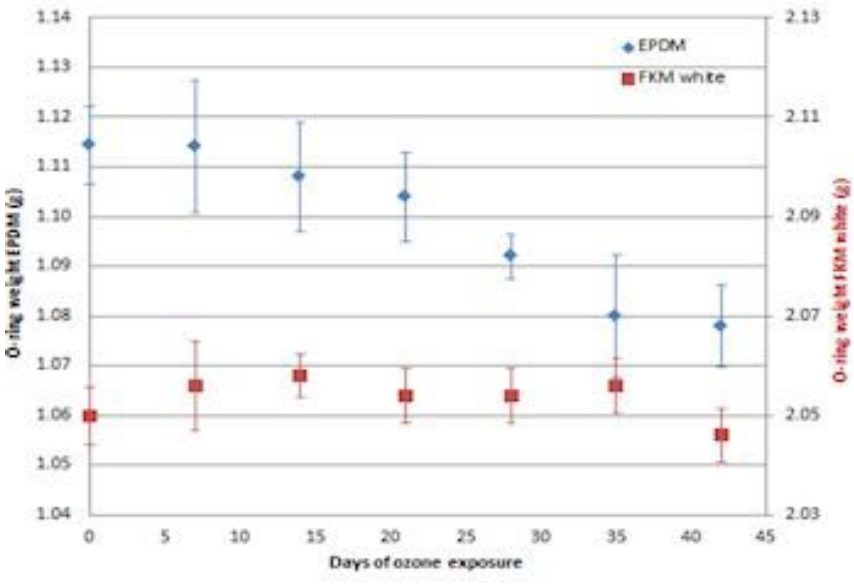

Figure 2. Weight development of FKM white and EPDM during testing time with 1 ppm ozone.

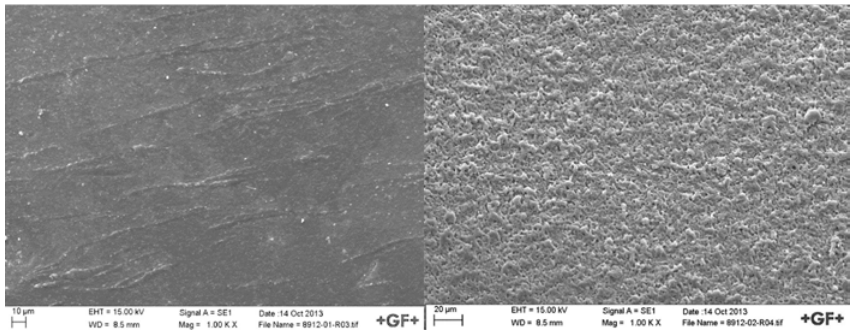

Figure 3. SEM pictures of EPDM, reference (left) and after exposure to 1 ppm ozone for 1,000 hours (right).

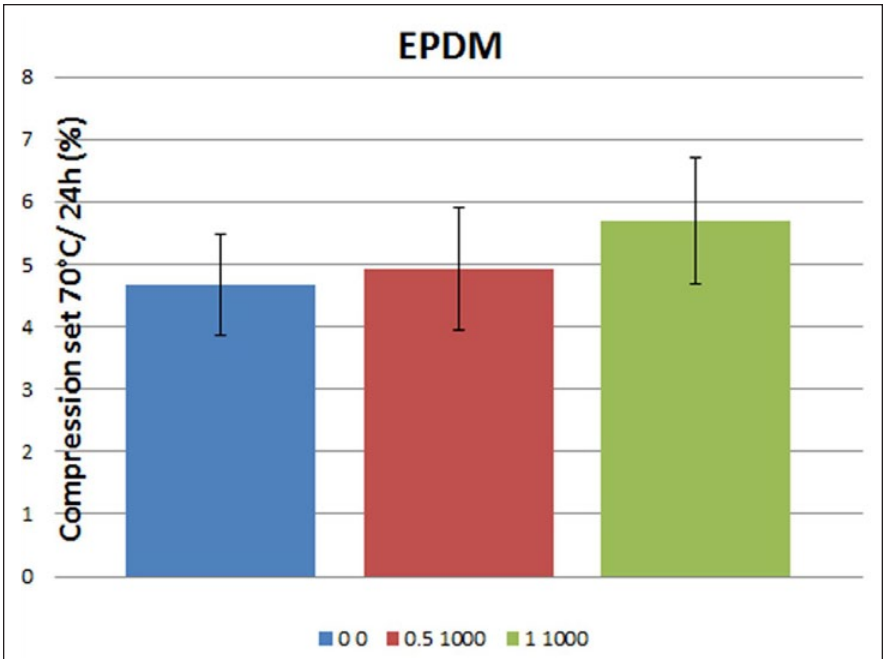

Figure 4. Compression set of EPDM, reference and after exposure to 0.5 and 1 ppm ozone for 1,000 hours.

