Paper #12

Effect of Different Nitrile Elastomers in Down Hole Drilling Applications With a Review of Testing and Failure Analysis

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With a Review of Testing and Failure Analysis

ABSTRACT

This paper discusses the use of rubber products in oilfield drilling applications and the analysis of their possible failure modes. Background information on the actual rubber products and their expected environment and service conditions is also presented. The effect of different nitrile butadiene rubber (NBR), hydrogenated nitrile butadiene rubber (HNBR), and carboxylated nitrile butadiene (XNBR), were evaluated in a down hole packer application. The effect of acrylonitrile content (% ACN) level within the elastomers was evaluated as well.

INTRODUCTION

Elastomers play a large role in oil field drilling and service equipment. These types of applications are demanding and require a highly engineered product from a variety of different elastomers. Elastomeric materials in oil field service protect workers, equipment, and the environment in addition to enhancing drilling and zone isolation to maximize well production.[1] These rubber parts are exposed to extremes in temperatures, high pressures, rapid gas decompression, and chemicals within their service lifetimes. These rubber components must be made without flaws and perform in these harsh environments with minimal failures. The most common types of polymers used in these applications are acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), carboxylated acrylonitrile-butadiene rubber (XNBR), and fluorocarbon terpolymers and tetrapolymers (FKM).

In recent years, changes in environmental policy have affected drilling applications, causing changes from oil based muds to synthetic based muds that comply more closely with environmental standards[2]. Although these synthetic fluids may be biodegradable and less toxic, some are incompatible with down hole elastomers. Particular components in synthetic based muds and their additives can often chemically and thermally degrade elastomers by altering such properties as volume swell, elongation, hardness, tear strength, and tensile strength[2]. Environmental policy changes will continue to push developments in cost reduction and new polymer technology.

OILFIELD APPLICATIONS, CONDITIONS

Oilfield Applications

Elastomers make up a variety of components for oilfield drilling applications. Some typical rubber oil field drilling components are shown in Table 1.

Table 1

Elastomeric Oilfield Components		
Gaskets	Drill Pipe Protectors	Down-hole Packers
O-rings	Drill Bit Seals	Inflatable Packers
Hoses	Annular Blowout Preventers	Valve Seals
Cables	Ram Blowout Preventers	Drilling Hoses
Cable Jackets	Drill Motor Seals	Pressure Accumulators
Pump Stators	Wellhead Seals	Swab Cups

Environmental Oilfield Service Conditions

Elastomers used in oilfield applications are routinely exposed to the below environmental conditions (see Table 2)

Table 2

Environmental Conditions
High temperatures, 150 -175°C - some as high as 300°C
Pressure of 20,000psi - spikes up to 30,000psi
Ambient temperature of -50 to 50°C
Geothermal steam
Abrasive mud, sand, and rock

Chemical Exposure Oilfield Service

Elastomers used in oilfield applications are also exposed to a variety of chemicals (see Table 3) that can be detrimental to the service life of the product. The rubber chemist needs to keep this in mind when developing rubber components for these applications.

Table 3

Chemical Exposures
Crude oil
Natural gas (methane)
Amine corrosion inhibitors
Hydrogen sulfide
Salt water (brine)
Carbon dioxide
Solvents such as methanol
Hydraulic fluids
Diesel oil
Inorganic and organic acids
Coolants

OILFIELD ELASTOMERS

Performance Criteria

For elastomers to operate in these harsh service conditions they need to comply with certain performance criteria. They need to have high temperature performance but, be able to operate at low temperatures without becoming brittle. They have to have excellent swell resistance or depending on the application a controlled swell when exposed to aggressive chemicals and fluids. Applications requiring a controlled swell must be able to swell while maintaining a certain percentage of the mechanical properties. Elastomers need to have high tear resistance, high abrasion resistance, low compression set and must be able to retain their shape at a variety of temperatures and exposure periods. Finally, resistance to failures due to rapid gas decompression (explosive decompression) when high pressures are released is needed.

Although many aspects of the rubber compound will affect how it performs, the most important property is the type of elastomer used within that particular compound. Table 4 is an elastomer property comparison chart for some common rubbers

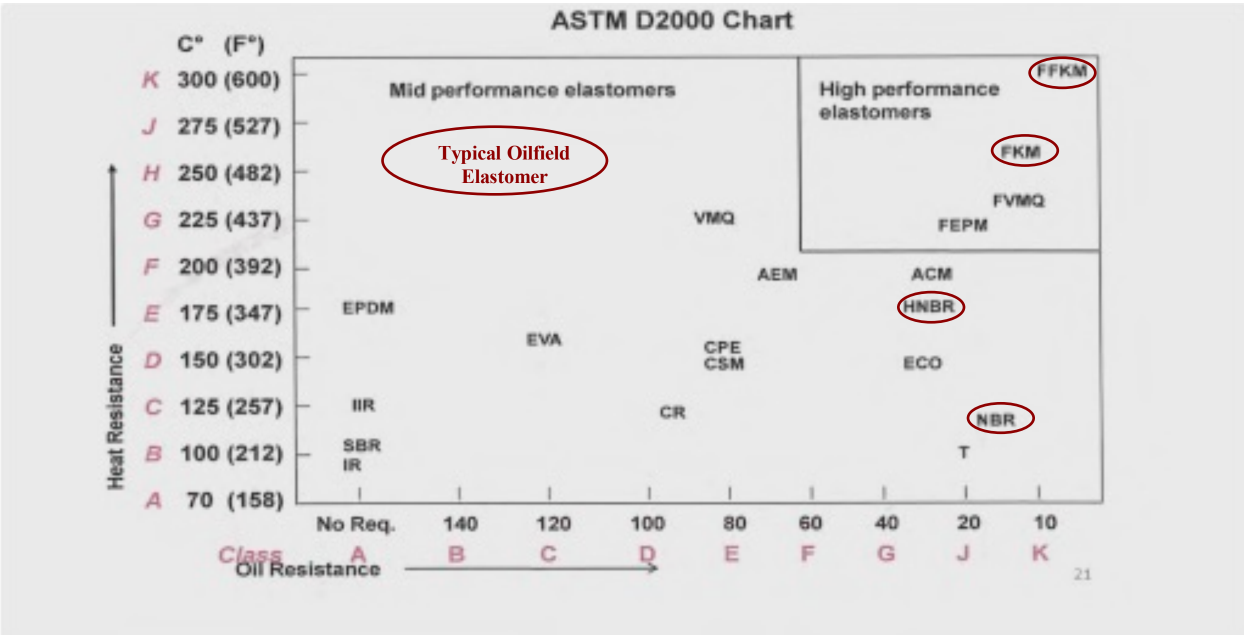
Table 4

Basic Property	NBR	HNBR	EPDM	FKM	CR	ACM	AEM	SBR	AU /EU	VMQ	FVMQ	NR
Economy of Material	1	4	2	3	2	3	4	1	3	3	4	1
Compression Set Resistance	1	1	1	1	2	4	2	2	3	2	2	1
Resilience (Rebound)	2	2	2	2	2	3	2	2	2	2	2	1
Tear Strength	2	1	2	2	2	3	2	3	2	4	3	1
Heat Aging Properties	3	2	2	1	3	1	1	3	1	1	1	3
Ozone Resistance	4	2	2	1	2	2	1	4	1	1	1	4
Resistance to Oil and Grease	2	2	4	1	2	1	3	4	2	3	1	4
Fuel Resistance	4	3	4	2	4	1	4	4	3	4	2	4
Water Swell Resistance	2	2	1	2	3	4	2	1	4	1	1	1
Gas Impermeability	2	2	3	2	2	3	2	3	2	4	4	3
Dynamic Service / Abrasion Resistance	2	2	2	3	2	2	2	1	1	4	4	1
High Temperature,°C	140	175	160	200	110	150	150	110	80	200	200	100
Low Temperature, °C	-40	-35	-60	-18	-40	-60	-40	-50	-60	-100	-50	-55

VERY GOOD = 1, GOOD = 2, AVERAGE = 3, POOR = 4

Figure 1 is the ASTM D2000 Chart which plots heat resistance versus oil resistance of some common rubber elastomers. Typical oilfield application rubber elastomers are NBR, acrylonitrile-butadiene rubber, HNBR, hydrogenated acrylonitrile-butadiene rubber, XNBR, carboxylated acrylonitrile-butadiene rubber, FKM/FFKM, fluorinated terpolymers and tetrapolymers of fluorocarbons.

Figure 1



OILFIELD RUBBER COMPOUND TESTING

The base elastomer should be chosen based on the criteria that the rubber component must meet including production processing, performance properties under all exposure environments required and economical considerations.

Processing Properties

The processing properties (see Table 5) measure how the rubber compound will handle in the production process. Good processing is important not just from an economic standpoint but more importantly, to produce defect free rubber components.

Table 5

Processing Property	Test Procedure
MDR Rheometer Cure Properties	ASTM D-5284
Mooney Viscosity, Scorch, Stress Relaxation	ASTM D-1646
API Extrusion Resistance, 175°C, 69 MPa	

.Physical Properties

The physical property testing of a rubber compound will tell you how the compound will behave mechanically (see Table 6).

