HNBR in CO$_2$

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ABSTRACT

Nitrile rubber ("NBR") remains one of the most popular oilfield elastomers. More recently, hydrogenated nitrile rubber ("HNBR") is being accepted in its place on account of its similar "toughness" and improved stability in the presence of heat and reactive chemical species. However, carbon dioxide (a naturally occurring gas that is frequently encountered in hydrocarbon environments) presents challenges for the NBR class of polymers. Relatively small concentrations of CO_2 in hydrocarbon mixtures can cause significant seal swelling if consideration is not given to the specific choice of polymer, cure, and elastomer reinforcement. More significantly, the effect of absorbed CO_2 upon rapid gas decompression can be catastrophic if the same consideration is not applied.

This study explores the interaction of CO2 and HNBR polymers. The relationships between CO2 and acrylonitrile level is examined. This study is a continuation of work conducted and presented at RAPRA's 2012 High Performance and Specialty Elastomer symposia but with an exclusive focus on HNBR. The study's objective is to provide reference data for both the application engineer and compounder when designing for applications where CO2 will be encountered.

INTRODUCTION

Carbon Dioxide (CO_2) is a naturally occurring colorless, odorless gas. It is frequently found in hydrocarbon reserves. CO_2, in the gaseous state, is denser than air with a specific gravity of 1.98 kg/m3.

CO_2 is a linear molecule of two oxygen atoms bonded to one carbon atom through double bonds (C=O=C). The molecule is symmetrical around the carbon atom and thus has no dipole moment. However, CO_2 being a linear triatomic molecule possesses four bending modes. The molecule presents symmetrical and unsymmetrical stretch modes. The third and fourth bending modes include bending in the plane of page or perpendicular to it ("doubly degenerate"). Given the CO_2's transient dipole moments, the molecule appears bent[i] (e.g. like an H_2O molecule). Thus, the simple rule of thumb of "likes dissolves likes" is misleading if you consider CO_2 as a linear molecule.

Carbon dioxide becomes a supercritical fluid and hence a solvent at relatively modest pressures and temperatures. The requisite parameters frequently exist in the reservoir and production conditions. Carbon dioxide is only able to exist in the liquid state at pressures above 0.517 MPa (74.9 PSI). The triple point[ii] of CO_2 is about .518 MPa (75.1 PSI) at -56.6 C. The critical point[iii] is 7.375 MPa (1070.4 PSI) at 31.1 C (88 F).[iv] In the course of this study, super-critical conditions were not present.

The solvating powers of CO_2 are well documented and applications utilizing supercritical CO_2 have been established for some time now. Unfortunately for the oil & gas field operator, these very same principles are at work sabotaging elastomeric seals and the equipment they are designed to serve when CO_2 is present in the hydrocarbon stream. Modest amounts of CO_2 present in the hydrocarbon reservoir can induce failure in elastomeric seals that otherwise perform admirably in high pressure gases. Usually, the damage occurs during rapid gas depressurization ("RGD").

This study was conducted using 5 MPa (750 PSI) of pure CO_2 which could be considered moderate pressure in terms of most field conditions. However, the implications of Dalton's "Law of Partial Pressures" should be considered when viewing this data. Specifically, Dalton postulated that the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone and occupied the same volume as the mixture of gases. Under most conditions, the molar fraction of CO_2 in a hydrocarbon gas mixture is substantially smaller than the molar fraction of the other gases present (e.g. N_2, He, O_2, CH_4, C_2H_6, C_3H_8, etc.). Thus, in the context of partial pressure, the CO_2 condition in this study would exist in well pressures of several thousand

PSI where the CO_2 molar fraction is only a few percentage points. On the other hand, in a situation such as CO_2 reinjection, field results might differ substantially from those observed herein. . For a more critical discussion of the theoretical dynamics and associated references, the author directs you to the published article "Elastomers in the Hot Sour Gas Environment" by Hertz, Jr.[v]

This study was undertaken to document HNBR's interaction with CO_2. HNBR is a copolymer of acrylonitrile ("ACN") and Butadiene. Unlike NBR, the copolymer is subsequently hydrogenated to increase saturation of the butadiene component. NBR and HNBR are primarily graded by their acrylonitrile content. By varying the ratio of ACN and butadiene, different properties are obtained. How this ratio affects HNBR behavior in CO2 was the question addressed by this study.

