Elastomers in CO_2

Presented at the
High Performance Elastomers & Polymers for Oil & Gas 2012
International Conference
Aberdeen, SCO, UK
20-21st April, 2012

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ABSTRACT

Carbon dioxide is a naturally occurring gas that is frequently encountered in hydrocarbon environments. The CO_2 molecule has unique characteristics causing popular oilfield elastomers to swell when in contact with it. Relatively small concentrations of CO_2 in hydrocarbon mixtures can cause significant seal swelling. More significantly, the effect of absorbed CO_2 upon rapid gas decompression can be catastrophic if consideration is not given to the choice of polymer, cure, and particle reinforcement.

This study utilized Taguchi's approach to experimental design that studied the effect of cure system and particle black reinforcement upon an elastomeric compound's swelling in CO_2. The elastomeric compounds studied included HNBR, EPDM, FKM Type I, FKM Type II, FKM Type III, FEPM (TFE/P), and FEPM (TFE/E/PMVE). Amine curatives in the FKM class materials were studied. Peroxide loading in the FEPM, FKM Type III and hydrocarbon elastomers was studied. Finally, particle black grades (N990, N550, and N330) and their respective loadings were studied.

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.

This study was an undertaking to document the *WHEREFORES* of elastomers' interaction with CO_2 rather than the *WHY* elastomers' interact with CO_2. 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]

OBJECTIVES

The first objective of this study is to offer a comparative analysis of elastomers' swelling in CO_2. The enclosed data might then serve as a quick reference for determining possible swelling of the referenced elastomers in reservoirs known to contain CO_2.

The second objective is to offer a comparative analysis of elastomers' swelling behavior subsequent to rapid gas decompression ("RGD") after soaking in CO_2.

The final objective is to offer details that will mitigate/exacerbate the swelling of elastomer compounds subject to CO_2 either while under pressure or subsequent to RGD. Specifically, differences attributable to the amount of cure, grades of fine particle reinforcement, and amounts of fine particle black have been examined for each of the subject elastomers.

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 causal factors that will ultimately define elastic modulus. 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 in an oilfield compound. Taguchi L_4 and L_9 Orthogonal Arrays were used to study factors and associated levels. Specifically, the controlled factors were:

1) The choice of polymer;
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, N550, and N330;
4) The level 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.

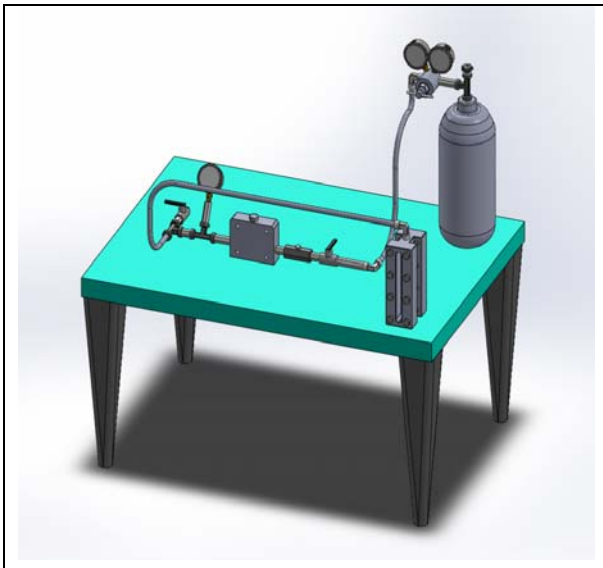

Figure 1A – Test Fixture Configuration

Figure 1B – Observation Vessel and test vials

ELASTOMERS:

The following popular oilfield elastomers included in this study are found in Table 1. Polymers were studied in three experimental groups as determined by their molecular structure and/or cure system:

1) Peroxide cured hydrocarbon polymers, both non-polar and polar,
2) Amine cured FKM class fluoroelastomers (Types 1 & 2),
3) Peroxide cured fluoroelastomers utilizing a triallyl-isocyanurate (“TAIC”) coagent, also referred to as “peroxy-TAIC” cured polymers.

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

Since the primary objective was a comparative analysis of elastomers, the experiment design used elastomers as a controlled factor. Obviously an effort was made to group similar elastomers. Any future study whose purpose is product improvement should treat a specific polymer structure as an uncontrolled factor except in instances where grades of a specific polymer type are being examined.

(Experiment #) Test Group	D1418 Designation	Trade name	Specific gravity
(#1) Hydrocarbon	HNBR	Zetpol® 2010	1.10
(#1) Hydrocarbon	EPDM	Royalene® 575	0.86
(#2) FKM Amine cure	FKM Type 1	Viton® A	1.80
(#2) FKM Amine cure	FKM Type 2	Viton® B	1.81
(#3) Peroxy-TAIC cure	FKM Type 3	Technoflon® PL 855	1.78
(#3) Peroxy-TAIC cure	FEPM	Aflas® 100H	1.55
(#3) Peroxy-TAIC cure	FEPM	Viton® ETP 600S	1.83

Table 1 – 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:

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 L_4 matrix used to test three (3) factors at two (2) levels.

	LEVEL	
FACTOR	**1**	**2**
A	A1	A2
B	B1	B2
C	C1	C2

Table 2 – Taguchi L_4 design of experiment

The resulting conditions (formulas) contain no unfair biasing when Orthogonal Arrays are utilized. Table 3 illustrates the resulting conditions utilizing a Taguchi L_4 Orthogonal Array.