Table 6

Physical Property	Test Procedure
Unaged Physical Properties- tensile, modulus, elongation	ASTM D-412
Durometer Hardness	ASTM D-2240
Tear Strength	ASTM D624
Compression Set	ASTM D-395
Low Temperature Brittle Point	ASTM D-2137
Low Temperature Retraction	ASTM D-1329

Aging and Fluid Resistance

The aging and fluid resistance testing indicate how a rubber compound will perform in different environments for an extended period of time. Typical aging and fluid tests for down hole drilling applications are shown in Table 7.

Table 7

Aging and Fluid Resistance Properties	Test Procedure
Heat Aging - 168 HRS. @ 125, 150, and 175°C	ASTM D-573
Fluid Immersion - 168 hrs @ 125, 150, 175°C in various fluids (water, brine, diesel, oils fuels, and mud)	ASTM D-471

Dynamic Properties

Dynamic property testing is important if you have a rubber component that will have to bend, flex, or slide against another substrate. Typical testing for dynamic properties in down hole applications are shown in Table 8.

Table 8

Dynamic Properties	Test Procedure
DeMattia Flex	ASTM D-813
DIN, Pico, or Tabor Abrasion	ASTM D-5963, D-2228, D-3389
DMA Dynamic Viscoelastic Properties	
Fatigue to Failure	ASTM D-4882

High Pressure and Chemical Aging

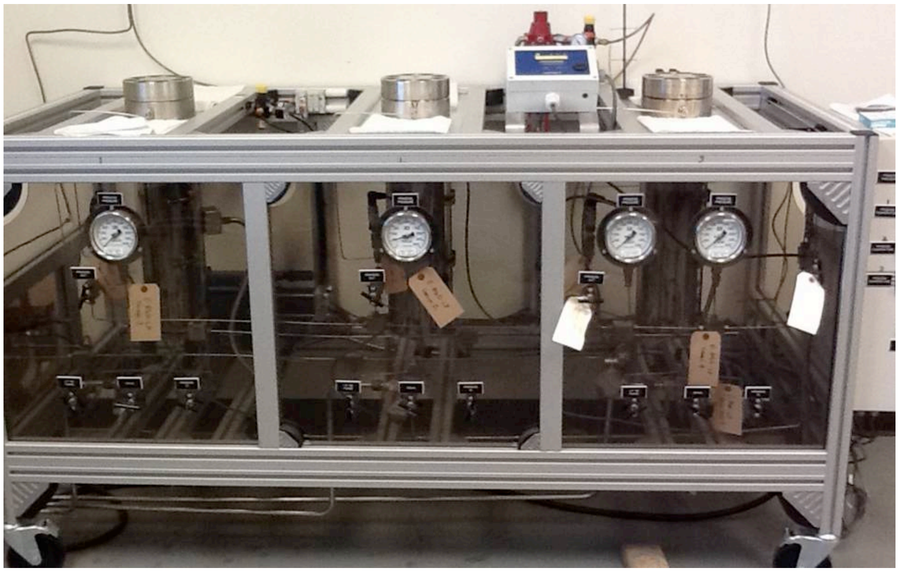
Many oilfield applications require certification to special standards like NORSOK or NACE to be used in these applications. NORSOK stands for Norsok Sokkels Konkuranseposisjon which is a set of standards developed by the Norwegian petroleum industry that have been adopted by regulating authorities in many countries. NACE standards are set by the International Corrosion Society and are also used to certify down hole drilling applications. The most common tests are shown in Table 9.

Table 9

High Pressure and Chemical Aging	Test Procedure
Chemical Aging	NORSOK M-710 (ANNEX A)
Rapid Gas Decompression (RGD)	NACE TMO 192-2003

Figure 2 is a picture of a Rapid Gas Decompression Chamber (RGD) used to perform NACE and NORSOK testing. Pressure capabilities are normally around 20,000 psi with a temperature capability of 300°C. Testing can be done in both Sweet Well (CH_4) and Sour Well (H_2S, CO_2) environments. Customized testing can be performed as well.

Figure 2



FAILURE ANALYSIS

Failures in oilfield drilling applications can be catastrophic, cost millions of dollars, and possibly result in legal or criminal action. It is imperative to understand the potential modes of possible failure for all parts involved. In 2006, Patel and Campion of RAPRA Technology Ltd. presented a comprehensive list of failure modes in their work "Oilfield Engineering with Polymers"[3] shown in Table 10.

Table 10

Failure	Description	Laboratory Prediction Test
Abrasion	Loss of material over time due to rubbing or fluid/gas flow	DIN, Taber, Pico Abrasion Testing
Bond Failure	Bonding between metal fittings or other components and elastomeric components can fail	Adhesion testing - pull out or peel strength under applicable conditions
Creep	Increase or deformation over time under constant load or from degradation of physical properties	Physical Properties and Tension Set ASTM D-412 D-2240, Heat Aging Properties ASTM D-573, or Fluid Immersion ASTM D-471
Chemical Degradation	Reduction in physical properties due to chemical attack, ozone, oxidation, etc. - resulting in degradation of physical properties	Physical Properties and Tension Set ASTM D-412 D-2240, Fluid Immersion ASTM D-471, NORSOK Chemical Aging
Fracture, rapid tearing	This happens when the ultimate strength properties of the Elastomers are exceeded.	NACE RGD, Tear Strength ASTM D-624, Physical Properties ASTM D-412 D-2240
Fatigue Crack Growth	Crack growth under repeated strain cycling under dynamic loads	DeMattia Flex ASTM D-813, Fatigue to Failure ASTM D-4882
Rapid Gas Decompression	Gas dissolved in the elastomer under high pressure comes out of solution and forms bubbles in the material when the pressure is removed. The bubbles can cause blisters and fractures in the elastomers	NACE TM0193-2003 Rapid Gas Decompression, Tear Strength ASTM D-624, Physical Properties and ASTM D-412 D-2240
Stress Relaxation	Reduction of load over time under constant deformation conditions. Can result in loss of sealing capabilities or loosening of fittings.	Compression Set ASTM D-395, Tension Set ASTM D-412, Stress Relaxation ASTM D-6147
Swelling	Absorption of fluids over time resulting in degradation of physical properties	Fluid Immersion ASTM D-471
Low Temperature	In cold climates, the ambient temperature in winter can be below or near the Tg of the elastomer causing the elastomer to become leather like near the Tg and glass like below the Tg. The rubber no longer has elastomer properties, which can lead to failure.	Brittle Point ASTM D-746 and D-2137, Low Temperature Retraction ASTM D-1329
Thermal Aging Oxidation	Hardening (usually) or sometimes softening of the rubber due to exposure to high temperatures leading to loss in physical properties, especially elongation	Physical Properties ASTM D-412 D-2240, Heat Aging ASTM D-573
UV and Ozone Degradation	Rubber parts exposed to UV and ozone can experience cracking	Ozone Aging ASTM D-1171 and D-1149

P. Martney also put together a list of the elastomeric components for oilfield drilling applications and their likely failure modes[4] shown in Table 11.

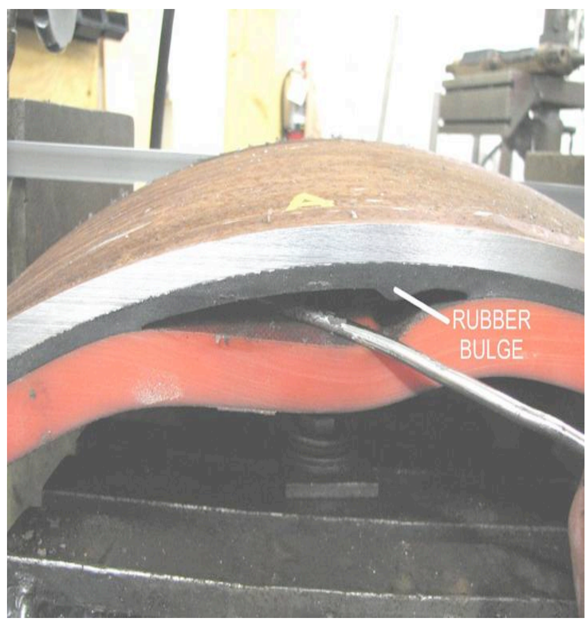
Table 11

Failure Mode	Static Seals	Packers Plugs	Repair Clamps	Dynamic Seals	Hoses	Flexible Joints	Valve Sleeves	Pulsation Bladder Bellows
Fracture	X	X	X	X	X	X	X	X
RGD	X		X		X	X		
Stress Relax	X		X	X	X			
Creep	X	X	X					
Swelling	X	X	X	X	X			
Thermal Contraction	X	X	X					
Chemical	X	X	X	X	X	X	X	X
UV / Ozone					X		X	
Fatigue				X	X	X	X	X
Abrasion				X	X			
Bond Failure					X	X		

Figures 3 and 4 are examples of an adhesion failure showing a rubber bulge causing a separation in the urethane / rubber interface.

Figure 3

Figure 4



Figures 5 and 6 shows another example failure due to chemical degradation of a rubber lined hydro transport and tailings pipe for tar sands. It can seen that the part is starting to crack and become brittle.

Figure 5

Figure 6

Microscopy Failure Analysis

Microscopy techniques are used to produce visible images of polymer microstructures or details that are too small to be seen by the human eye. The three main types of microscopes used for this type of analysis are Optical, Electron, and Scanning Probe. Two popular types of electron microscopes are scanning electron microscopes (SEM) or transmission electron microscopes (TEM). Optical and Electron microscopy both work based on the fact that diffraction, reflection, and refraction of radiation instigates the development of an image.