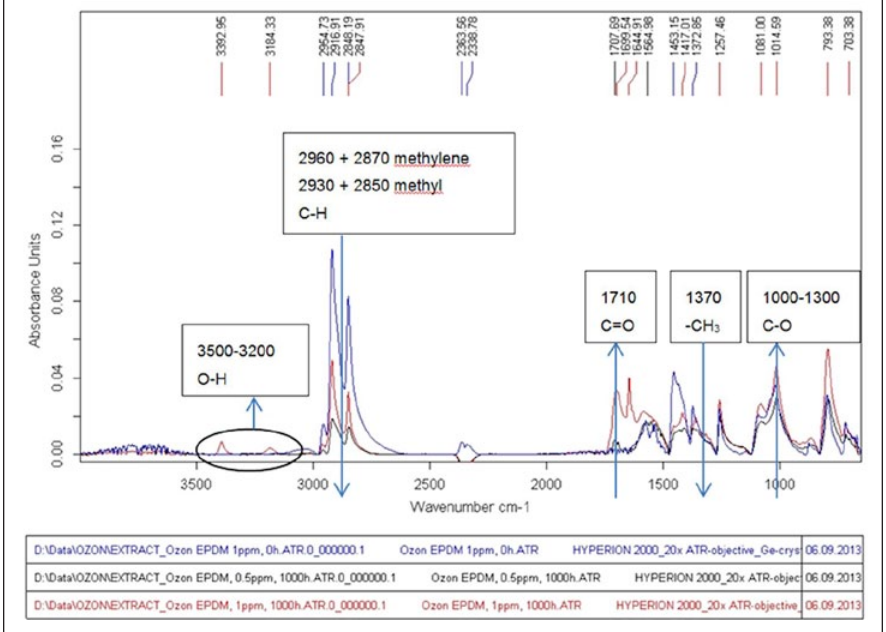

Figure 5. IR Spectroscopy of EPDM after exposure to 0.5 and 1 ppm ozone for 1,000 hours

surface of the EPDM as seen in Figure 3.

Figure 4 shows the change of the compression set after exposure to 0.5 and 1 ppm ozone for 1,000 hours. There is a trend to a higher compression set, meaning loss of elasticity, and therefore sealing force. Nevertheless, the value below 6% is still very good after ozone exposure compared to the initial values of other elastomers.

The findings described for EPDM go perfectly in line with what Miwa, et al. (11) have described in a study using 5.5 ppm ozone in water. They, too, observed mass loss and a smeary surface. They also described the degradation mechanism in contact with ozonated water, and used several analytical methods to prove "that the adhesive substance which appeared at the surface was composed of lower molecular weight components caused by the chain scission of EPDM." The findings that make this study especially interesting for high-purity water is that Miwa, et al. not only measured a weight change, but in parallel an increase in TOC in the ozonated water.

In order to confirm that the degradation mechanism was the same in our experimental setup and at the much lower concentration of ozone, IR spectroscopy was used, see Figure 5.

Although the results are not quite as consistent as the ones found by Miwa, it is clearly observable that the methylene- and methyl groups present in EPDM are reduced in their intensity during ozone attack, whereas oxygen-containing groups increase because of oxidation of the material. The formation of ketone, carboxy-, and hydroxy- groups during oxidation of ethylene propylene elastomers in the presence of ozone has already been described earlier (12). Therefore, we can assume that the surface of the EPDM got degraded by ozone forming low-molecular weight residues that have been introduced into the water as TOC. This attack would proceed with longer exposure times.

Results on FKM

The weighing results and the handling of the FKM O-rings during the weighing process already lead to the assumption that the black and white O-rings show a different behavior in ozone resistance. Figure 6 shows the images of the surfaces taken with the stereomicroscope.