OBJECTIVES

The first objective of this study was to offer a comparative analysis of various HNBR grades' swelling in pressurized CO_2 and swelling subsequent to rapid gas decompression ("RGD"). The enclosed data might then serve as a quick reference for determining possible swelling of HNBR compounds in reservoirs known to contain CO_2.

The second objective was to offer details that could mitigate/exacerbate the swelling of HNBR compounds subject to CO_2 either while under pressure or subsequent to RGD. Specifically, this study examined differences attributable to the amount of acrylonitrile, the amount of curative, grades of fine particle reinforcement, and the amount of fine particle black.

SCOPE

CONTROLLED FACTORS:

Elastic modulus is a primary consideration of seal design. It is also one attribute affecting an elastomer's behavior under pressure and during RGD. However, there are several factors that will ultimately define elastic modulus as well as other material attributes. An experimental array would be unwieldy if all these factors and their possible levels were all examined. For purposes of this experiment, the author chose only the most fundamental factors used to develop elastic modulus and solubility behavior of an HNBR oilfield compound. A Taguchi L_9 Orthogonal Arrays was used to study the factors and their associated levels. Specifically, the controlled factors were:
1) The Acrylonitrile content;
2) The degree of cross-linking as controlled by part-per-hundred ("phr") of curative;
3) The particle size/structure of carbon black, controlled by grade of carbon black, specifically N990, N762, and N330;
4) The loading of carbon black reinforcement, controlled by phr of carbon black.

ENVIRONMENT:

Gas composition and testing temperature, while constant, were treated as uncontrolled factors in the experiment. A pressure vessel, with a built in observation window, per Figure 1B, was flushed and charged with a connected canister of 99.9% pure CO_2 at room temperature 22.7 C (73 F) to evaluate the specimens placed within it. The configuration is schematically detailed in Figure 1A.
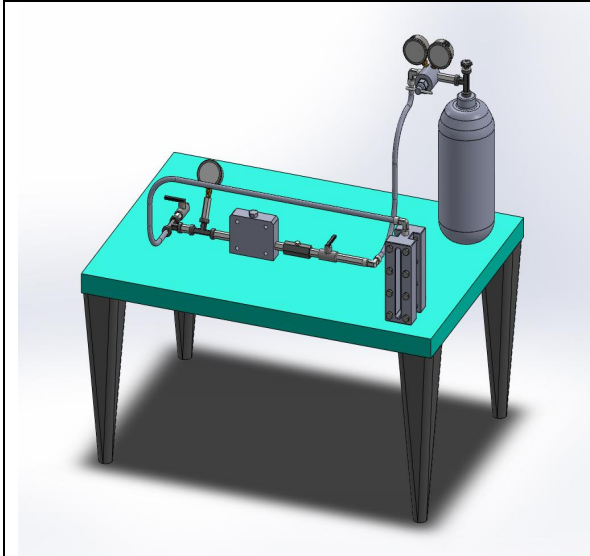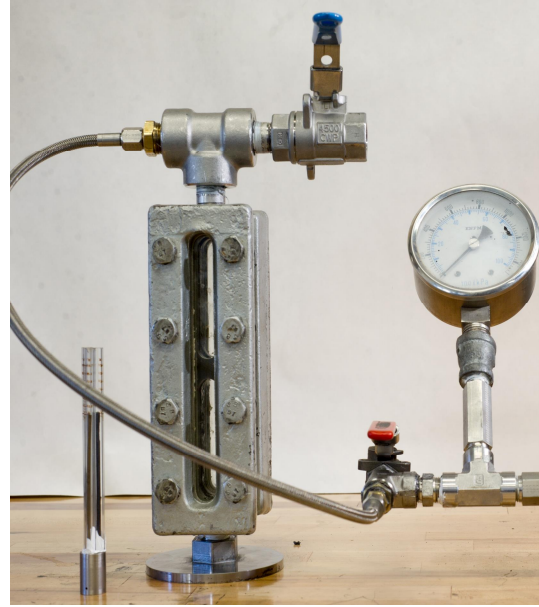
| Figure 1A . Test Fixture Configuration | Figure 1B . Observation Vessel and test vials |

ELASTOMERS:

For the rubber compounder and application engineer, HNBR polymer is normally graded on the following attributes:
1) Percentage content of acrylonitrile,
2) Degree of saturated butadiene in the backbone,
3) Mooney viscosity.