Energy Dispersive X-RAY (EDX) detects elements within a sample using X-RAYS generated by the SEM. This can also be expressed as Elemental Analysis and Multi- Element Dot Mapping. Light Optical Microscopy (LOM) is used to look for physical defects and failures. An Optical Comparator (OC) can be used for micro measurements on parts to make sure they are in specification. Typical failures that can be analyzed by microscopy are show in Table 12.

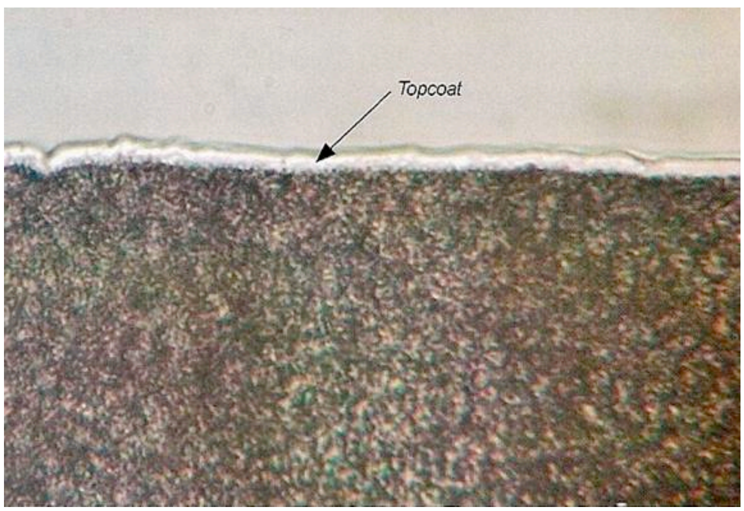
Table 12

Failures Analyzed by Microscopy	Microscopy Method
Coating and Film Thickness	LOM, OC, SEM, EDX, TEM
Dispersion Analysis	LOM
Element Composition	EDX
Metal to Rubber Bonding	SEM, EDX

Many modern rubber and plastic products are manufactured with different layers (co-extrusions, laminates, and/or surface coatings and treatments) that perform certain functions. These can be analyzed by embedding and microtoming cross-sections through the different layers and evaluating them microscopically using the OC or LOM microscopes. A determination can be made of the number of layers and their thicknesses. This type of analysis can help to understand if the layers are degrading over time. Swelling, separations, and chemical degradation can be seen.

Subsequent analysis of the microtomed sections by microscope, FTIR and SEM/EDX can also determine organic and inorganic compositions of the different layers. TEM can resolve very thin sections that cannot be seen by other methods (see Figure 7).

Figure 7



Topcoat thickness measurement by LOM – 15 micron

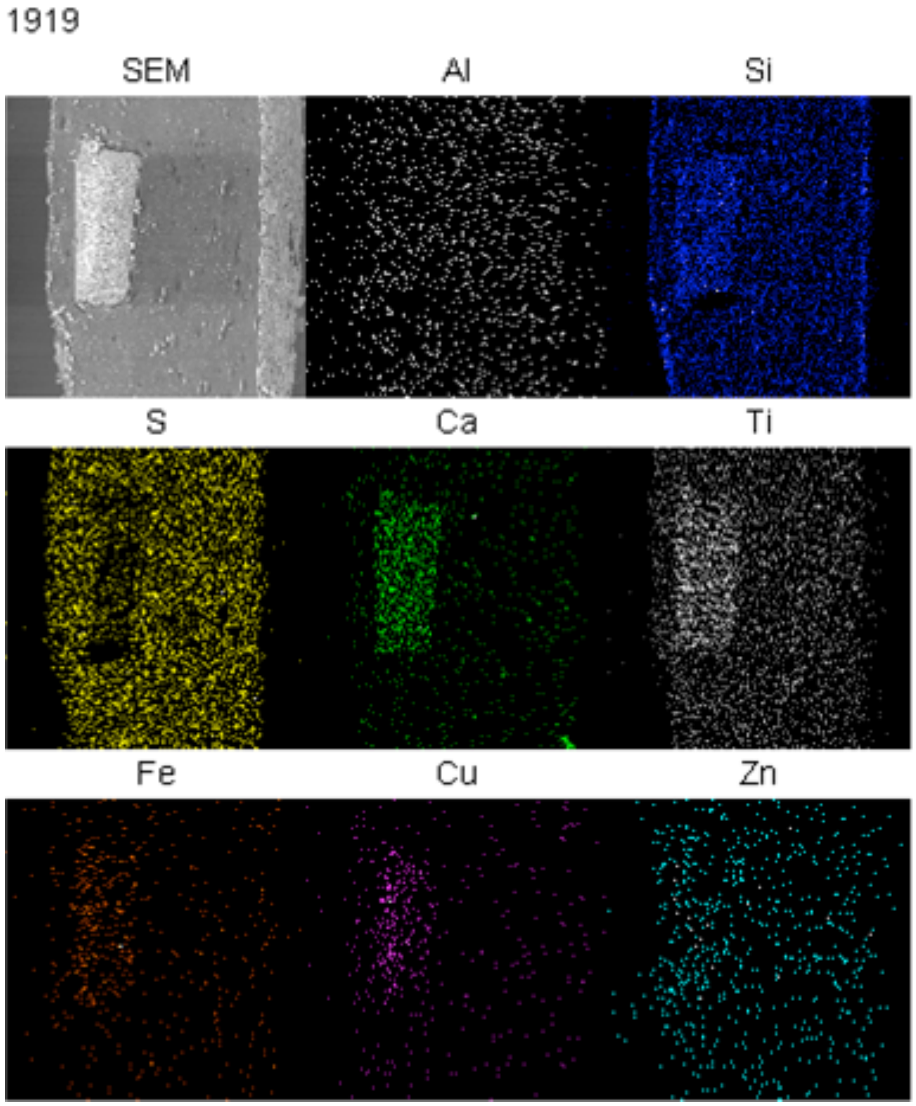
Dispersion of carbon black or inorganic fillers can be determined by cutting or microtoming the rubber and analyzing with reflected light, transmitted light, or electron microscope. The most common carbon black dispersion analysis is done with an LOM microscope using reflected light in a method commonly known as Phillips Dispersion Rating. More precise carbon black dispersion analysis can be done by microtoming thin sections and using transmitted light (TEM) as shown in Figure 8.

Figure 8

Phillips Dispersion by LOM – 665 micron

SEM analysis uses atomic number contrast from backscattered electron images to determine the dispersion of inorganic fillers. In this type of analysis the inorganic fillers appear lighter (higher atomic number) than the surrounding polymer (low atomic number). This type of SEM analysis is beneficial when reviewing inorganic structures while other means of analysis such as FTIR and GC/MS are beneficial when evaluating organic structured contaminants. Positions and concentrations of different elements in a composite can be determined with either multi-elemental X-Ray dot mapping or line scan analysis as shown in Figure 9.

Figure 9

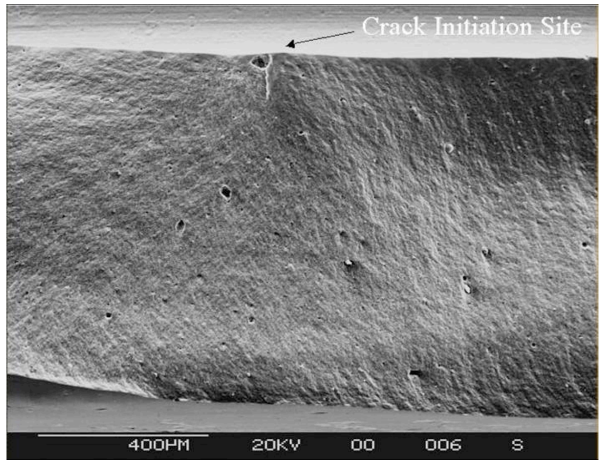


Electron Dot Map

Metal to rubber bonding failures are one of the most common failures within the rubber industry. Cord adhesion and other metal to rubber bonds can be looked at in the SEM using image and elemental analysis as shown in Figure 10. Techniques such as freeze fracturing and polishing of sample cross-sections can be employed to get a close look at the interfaces in question. Multi-elemental X-RAY dot mapping and line scan techniques can then be used to measure layer thickness and identify elements present that are specific to primers and adhesives. Another example of SEM analysis is the view of a crack initiation site and the subsequent crack growth as show in Figure 11.

Figure 10 **Figure 11**

Tire Cord Analysis by SEM



SEM Image of Failure Site

Chemical Failure Analysis

Chemical analysis of a failed part can be very a critical part of failure analysis. It can identify foreign contamination, if the correct raw materials were originally used, and if the crosslink density of the compound has changed, indicating aging or ozone issues within the compound. The most common chemical analysis tools are:

Table 13

Chemical Analysis Methods	Uses
Fourier Transform Infrared Spectroscopy, FTIR	Identifies type of polymer, blends of polymers, bloom, and contamination
Thermogravimetric Analysis, TGA	Breaks down compound into measurable categories - Highly volatile, Medium volatile, combustibles, and Ash
Chemical Analysis per ASTM D-297	Can identify fillers, sulfur analysis, antidegradants, specific gravity, accelerators, plasticizers, and hydrocarbon content, etc.
Thin Layer Chromatography	Used to identify antidegradants
Pyrolysis GC/MS	Plasticizers, antidegradants, accelerators, resins, process aids, etc
Differential Scanning Calorimetric, DSC	Determines Tg, melt points, can give estimation on polymer blends.
Crosslink Density	Comparative test to see if the level of crosslink's has changed over time

NITRILE RUBBER STUDIES IN A PACKER SEAL COMPOUND

Packer Seal

A packer is a sealing device used down hole to block the flow of fluids through the annular space between the drill pipe and the wall of the hole[1]. The packer consists of a tubing string encased in a packing element. The packing element is a rubber component that expands to block the annulus and allow fluids to flow only though the encased tubing (see Figure 12). Packers are classified according to their function, configuration, and method of setting. Down hole packers may see pressure differentials of 15,000 psi and seal gaps as large as ¼ inch wide[1]. A packer seal needs to be an elastomeric type of material that can expand to fill the void. Properties needed for packers include heat, chemical, and cured extrusion resistance.