Interestingly, the surface of both black FKM O-rings developed stickiness upon ozone exposure. FKM black 1 formed a black layer throughout the whole surface. This increased in thickness with higher ozone content. The surfaces show areas where the sticky material has been torn away, probably by contact to other O-rings and gloves, among other things. In contrast, FKM black 2 showed brownish drops on the surface with the quantity also depending on ozone concentration.

White FKM, which did not stick but just developed some tack, showed black spots on the surface when examined after ozone exposure. Unfortunately, this is sticky material from the black FKM O-rings, which left residues on the white material as all samples were stored in one container during testing. On detailed inspection under the microscope some brownish areas on the surface of the exposed O-rings became visible. Maybe this is an effect of ozone on the material.

The compression set of both black

FKM materials shows a slight upward trend (Figure 7), with Formulation 2 being worse both in the initial value and the increase in compression set upon ozone exposure. This shows that the surface effect also led to a certain reduction of elasticity.

The compression set of FKM white is at a similar starting level as that of FKM black 1, but seems to be less changed (Figure 8).

Compression set thus confirms the optical impression of different resistance that the O-rings gave regarding their reaction to ozone, but also shows that the two formulations of black FKM were already significantly different in their initial compression set values. Though IR spectroscopy was done on all tested samples, we are not able so far to clearly determine where the differences between the FKM O-rings came from as the formulations are a trade secret of the suppliers. Some more work will be put into understanding the effects that were observed as only the understanding of the mechanism of attack can lead to the implementation of specific improvements to the materials.

So far it can only be said that the white formulation as used for high-purity products showed the best performance to ozone resistance of the tested grades, followed by the black formulation used for non-high-purity products in Europe.

Results on FFKM and FEP-coated FKM

Both fully fluorinated sealing solutions showed no visible surface effect upon ozone exposure.

The encapsulated FKM gave the optical impression of trapped liquid between the coating and the inner material, but since this was already the case in the reference sample this was not considered a testing effect. At closer visual inspection, the exposed samples gave the impression that brownish spots appeared on the FKM surface below the FEP coating after ozone exposure. This