This is not an exhaustive list of attributes, but those most indicative of the materials behavior. This study focused primarily on the acrylonitrile content while attempting to hold the other attributes constant. Because the acrylonitrile content primarily defines the molecular composition of HNBR and its resistance to non-polar (e.g. hydrocarbons) and polar (e.g. water) substances, it was the primary focus of this study.

All of the HNBR compounds herein were mixed on an open 12-inch roll mill.

HNBR code	Median Percent Acrylonitrile (%)	Median Percent Saturation (%)	Median Mooney Viscosity
1010	44%	96%	85
2010	36%	96%	85
3310	25%	95%	80
4310	17%	95%	72

Table 1 ó Elastomer Test Groups and Specimens

TEST SPECIMENS:

Specimens conforming to those defined by ASTM D1460-86 (2010) Section 7.1 were utilized. The specimens were die cut from ASTM slabs and measured 100 mm (4.0 in.) in length by ~1.6 mm (0.063 in.) wide by ~ 2.0 mm (0.075 in.) thick. By so doing, the author could make reliance upon Table 1 of ASTM D1460-86 (2010) for approximating the percentage change in volume[vi].

EXPERIMENTAL

METHODOLOGY:

In Experiment 1, the acrylonitrile content was isolated while holding all other variables constant to the extent this was possible. Four experimental compounds were mixed, tested, and measured as described *infra*.

In Experiment 2, specimen formulas were designed using Orthogonal Arrays, per Taguchi, and are detailed *infra*. Orthogonal arrays are tables of numbers that allow for effective combinations of factors and levels for an experiment. This approach allowed the study of a small fraction of the possible combinations of factors (elastomer ingredients) and levels (ingredient loadings) to yield unbiased and meaningful results. Table 2 illustrates the L9 matrix used to test four (4) factors at three (3) levels.

FACTORS		LEVELS		
		1	2	3
A	POLYMER	A1	A2	A3
B	CURE PHR	B1	B2	B3
C	FILLER TYPE	C1	C2	C3
D	FILLER PHR	D1	D2	D3

Table 2 - Taguchi L_9 design of experiment

The conditions (i.e. compound formulas), numbered 1 through 9, contain no unfair biasing when Orthogonal Arrays are utilized. Table 3 illustrates the resulting conditions utilizing a Taguchi L_9 Orthogonal Array. The measured result is the percent volume change during exposure to pressurized CO2 and subsequent to RGD.

Condition	Result	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
#1	a	a			a			a			a		
#2	b	b				b			b			b	
#3	c	c					c			c			c
#4	d		d		d				d				d
#5	e		e			e				e	e		
#6	f		f				f	f				f	
#7	g			g	g					g		g	
#8	h			h		h		h					h
#9	i			i			i		i		i		
	Total	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9
	Avg	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9	#1:9

Table 3 . Taguchi L$_9$ Orthogonal Array

An L9 Orthogonal Array provides all combinations of any four factors, so that each level of each factor is combined with each level of every other factor. The L9 array contains an equal number of conditions for each factor, so each factor level is tested an equal number of times.[vii].

Taguchi pleads "dig wide, not deep". Orthogonal arrays are designed to offer an efficient approach to discover effects and indicate where more comprehensive examination may be warranted.

MEASUREMENTS:

The 100 mm long high aspect ratio (50:1) test specimens were inserted into glass tubes printed with 1 mm increments beginning at 100 mm (see Figure 2A). The glass tubes were then stood upright and sealed within the pressure vessel such that the specimens could be observed and measured against the 1 mm increments (see Figure 2B). The vessel was flushed once with CO_2 and then charged and held at 750 PSI for 24-hours ("24 Hr soak"/ "soaking period"). During the soaking period, visual observation was made of the change in linear length and the values recorded. The value after a 24-hour soaking period was used in this study. Likewise, subsequent to RGD, visual observation was made of the change in linear length and the values recorded. The value two (2) minutes after the RGD event was used in this study.
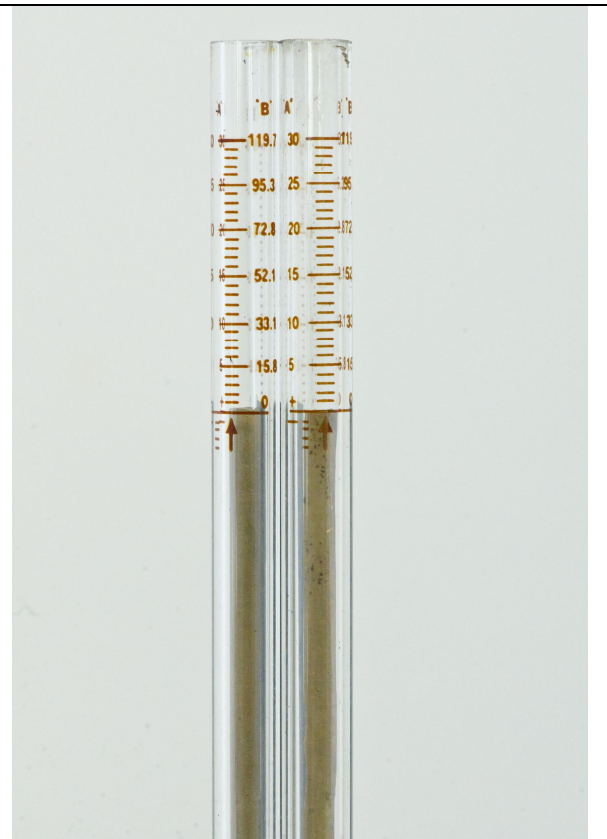