Figure 12

Examples of Packer Seal

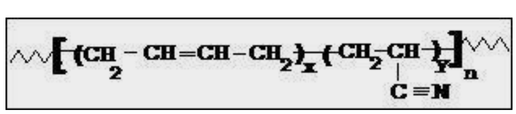
In this study, packer seal compounds were made from different NBR, HNBR, and XNBR were compared. Not only were the different types of nitriles compared but varying %ACN (acrylonitrile) levels as well.

Nitrile Rubber, NBR

Nitrile (NBR) is a co-polymer of polybutadiene and acrylonitrile (see Figure 13). Its properties such as physical strength and resistance to various solvents, oils, etc. are very dependent upon the amount of acrylonitrile (ACN) in the polymer. The glass transition temperature varies with the acrylonitrile (ACN) content.

- Low ACN content -45°C Tg
- Medium ACN content -34°C Tg
- High ACN content -20°C Tg

Figure 13

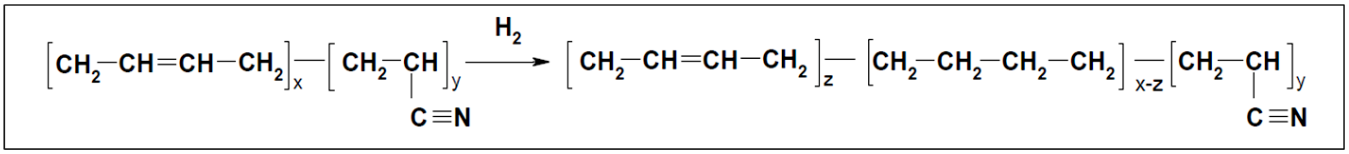


NBR Polymer Structure

Hydrogenated Nitrile Rubber, HNBR

HNBR is produced from NBR after the dissolution process is complete. Hydrogen gas and a precious metal catalyst hydrogenate the backbone resulting in a highly saturated HNBR polymer which improves physical properties, heat aging, and weather resistance (see Figure 14). HNBR is used in applications requiring better aging resistance than standard NBR polymers. As with NBR, HNBR Tg increases with increasing ACN content.

Figure 14

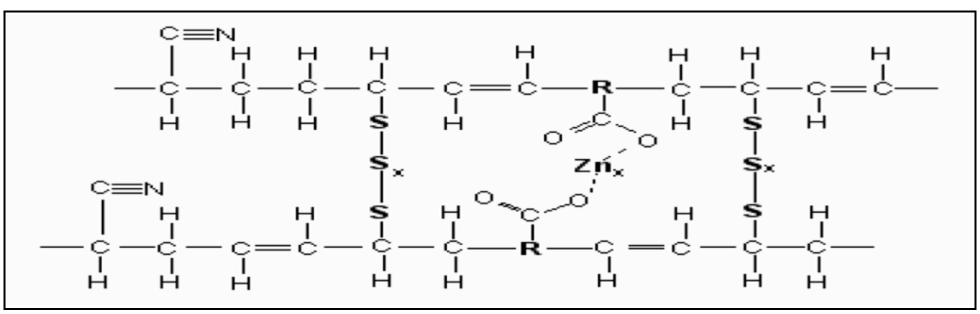


HNBR Polymer Hydrogenation and Structure

Hydrogenated Nitrile Rubber, HNBR

The third type of nitrile used is crosslinked NBR or XNBR. XNBR polymers are used in applications requiring fluid and aging resistance and excellent abrasion resistance. According to the R.T. Vanderbilt Rubber Handbook carboxylic acid groups are added to the polymer back bone which alters process and cure properties by providing a network of ionic bonds that supplement the sulfur and or carbon vulcanization bonds[5] (see Figure 15). The Tg of the XNBR increases with increasing ACN content.

Figure 15



XNBR Polymer Structure

ACN Content and Rubber Compound Properties

The % ACN of an NBR or HNBR compound can have significant effects on the end product. The rubber compounder must understand the differences that the different polymers make. A table indicating basic comparative properties is attached.

Table 14

Property	High ACN Content	Low ACN Content
Processability	Better	Worse
Cure rate with sulfur cure system	Faster	Slower
Cure rate with peroxide cure system	Slower	Faster
Oil / Fuel resistance	Better	Worse
Resilience	Lower	Higher
Hysteresis	Higher	Lower
Compatibility with polar polymers	Better	Worse
Low temperature flexibility	Worse	Better
Air / Gas impermeability	Worse	Better
Tensile	Better	Worse
Abrasion resistance	Better	Worse
Heat Aging	Better	Worse

Nitrile Elastomers Used in Studies

The polymers evaluated in this study were supplied by Zeon Chemicals. The polymers used are listed in Table 15.

Table 15

Nitrile	Type	% ACN	Mooney ML 1+4, 100°C	Cure Type
Zetpol 3301	HNBR	25	80	peroxide
Zetpol 2010	HNBR	36	85	peroxide
Zetpol 1010	HNBR	44	85	peroxide
Nipol NX775	XNBR	36	45	peroxide
Nipol 1032	NBR	33	63	Sulfur
Nipol 1051	NBR	41	68	Sulfur
Nipol DN003	NBR	50	78	Sulfur

Study Formulations

The packer seal formulations used are show in Table 16. The compounds were two pass mixed in a BR lab banbury, then sheeted out on a two roll mill. Mixing was done by Zeon Chemicals.

Table 16

Description	1 HNBR ACN 44 Mooney 85 Peroxide	3 HNBR ACN 36 Mooney 85 Peroxide	6 HNBR ACN 25 Mooney 80 Peroxide	7 XNBR ACN 26 Mooney 45 Peroxide	8 NBR ACN 50 Mooney 78 Sulfur	9 NBR ACN 41 Mooney 68 Sulfur	10 NBR ACN 33 Mooney 63 Sulfur
Elastomer Name	Zetpol 1010	Zetpol 2010	Zetpol 3310	Nipol NX775	Nipol DN003	Nipol 1051	Nipol 1032
Polymer Type	HNBR	HNBR	HNBR	XNBR	NBR	NBR	NBR
Acrylonitrile Content	44	36	25	26	50	41	33
Polymer Mooney Viscosity @ 100°C	85	85	80	45	78	68	63
Cure Type	peroxide	peroxide	peroxide	peroxide	sulfur	sulfur	sulfur
FORMULATION							
Elastomer PHR	100.00	100.00	100.00	100.00	100.00	100.00	100.00
N550 Carbon Black	85.00	85.00	85.00	40.00	60.00	60.00	60.00
N774 Carbon Black					60.00	60.00	60.00
N990 Carbon Black					40.00	40.00	40.00
Magnesium Oxide	5.00	5.00	5.00				
Zinc Oxide				5.00	5.00	5.00	5.00
Stearic Acid					1.00	1.00	1.00
4, 4'-Bis (alpha, alpha-dimethylbenzyl) diphenylamine	1.50	1.50	1.50	3.00	2.00	2.00	2.00
2-mercaptotoluimidazole	1.00	1.00	1.00				
Polyester Sebacate	10.00	10.00	10.00				
Ether/Ester Type Plasticizer				5.00	5.00	5.00	5.00
a,a,'-Bis(tert-buylperoxyy)-diisopropylbenzene Peroxide curing agen, 40% active on clay	9.00	9.00	9.00				
Dicumyl peroxide curing agent, 40% active on calcium cabonate and silica				4.00			
Spider Sulfur					0.50	0.50	0.50
2,2'-Dibenzothiazolyl disulfide, MBTS accelerator					1.00	1.00	1.00
Tetramethylthiuram disulfide, TMTD accelerator					1.00	1.00	1.00
Tetraethylthiuram disulfide, TETD acclerators					1.00	1.00	1.00
TOTAL phr	**211.50**	**211.50**	**211.50**	**157.00**	**276.50**	**276.50**	**276.50**

Testing

All compounds were tested for physical properties ASTM D-412 Shore A hardness ASTM D-2240, fluid immersion in IRM 902 ASTM D-471, tear resistance ASTM D-624, low temperature retraction ASTM D-1329, brittle point ASTM D-2137, and NACE TMO-192 rapid gas decompression. The NACE testing conditions were as are listed below:

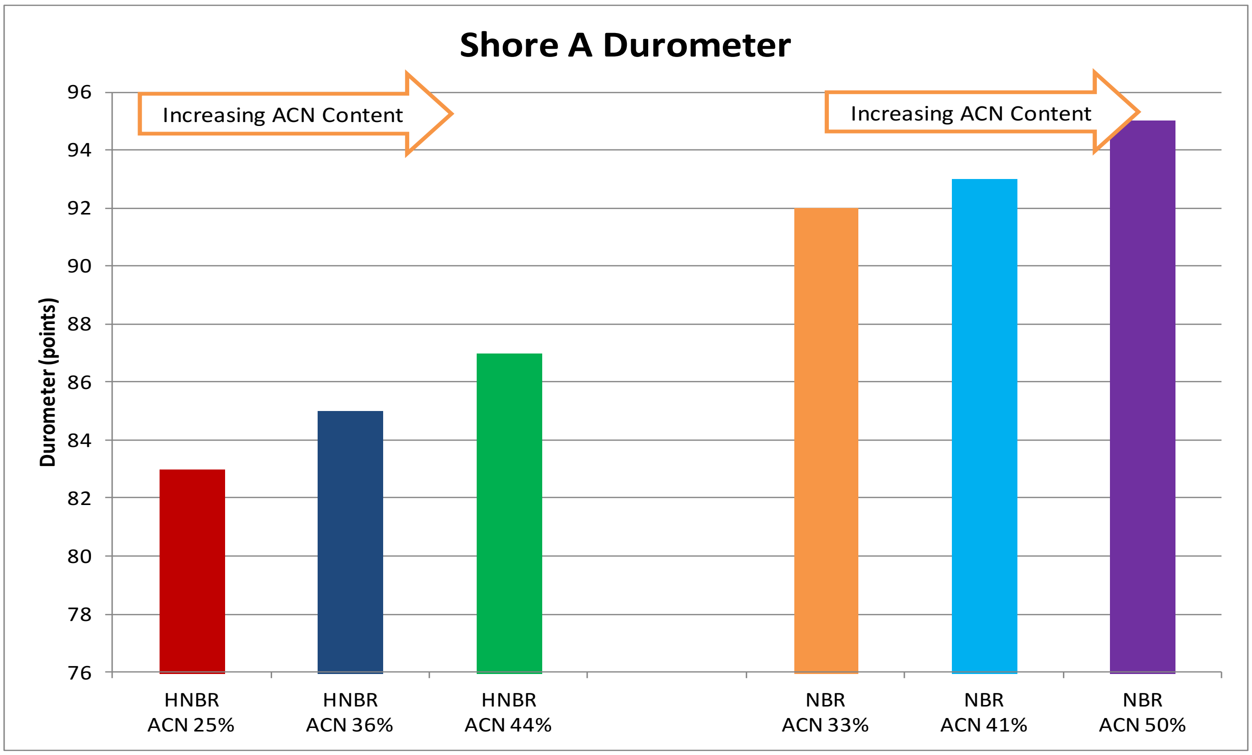
- Test Media: 100% carbon dioxide gas
- Test Pressure: 5.2 MPa
- Test Exposure Period: 24 hours
- Decompression Time: < 60 seconds

Only key test results are being presentation to keep the length of the paper reasonable.

Results - Varying ACN Content in NBR and HNBR

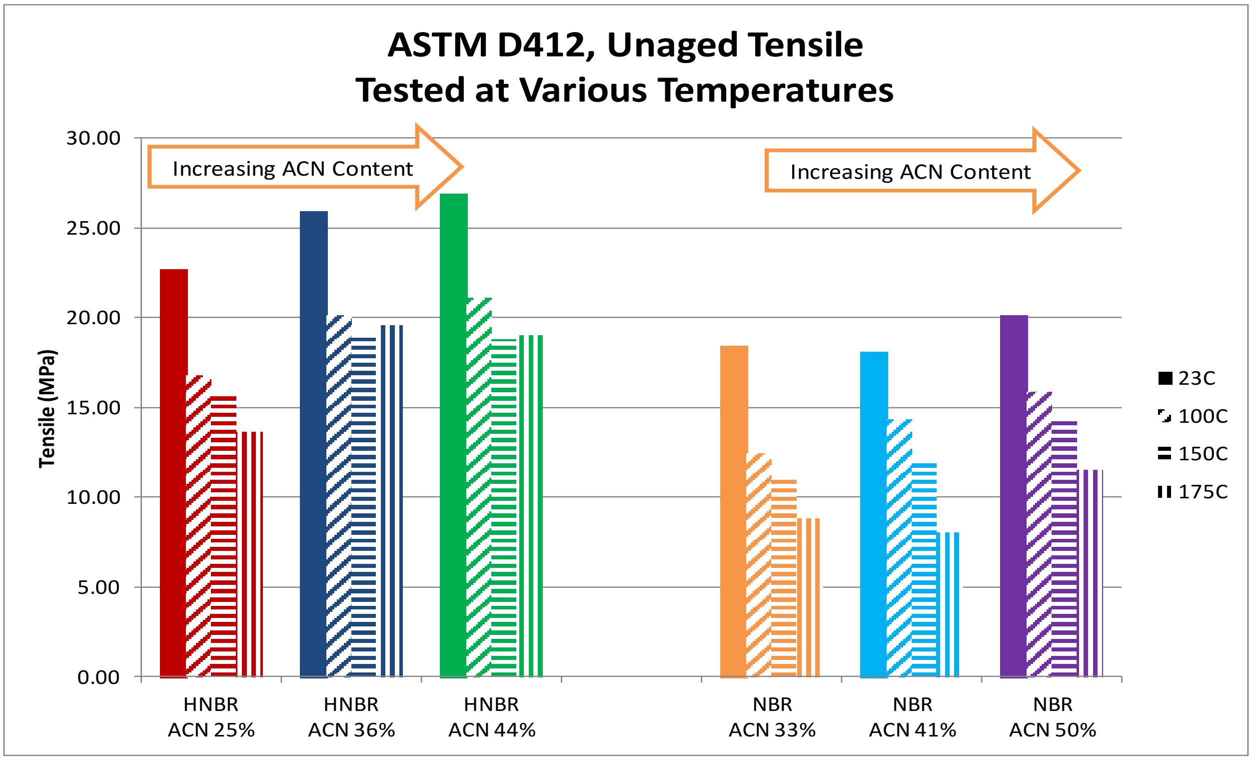
Both NBR and HNBR compounds with varying ACN contents were evaluated while keeping the other polymer properties such as raw Mooney viscosity as close as possible. It must be kept in mind that direct comparisons between NBR and HNBR are difficult because there are differences not just in polymer type but, the NBR and HNBR formulations differ in loading systems and cure systems. The design of the this study was to look at variations in ACN content within a polymer type.

Figure 16



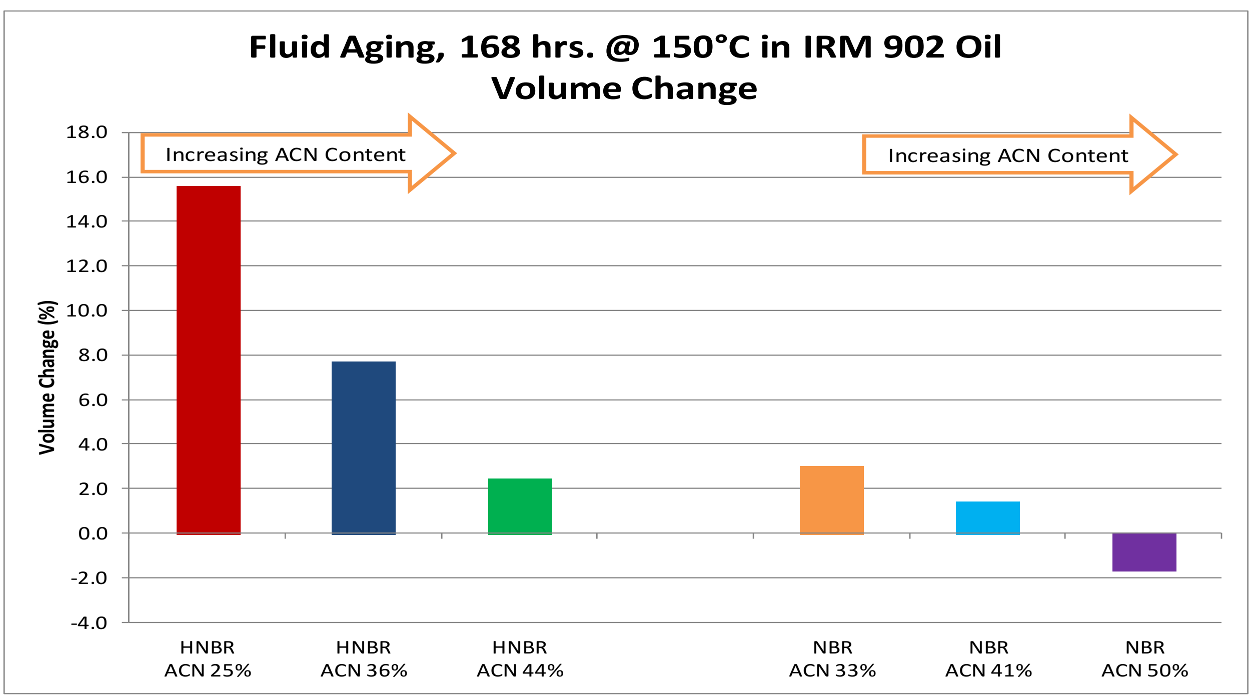
The compounds were tested for unaged durometer and results show that the higher ACN content results in higher durometer values both in the HNBR and NBR compounds.