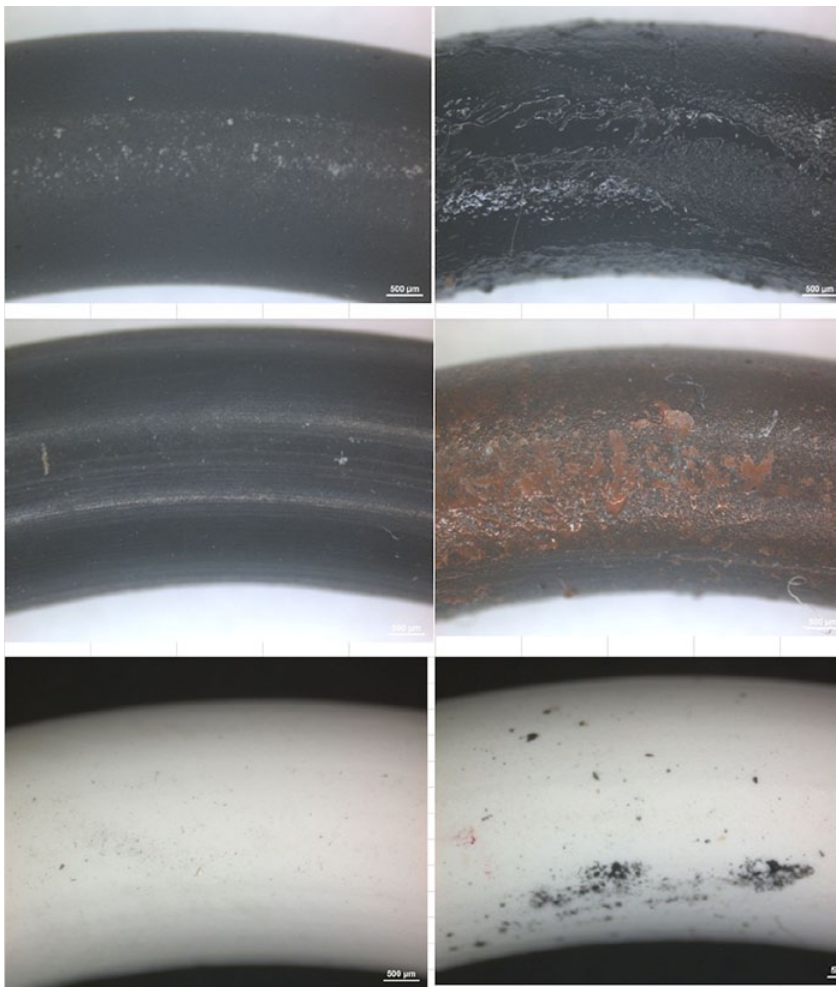

Figure 6. Top: Macroscopy on FKM black 1, reference (left), and after 1,000 hours at 1 ppm ozone exposure; Middle: Macroscopy on FKM black 2, reference (left), and after 1,000 hours at 0.5 ppm ozone exposure; and Bottom: Macroscopy on FKM white, reference (left), and after 1,000 hours at 1 ppm ozone exposure.

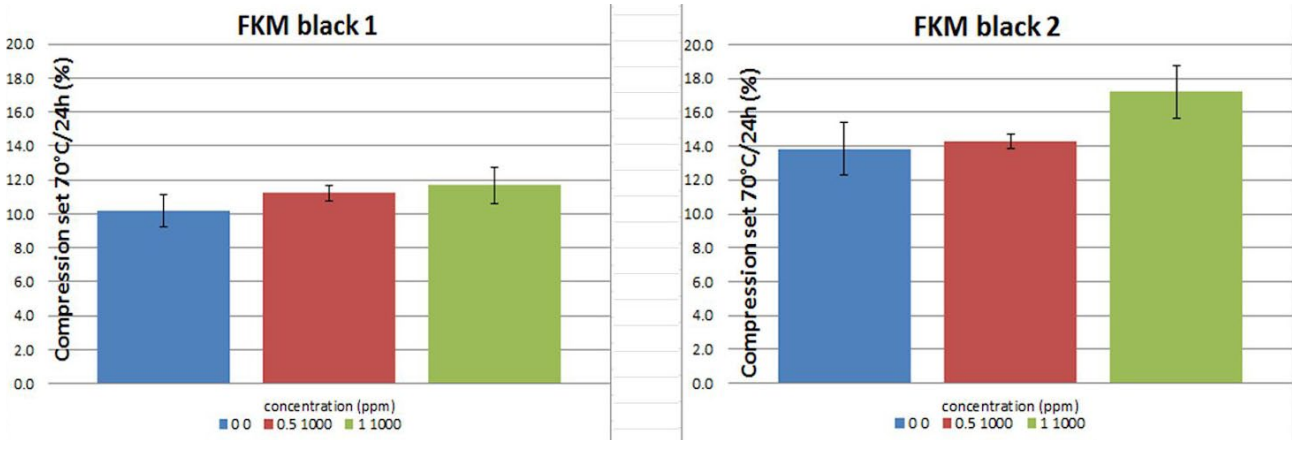

Figure 7. Compression set of FKM black 1 and 2, reference and after exposure to 0.5 and 1 ppm ozone for 1,000 hours.