Figure 2A . Test vials

Figure 2B . Vial increments

Evaluation of the HNBR compounds was based upon the specimen's change in volume ("Δ Vol %") as set forth in Equation 3. The original specimen volume is calculated per Equation 1. Since observations are measured as "length" in millimeters, the percent change in length is calculated per Equation 2 as an intermediate step in calculating the percent change in volume. .

Eq. 1 : $Volume_{initial} = Vol_i = Length_{Initial} \times Width_{Initial} \times Depth_{initial}$

Eq. 2 : $\Delta Length \% = \Delta Len\% = (Length_{final} - Length_{initial}) / Length_{initial}$

Eq. 3 : $\Delta Vol \% = \{ [Length_I \times (1 + \Delta Len\%)] \times [Width_I \times (1 + \Delta Len\%)]$
$\times [Depth_I \times (1 + \Delta Len\%)] . Vol_i \} / Vol_i$

PROCEDURE:

Test specimens were cut and placed in the measuring tubes. Three measuring tubes at a time were placed inside a pressure vessel that was subsequently flushed with 99% CO_2. After a single flushing with CO_2, the pressure vessel was pressurized with fresh CO_2 to 750 PSI. This pressure was held for four (4) hours at room temperature. After four hours, this pressure was released through a regulator over a two minute period (350 PSI/minute). Upon reaching ambient pressure, the time was marked and measurements were made after 2 minutes, 10 minutes, 30 minutes, 1 hour, and 2 hours.

EXPERIMENT 1 - EFFECT OF ACRYLONITRILE IN A MARGINALLY REINFORCED HNBR WHEN IMMERSED IN CO2.

The first objective was to isolate the acrylonitrile content of HNBR and study its behavior when subject to CO_2. Four grades of HNBR polymer of similar saturation (95% . 96%) and viscosity (72 . 85 mooney) were examined. Several criteria were used to determine the test formulas: 1) minimize the number of ingredients, 2) achieve a state-of-cure that would merely facilitate preparing the samples, and 3) minimize the interaction of carbon-black and polymer.

The effect that different reinforcing particle sizes have upon swelling in high pressure gas relative to other particle sizes has been previously reported by Hertz[viii]. N990 was settled upon since it is the largest particle size with the least amount of elastomer reinforcement. It was determined that this particle size and a moderate loading would minimize polymer-to-filler interaction and allow better observation of the polymer's behavior. The change in volume of the first trial specimens, subsequent to RGD, exceeded the measuring apparatus. Thus, in this experiment, an additional trial used specimen lengths of 80 mm so that their substantial change in volume could be accurately measured.

The polymers, filler, and cure system were mixed on an open roll 12 inch mill. The formulas used to study the effect of acrylonitrile content in CO_2 are listed in Table 4. Stress-strain data for these compounds was calculated using ASTM D412 Test Method "A" and compiled in Table 4a. Normalizing the formulas' modulus was not only impractical given the differences in acrylonitrile content, but unnecessary since there is no correlation between volume change of the specimens and their measured modulus.