Figure 17



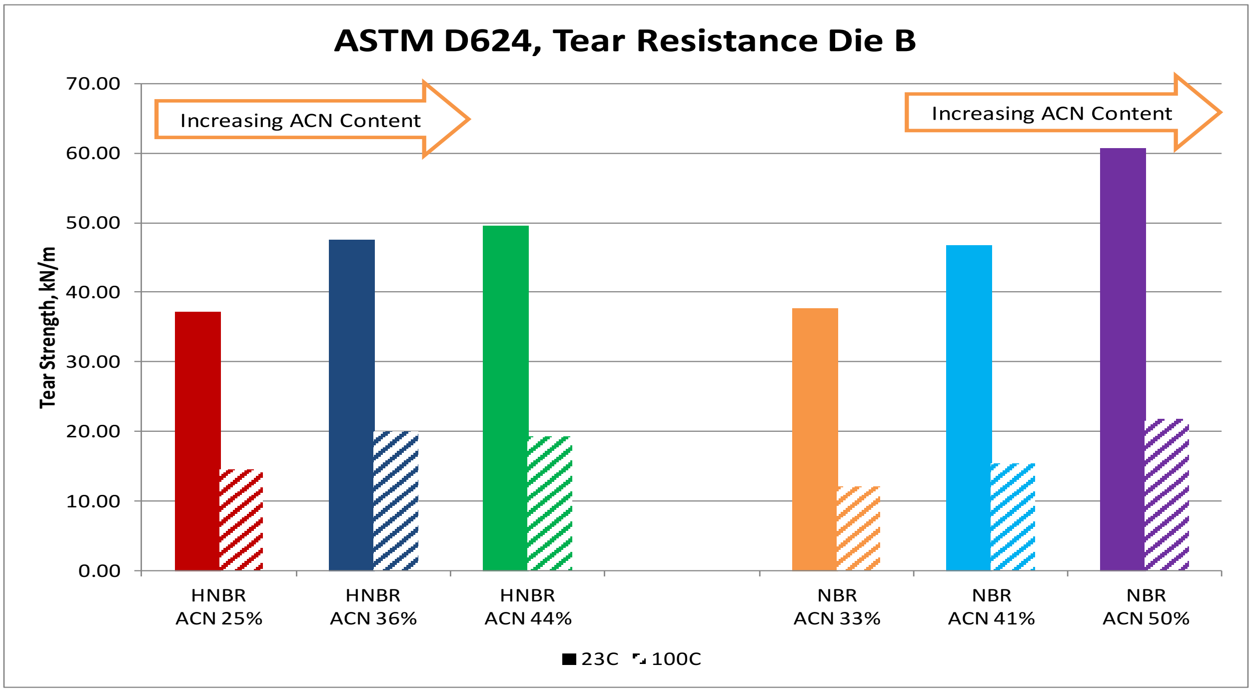
Unaged tensile properties were tested at 23, 100, 150, and 175°C. Tensile generally increases with increasing ACN content within the compound. Tensile is lower at elevated temperatures as expected.

Figure 18



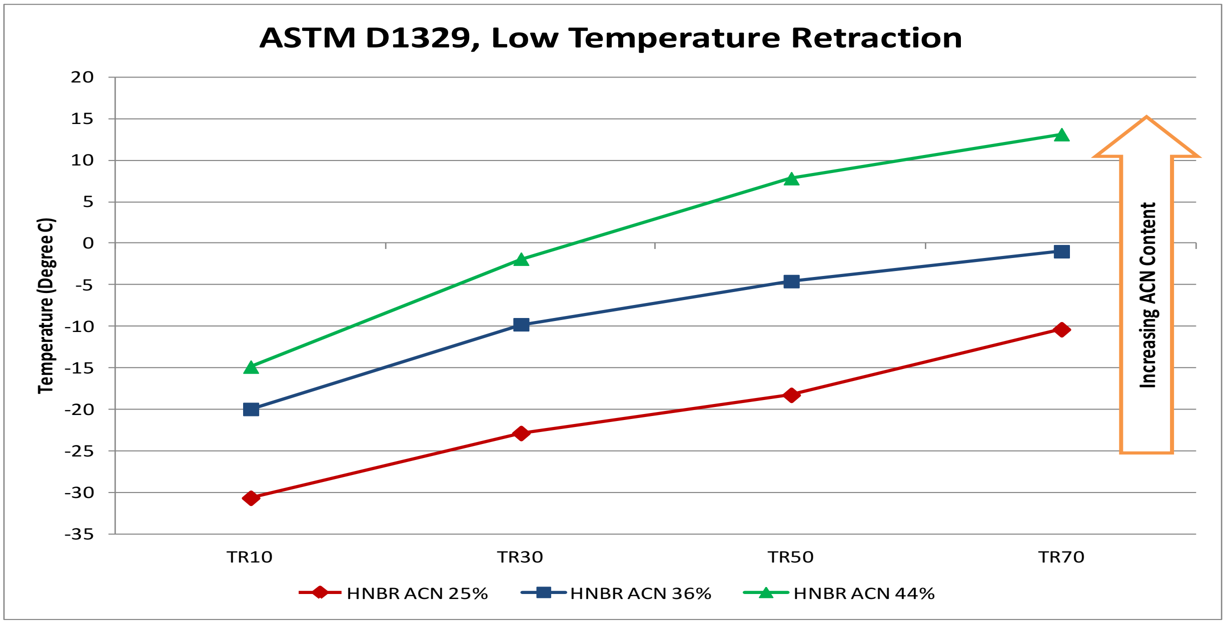
Volume change after immersion in IRM 902 oil shows less swelling with increasing ACN content in both NBR and HNBR formulations.

Figure 19



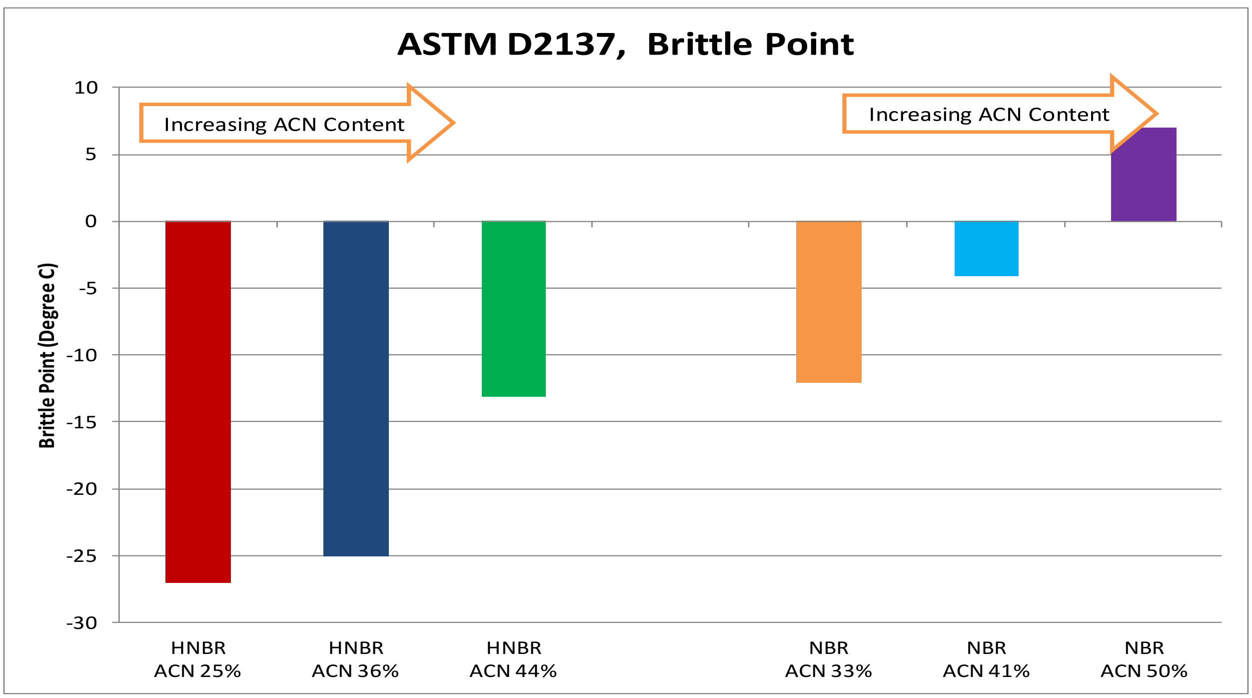
Tear resistance generally increases with increasing ACN content in both NBR and HNBR compounds.

Figure 20



Low temperature retraction is better with lower ACN content in both NBR and HNBR.

Figure 21



Brittle point increases with increasing ACN content in both HNBR and NBR formulations.