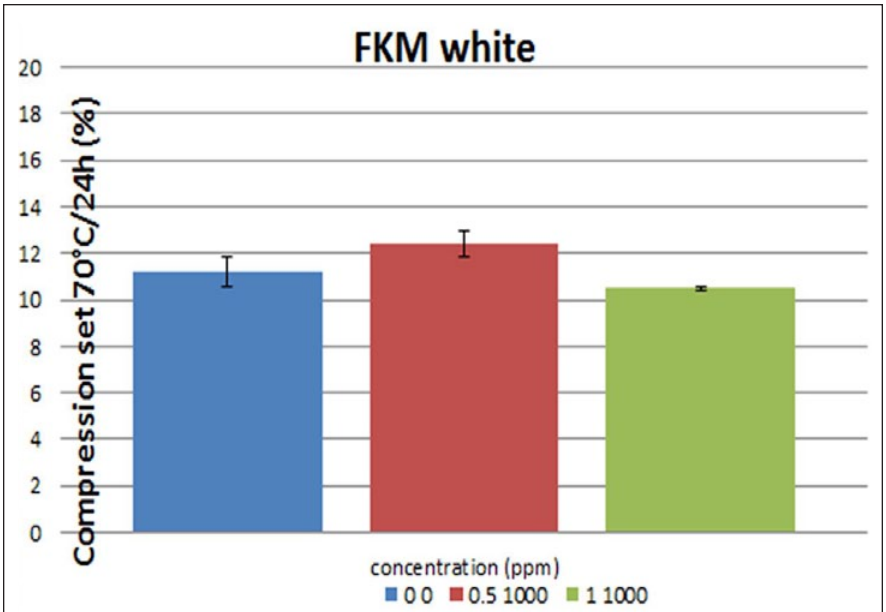

Figure 8. Compression set of white FKM, reference and after exposure to 0.5 and 1 ppm ozone for 1,000 hours.

looks similar to the brownish drops appearing on the surface of FKM black 2 and could be a hint that, though the FEP resists ozone attack, there could be ozone diffusion through the protective layer attacking the inner FKM. Although this attack is barely visible after 1,000 hours, it may become more significant under more severe conditions like higher ozone concentrations, longer exposure times or elevated temperature.

FFKM and the FEP- coated O- rings did not change their compression set when exposed to ozone for 1000 hours. Nevertheless it is interesting to observe that the compression set of the FFKM reference was by far the worst compression set value of all tested O- rings, whereas the FEP- coating of the FKM did not significantly alter the properties regarding compression set when compared to the uncoated FKM.

Summary and Conclusions

Ozone is a common additive within high-purity water systems used in advanced microelectronic fabs. However, very little research and publication of studies regarding the compatibility of high-purity water piping system materials to ozone exposure has been made. This is especially true when looking at the elastomeric seal found in unions and flanges of high-purity water piping systems. Specifically, studies regarding the resistance of fluoroelastomers resistance to ozone do not exist. As years of experience have shown that the commonly used FKM seals do not cause failures in high-purity water systems, endusers do not think about this single point of potential failure or contamination much.

This study was a comprehensive effort to thoroughly test and understand the resistance of both thermoplastic pipe materials as well as elastomers to relevant concentrations of ozone. Because of the large scale of the test assembly, parameters were harder to control than in small test setups, with the evaluation of the ozone impact on the thermoplastic piping system still pending. In spite of the challenges, the impact of 0.5 and 1 ppm of ozone on the tested elastomers is obvious. All of the non- or partially fluorinated elastomers underwent visual and haptic surface changes compared to the initial state that were also reflected in the use properties, as represented by compression set.

Our results on EPDM fully confirmed the existing literature regarding its reaction with ozone. The material degrades in contact with the strongly oxidizing ozone, forming a smeary surface consisting of low molecular weight degradation products that end up as TOC and/or particles in the water. The sealing properties as represented by the compression set are slightly influenced, but remain at an acceptable level. In actual installations, the low surface area of the EPDM seal might make this material a real option if TOC and particles are not an issue in the application.

The tests on three FKM grades, common choices for high-purity water applications, showed a significant dependence of the properties and amount of attack on the formulation of the O-ring material. Both black formulations tested formed a sticky surface upon testing. It can be assumed, though this would need to be proven scientifically, that this material also ends up in the high-purity water as TOC and particles. Therefore the correct choice of the O-ring FKM formulation is important for sensitive applications.

Both fully fluorinated solutions tested, FFKM and FEP coated FKM, were very good regarding their resistance to ozone. FFKM has a weakness regarding its compression set properties and is very expensive, but could be an option where excellent resistance and low particle and TOC emission are essential. The FEP coating appears to allow some diffusion of the ozone molecules to the inner FKM O-ring that got slightly attacked under the testing conditions of this study, but surely adds much less contamination to the process than does EPDM or uncoated FKM.

To fully understand the effects that have been found, further sound scientific research and study is needed.

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The late Marty Burkhart was an author of this paper, providing his knowledge and insights to the other authors. Prior to his passing, he was a consultant to Georg Fischer Piping Systems, providing technical support for high-purity products. Between 1992 and 1996, he was employed by Georg Fischer as the technical marketing manager for high-purity products in Switzerland. He also worked 13 years with Texas Instruments in Dallas, TX, and was very active in SEMI's standards method development program.

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