TEST FORMULAS:

44% acn		36% acn		25% acn		17% acn	
Ingredient	Phr	Ingredient	Phr	Ingredient	Phr	Ingredient	phr
Zetpol 2010	100	Zetpol 2010	100	Zetpol 3310	100	Zetpol 4310	100
Zinc Oxide	5	Zinc Oxide	5	Zinc Oxide	5	Zinc Oxide	5
Peroxide	5	Peroxide	5	Peroxide	5	Peroxide	5
N990 black	30	N990 black	30	N990 black	30	N990 black	30

Table 4 . Peroxide cured, 95-96% saturated HNBR polymers

ASTM D412 Test Method A - RESULTS:

HNBR Code	ACN%	M25	M50	M100	M300
HNBR-1010	44%	146 psi	175 psi	213 psi	688 psi
HNBR-2010	36%	136 psi	161 psi	190 psi	625 psi
HNBR-3310	25%	106 psi	130 psi	171 psi	746 psi
HNBR-4310	19%	100 psi	132 psi	211 psi	994 psi

Table 4a . ASTM D412 Test Method A data

RESULTS AND DISCUSSION:

The swelling of elastomers under pressure in CO_2 are merely a prelude to future behavior. A significantly different story emerges subsequent to rapid gas decompression ("RGD"). Release of the hydrostatic load on the materials' surface allows the absorbed gas to expand causing significant swelling. Over a brief amount of time, however, the gas diffuses from the elastomers allowing them to return to their initial geometry. Figure 4 illustrates swelling under pressurized CO_2 and subsequent to RGD. Assuming elastomers to be isotropic materials, the % linear change in the test specimens reflects approximately a 3X change in volume. The changes in volume attributable to CO_2 absorption presumably precede seal failure modes.

Previous work by Hertz III found that EPDM swelled slightly less than HNBR under pressurized CO2. However, upon RGD, the EPDM swelled slightly more than HNBR but degassed more quickly and returned to normal size more quickly[ix]. This past observation is relevant to the current study. In a limited sense, an HNBR with 19% acrylonitrile content is more similar to an EPDM than an HNBR grade with higher ACN content.

In this study, the amount of ACN content had minimal effect on swelling in CO2 under pressure during the first 4 hours (240 minutes). The measured differences attributable to ACN content are mixed. Likewise, during the first 10 minutes of an RGD event, the relationship of ACN to swelling was mixed. However, shortly thereafter, the less ACN content there was in the HNBR the more quickly the compound released CO2.

The implications of the post RGD observation may be complicated for the seal engineer. Upon an RGD event, the question becomes at which point in time does the elastomer compound suffer mechanical damage?

The results of this experiment are recorded in Table 5 and depicted graphically in Figure 4.

Elastomers	4 hours 750 PSI	2 minutes post RGD	10 minutes post RGD	30 minutes Post RGD	60 minutes Post RGD	120 minutes Post RGD
HNBR 44% ACN	16%	139%	255%	264%	255%	229%
HNBR 36% ACN	13%	133%	221%	205%	153%	73%
HNBR 25% ACN	13%	272%	300%	167%	33%	8%
HNBR 19% ACN	16%	205%	264%	120%	12%	0%

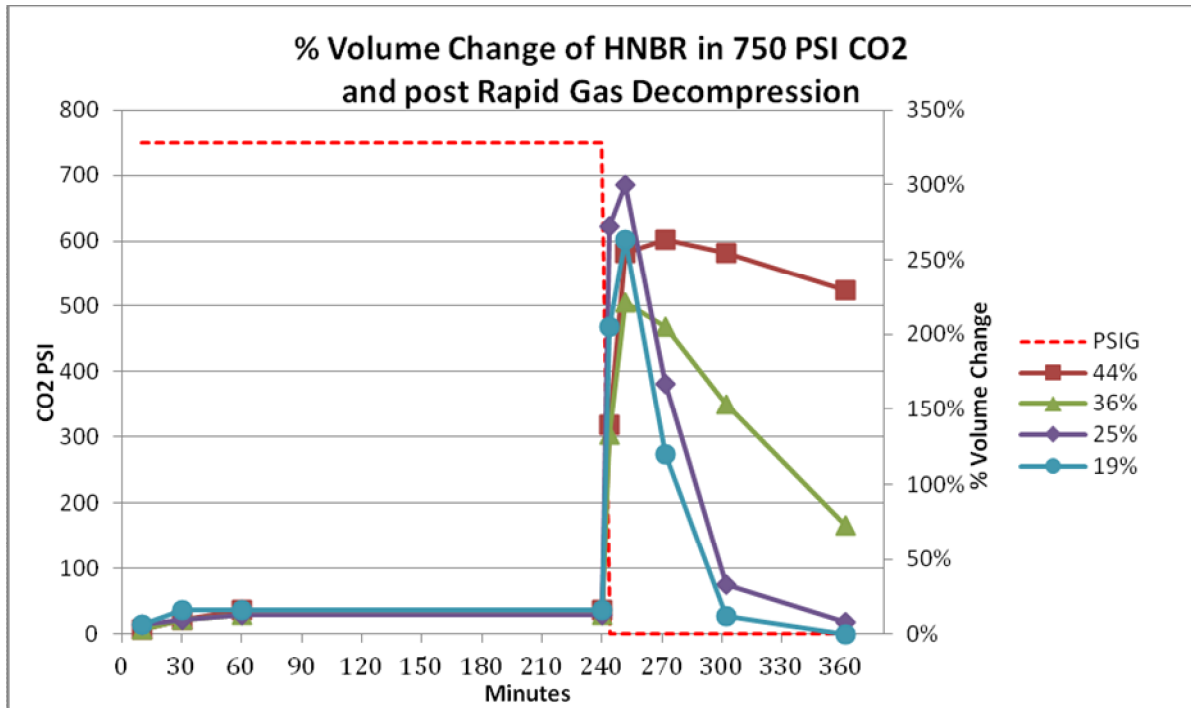Table 5 . HNBR % change in volume in CO2 under pressure and subsequent to RGD.