Figure 22

NBR Compounds NACE TMO-192 Rapid Gas Decompression

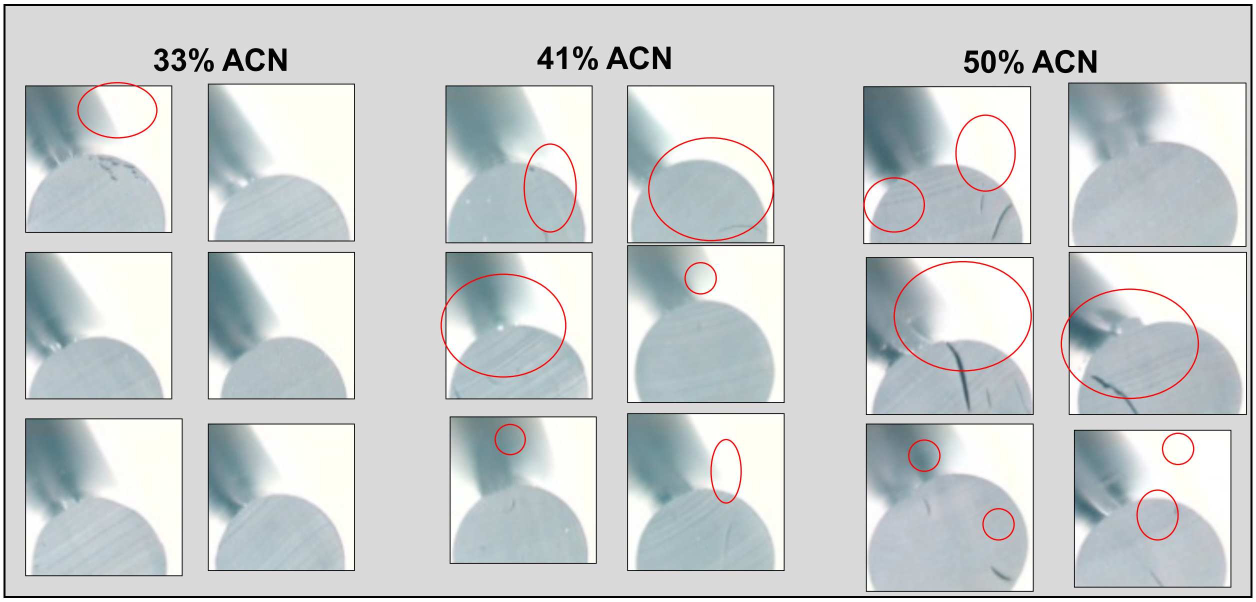
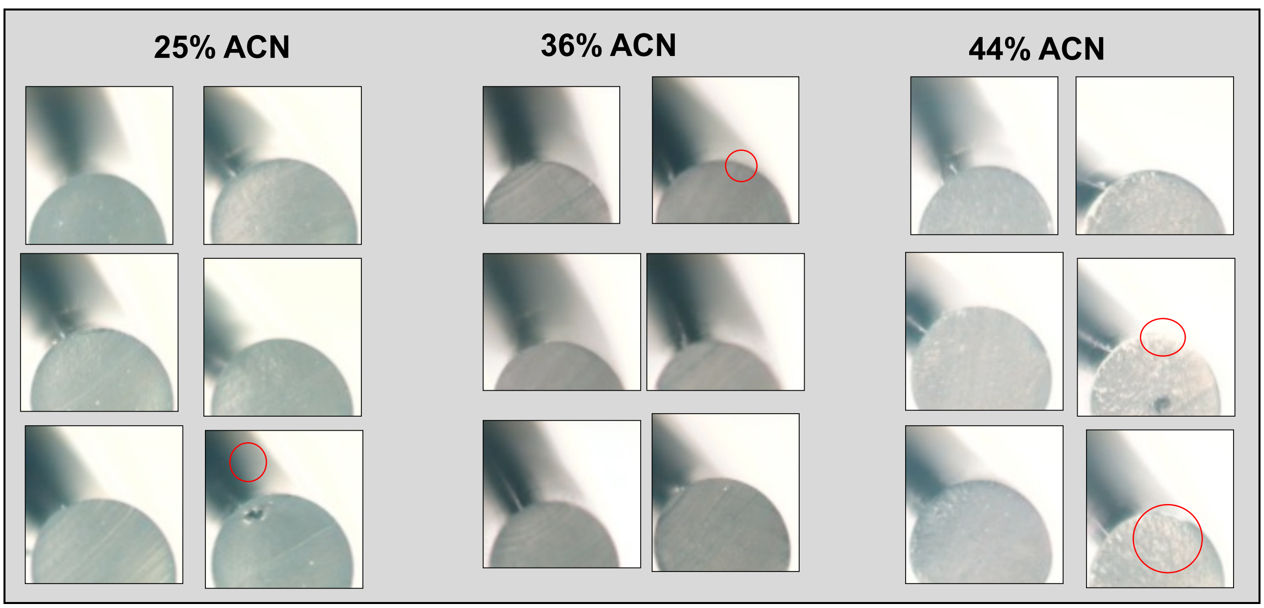


Figure 23

HNBR Compounds NACE TMO-192 Rapid Gas Decompression



In the NACE TMO-192 RGD testing more fractures are seen with higher ACN content in the NBR compound see Figures 22 and 23). Fractures are highlighted with a red circle/oval. The HNBR compounds seemed more resistance to fractures than the NBR compound but, at the highest AC content (44%) it had larger fractures than at the lower ACN contents (25 and 36%). There is conflicting reports in the literature on whether high ACN content is worse or better for rapid decompression resistance but our studies showed more fractures high ACN content nitriles than the lower ACN content nitriles. It is felt the reason for this result is that air permeability increases with higher ACN content allowing for more gas to permeate into the rubber.

Results - HNBR versus XNBR

Comparisons were made between HNBR and the XNBR compound for the following tests: heat aged 168 hrs at 125°C and 168 hrs. at 150°C per ASTM D-573, fluid immersion for 168 hrs. at 150°C in IRM 902, water, and salt water, and NACE TMO-192 rapid gas decompression (RGD) testing. Both polymers had an ACN content of 25% and were peroxide cured.

Figure 24

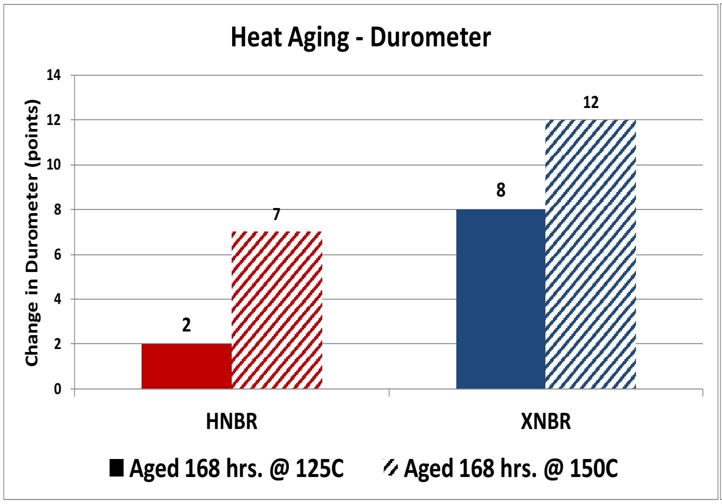


Figure 25

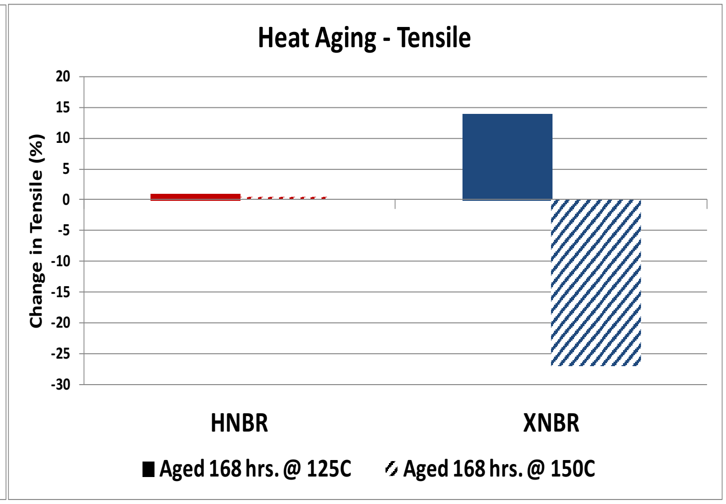


Figure 26

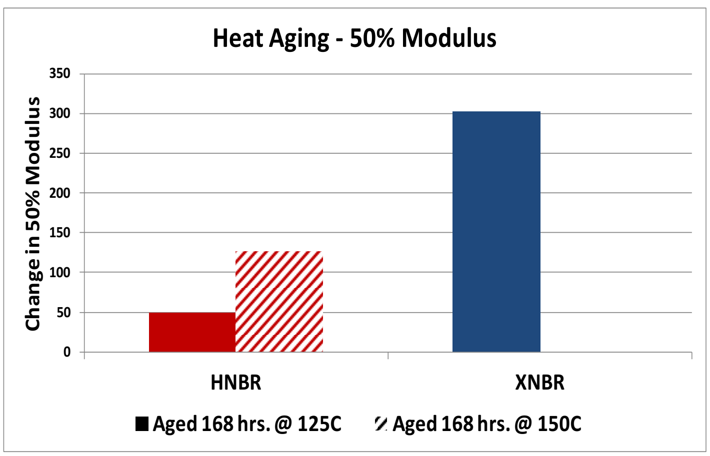
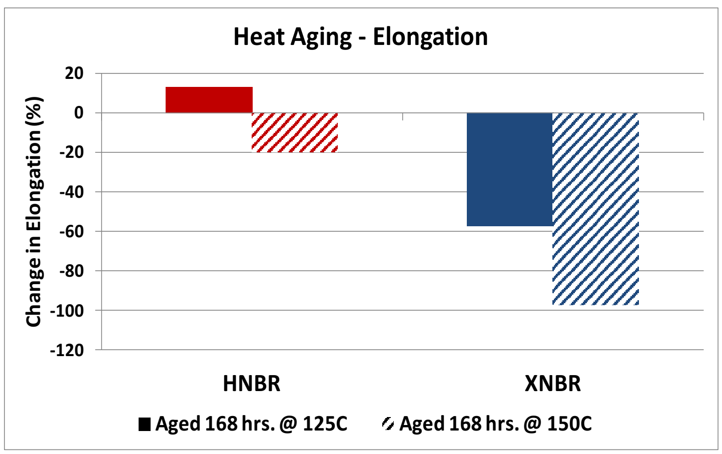


Figure 27



The HNBR compound had less change in physical properties when aged for 168 hours at both 125° and 150°C than the XNBR compound (see Figures 24 through 27).