Figure 4 . Chronologic plot of HNBR swelling under pressure and subsequent to RGD

EXPERIMENT 2 - EFFECT OF ACRYLONITRILE, CURE, AND REINFORCEMENT ON HNBR WHEN IMMERSED IN CO2.

The objective of Experiment 2 was to study the effects of CO2 on compositions of varying acrylonitrile content, different grades of particle black (%carbon black+), different loadings of carbon black, and different levels of cure. Evaluation was conducted using a Taguchi L_9 Orthogonal Array. The test matrix is documented in Table 6. Zinc oxide loading (5 phr) was constant and uncontrolled in this study. The percent saturation of these polymers ranged from 95 to 96%.

		LEVELS		
FACTORS		1	2	3
A	POLYMER	36% ACN	25% ACN	19% ACN
B	CURE PHR	4	5	6
C	FILLER TYPE	N330	N762	N990
D	FILLER PHR	30	50	70
uncontrolled	ZnO	5	5	5

Table 6 . Factors and associated levels for HNBR study

The test matrix in Table 6 results in the Taguchi L_9 Orthogonal Array depicted in Table 7. The results of this testing are found in Tables 8 and 9.

Condition	Polymer	Cure PHR	Filler type	Filler PHR	4hr soak % Vol Δ	Post RGD % Vol Δ
#1	36% ACN (A1)	4 (B1)	N330 (C1)	30 (D1)	9%	186%
#2	36% ACN (A1)	5 (B2)	N762 (C2)	50 (D2)	12%	110%
#3	36% ACN (A1)	6 (B3)	N990 (C3)	70 (D3)	9%	60%
#4	25% ACN (A2)	4 (B1)	N762 (C2)	70 (D3)	19%	238%
#5	25% ACN (A2)	5 (B2)	N990 (C3)	30 (D1)	12%	186%
#6	25% ACN (A2)	6 (B3)	N330 (C1)	50 (D2)	12%	52%
#7	19% ACN (A3)	4 (B1)	N990 (C3)	50 (D2)	16%	186%
#8	19% ACN (A3)	5 (B2)	N330 (C1)	70 (D3)	12%	40%
#9	19% ACN (A3)	6 (B3)	N762 (C2)	30 (D1)	9%	82%

Table 7 . Taguchi L_9 Orthogonal Array for HNBR study

Volume Change after 4 hour soak in 750 PSI CO2 at room temperature

	36% A1	25% A2	19% A3	4phr cure B1	5phr cure B2	6phr cure B3	N330 C1	N762 C2	N990 C3	30phr black D1	50phr black D2	70phr black D3
#1	9%			9%			9%			9%		
#2	12%				12%			12%			12%	
#3	9%					9%			9%			9%
#4		19%		19%				19%				19%
#5		12%			12%				12%	12%		
#6		12%				12%	12%				12%	
#7			16%	16%					16%		16%	
#8			12%		12%		12%					12%
#9			9%			9%		9%		9%		
Total	0.31	0.44	0.38	0.44	0.37	0.31	0.34	0.41	0.38	0.31	0.41	0.41
Avg	0.10	0.15	0.13	0.15	0.12	0.10	0.11	0.14	0.13	0.10	0.14	0.14

Table 8 - % Volume Change after 4 hour soak in 750 PSI CO2

Volume Change subsequent to RGD

	36% A1	25% A2	19% A3	4phr cure B1	5phr cure B2	6phr cure B3	N330 C1	N762 C2	N990 C3	30phr black D1	50phr black D2	70 phr black D3
#1	186%			186%			186%			186%		
#2	110%				110%			110%			110%	
#3	60%					60%			60%			60%
#4		287%		287%				287%				287%
#5		186%			186%				186%	186%		
#6		52%				52%	52%				52%	
#7			261%	261%					261%		261%	
#8			40%		40%		40%					40%
#9			82%			82%		82%		82%		
Total	3.56	5.25	3.83	7.34	3.37	1.94	2.79	4.78	5.07	4.54	4.22	3.88
Avg	1.19	1.75	1.28	2.45	1.12	0.65	0.93	1.59	1.69	1.51	1.41	1.29

Table 9 - % Maximum Volume Change subsequent to RGD

RESULTS AND DISCUSSION:

The swelling of HNBR compounds in CO2 under pressure is appreciable. A range of volume increases from 9% to 19% was observed. However, upon RGD, the amount of swelling in HNBR is substantial. Ranges of 40% to 238% were observed. Nevertheless, the reader should not simply conclude that HNBR is unsuitable for CO2. These test compounds were designed to provide guidance rather than optimal solutions.

Clearly, CO2 contra-indicates the use of HNBR in applications where the gas is present in appreciable quantities. However, the seal engineer frequently finds the other merits of HNBR to require its use in spite of this particular shortcoming.

The data clearly indicated that crosslink density, which is a function of the amount of curative (and the HNBR grades degree of saturation) had the greatest impact on swelling subsequent to RGD. For this very reason, an attempt was made to test materials possessing a similar degree of saturation. A reduction in saturation would allow for a higher crosslink density.

It was further apparent that smaller particle size carbon black also mitigated swelling. N330 carbon black is comprised of particles measuring 28 to 36 nm. N762 particles measure 60 to 100 nm while N990 particles measure 250 to 350 nm. A smaller particle size presents greater surface area per unit of weight and hence more reinforcement.

Higher loadings of carbon black demonstrate diminishing returns on mitigating swelling. The experienced rubber compounder knows that these relationships will likely cause problems in achieving other material attributes when designing an HNBR compound.
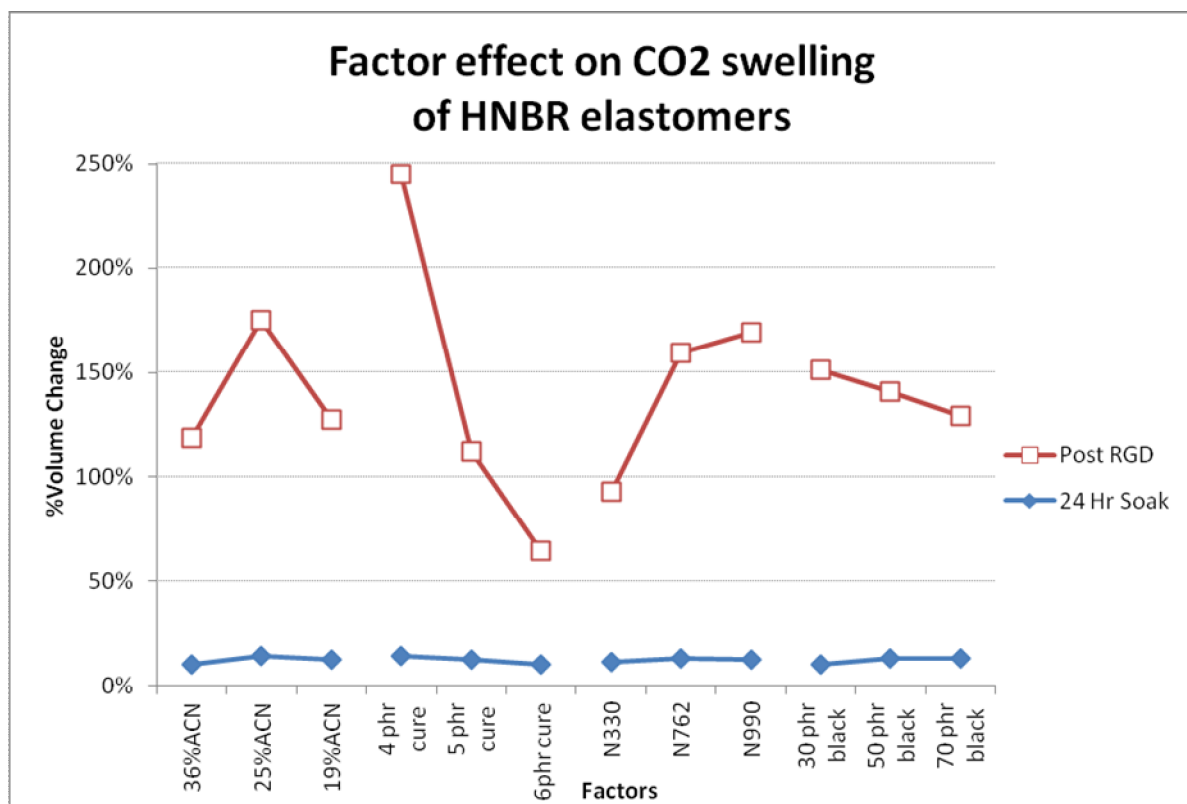