Figure 28

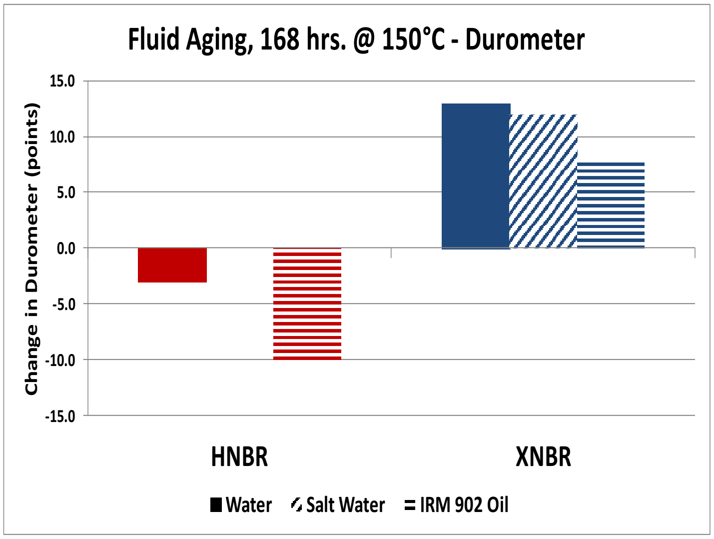


Figure 29

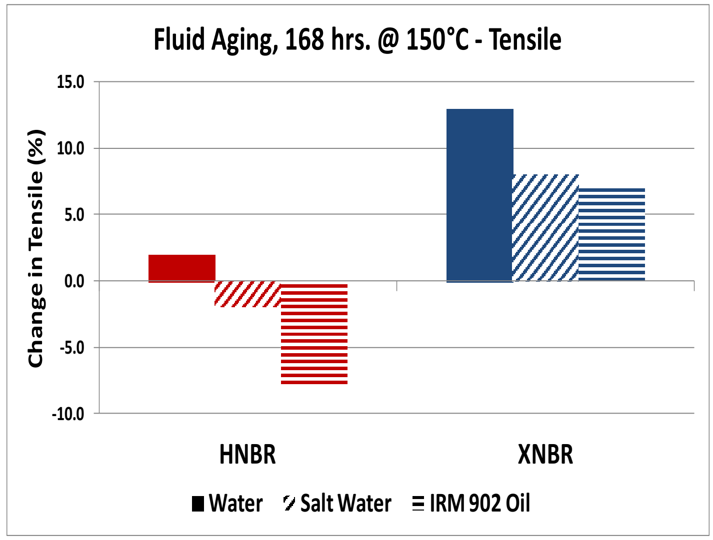


Figure 30

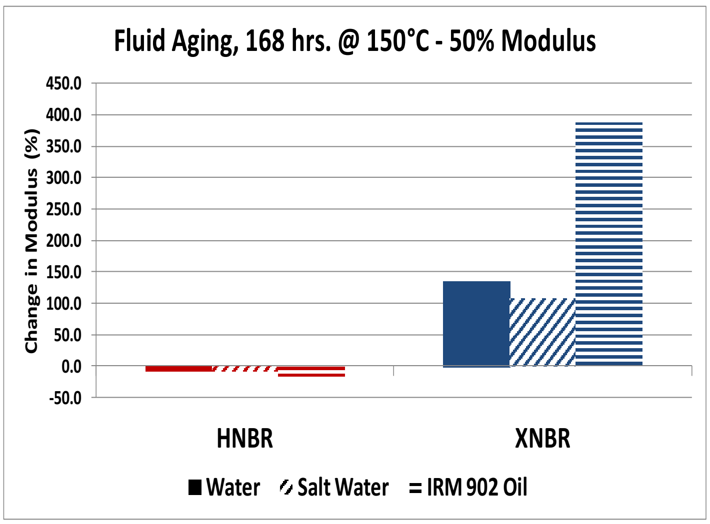
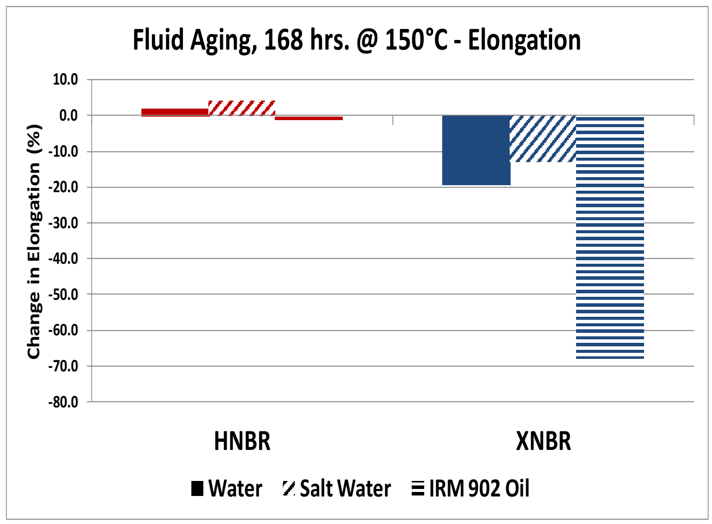
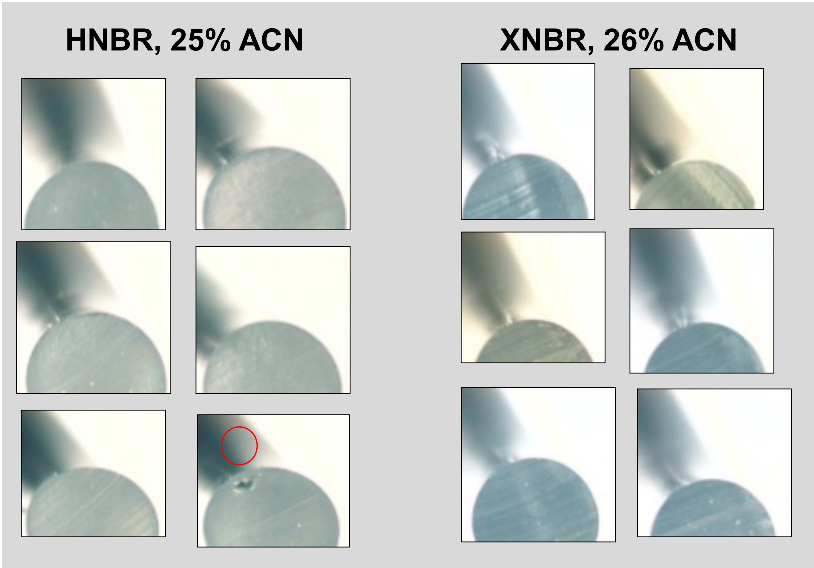


Figure 31



The HNBR compound had less change in physical properties after being immersed in IRM 902, water, and salt water for 168 hours at 150°C (see Figures 28 through 31).

Figure 32



In the NACE TMO-192 RGD testing the XNBR compound had no fractures while the HNBR had one fracture.

Discussion and Conclusions

Studies on ACN content in NBR and HNBR show similar trends to what has been reported in the literature:

- Physical strength properties such as durometer, tensile and tear resistance increase with increasing ACN content in both NBR and HNBR compounds
- Higher ACN content results in poorer low temperature properties such higher retraction and brittle point temperatures
- NACE rapid gas decompression fractures increase with increasing ACN content particularly in the NBR compounds and in the high ACN content (44%) HNBR compound

Studies comparing an HNBR compound to a XNBR compound, both peroxide cured showed that:

- The HNBR compound had better heat aged resistance
- The HNBR compound had had less change in physical properties after immersion in water, salt water and IRM 902 oil than the XNBR compound
- Both the HNBR and XNBR compounds had excellent resistance to fractures after NACE rapid gas decompression testing

There are a variety of different failure modes for oilfield applications. Recent changes in environmental policy have caused failures in established compounds that have required new formulations to be developed because the old ones cannot withstand the new synthetic based muds and additives. Complete testing including processing, unaged physical properties, heat aged properties, retention of properties after immersion in fluids the component will exposed as well as rapid gas decompression is necessary to evaluate a new compound. It is essential for the rubber compounder to understand the service conditions, test specifications, and possible failure modes of the formula they are developing.

The most common polymers used in oilfield applications are NBR, HNBR, and XNBR compounds. The ACN content can have a significant impact on the fluid immersion and low temperature properties of a compound. These are both crucial requirements in down-hole drilling applications and one may need to be sacrificed for the other depending on the application; however, a balance of both is preferred.

Acknowledgements

We want to thank Zeon Chemicals and particularly, Andy Anderson of Zeon for their help with this project. They provided all of the nitrile elastomers, did the mixing and some of the testing for this project.

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