Figure 8- Factor/Level effects on HNBR compound swelling in CO2.

SOURCES OF ERROR

Changes in specimen length were recorded by visual examination. As such, a significant source of error could be introduced. A one (1) millimeter error in reading the specimen length translates to roughly a $3mm^3$ error in volume. In evaluating data, the reader may want to consider volume change within a range rather than as a single point.

All mixing of test batches was conducted on open roll mills, subject to loss of ingredients during the mixing process or marginal errors during ingredient weigh up. Test batch weigh-up was conducted on industrial scales with ±0.1 gram accuracy. Test compounds were mixed using 500

grams of polymer. With curatives weighed as low as 4 phr (25 grams per batch), a 0.5 gram error would amount to a 2% deviation from the test formula.

CO_2 Pressure was regulated for the 750 PSI soak. Depressurization was also regulated to 375 PSI/minute. Volume changes were rapid within the first 10 minutes of RGD and a simultaneous read of all three samples was not practical. Thus, it is reasonable to assume a specimen length tolerance of ±1mm for the post RGD data.

SUMMARY

This study utilized "Design of Experiments" to reveal significant relationships with an HNBR compound that affect its interaction with CO2. No attempt was made to optimize these compounds. Percent saturation of the HNBR, while mostly similar amongst the test compounds, was uncontrolled.

1) The predominant factor in reduction of CO2 induced swelling subsequent to RGD is the amount of curative utilized.

2) The acrylonitrile content in HNBR is inconsequential to swelling in CO2 while the material is under pressure. On the other hand, the acrylonitrile content of HNBR is a significant determinant of the propensity to swell subsequent to an RGD event. While other factors may predominate in determining the maximum swell of HNBR immediately subsequent to RGD, the rate of degassing clearly increases as the amount of acrylonitrile decreases.

3) Smaller carbon black particle sizes mitigate swelling subsequent to an RGD event. Likewise, increasing the loading of carbon black appears to mitigate swelling but with diminishing returns as loading increases.

ACKNOWLEDGEMENTS

TRADEMARKS

Zetpol® is the registered trademark of Zeon Chemicals

[i] Knox, J.H., "Molecular Thermodynamics", p129-130, John Wiley & Sons (Rev.Ed. 1978)

[ii] The temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium.

[iii] The state of fluid in which the fluid and gas both have the same density.

[iv] Lide, David R.,CRC, "Handbook of Chemistry and Physics", p.6-54 (77th Ed.1996).

[v] Hertz, Jr., D.L., "Elastomers in the Hot Sour gas Environment", Elastomerics (Sept 1986).

[vi] The ASTM table simply calculates percent volume change as the difference between initial calculated volume and final calculated volume divided by the initial volume. The final volume assumes an isotropic material response such that percent change in length will be the same across all three dimensions.

[vii] "Taguchi Approach to Quality Optimization Series", Technicomp,Inc., Cleveland, OH, p 2-2, (4th Printing, 1988).

[viii] Hertz, Jr., D.L., "Sealing Technology", Rubber Products Manufacturing Technology, p.786, Marcel Dekker, Inc. (1994).

[ix] Hertz III, D.L., "Elastomers in CO2", High Performance Elastomers & Polymers for Oil & Gas 2012, Int'l Conference, Aberdeen, SCO, UK (April 2012)