Factor:		A	B	C	Results	A1	A2	B1	B2	C1	C2
Condition	#1	A1	B1	C1	w	w		w		w	
	#2	A1	B2	C2	x	x			x		x
	#3	A2	B1	C2	y		y	y			y
	#4	A2	B2	C1	z		z		z	z	
					Total	∑ #1, #2	∑ #3, #4	∑ #1, #3	∑ #2, #4	∑ #1, #4	∑ #2, #3
					Average	X #1, #2	X #3, #4	X #1, #3	X #2, #4	X #1, #4	X #2, #3

Table 3 – Taguchi L_4 Orthogonal Array

Orthogonal Arrays provide all combinations of any two factors, so that each level of each factor is combined with each level of every other factor. The arrays contain 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 twice 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.

Evaluation was primarily based upon the change in length dimension per Equation 2. Analysis and discussion are based upon the corresponding calculated percent change in volume (“Δ Vol %”) of the specimen per Equation 3.

Eq.1 : $\text{Volume}_{\text{initial}} = \text{Vol}_i = \text{Length}_{\text{Initial}} \times \text{Width}_{\text{Initial}} \times \text{Depth}_{\text{initial}}$

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

Eq. 3 : $\Delta\ \text{Vol}\ \% = \{\ [\text{Length}_I \times (1 + \Delta\text{Len}\%)] \times [\text{Width}_I \times (1 + \Delta\text{Len}\%)] \times [\text{Depth}_I \times (1 + \Delta\text{Len}\%)] - \text{Vol}_i\ \} / \text{Vol}_i$

Elastic modulus of the sample materials was obtained using DMRT (ARES) operating at the same room temperature, 0.1 Hz, 0.5 % strain.

Figure 2A – Test vials

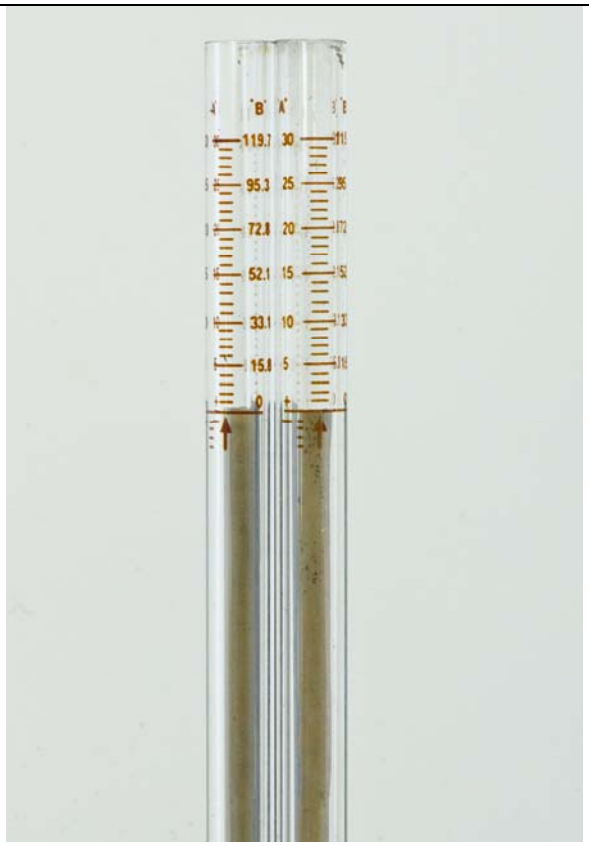

Figure 2B – Vial increments

CURED GUM POLYMER, NON-REINFORCED

Commercially available fluoroelastomer and hydrocarbon class polymers were selected based upon their acceptance and perception as high performance polymers in the oilfield. HNBR was selected over NBR since it is perceived as a high performance polymer and differs only in backbone saturation.

Reinforcing fillers were omitted during the examination of cured gum polymer swelling in CO_2. In subsequent experiments different grades of particle black ("carbon black") were incorporated. Specific gravity of the polymers is noted in Table1 should the reader want to consider differences in weight to volume when comparing volume swell of the different reinforced polymers. 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].

First, an evaluation of non-reinforced polymers was undertaken. The polymers and their respective cure systems were mixed on an open roll 12 inch mill. The formulas for non-reinforced, cured gum polymers are tabulated below in Tables 4 through 6.

TEST FORMULAS:

GROUP 1 - Hydrocarbon Elastomers, peroxide cured

HNBR		**EPDM**	
Ingredient	PHR	Ingredient	PHR
Zetpol® 2010	100	Royalene® 575	100
Peroxide	6	Peroxide	5

Table 4 – Peroxide cured hydrocarbon gum polymers

GROUP 2 – FKM Class polymers, Amine-BPAF cured

FKM Type 1		**FKM Type 2**	
Ingredient	PHR	Ingredient	PHR
Viton® A	100	Viton® B	100
Diak® 1	2	Diak® 3	3
MgO	15	MgO	15

Table 5 – Amine cured FKM class gum polymers

GROUP 3 – Fluoroelastomers, peroxide-TAIC cured

FEPM (TFE/P)		**FEPM (TFE/E/PMVE)**		**FKM Type 3**	
Ingredient	PHR	Ingredient	PHR	Ingredient	PHR
Aflas® 100H	100	Viton® ETP 600	100	Technoflon® PL855	100
TAIC	5	TAIC	5	TAIC	5
Peroxide	3	Peroxide	3	peroxide	3

Table 6 – Peroxide-TAIC cured no/low VDF gum polymers

RESULTS AND DISCUSSION:

One could reasonably assume that the amount of elastomer swelling in CO_2 might be a function of elastic modulus. Table 7 documents the measured elastic modulus (G') of the specimens prior to the soaking period and the recorded change in length and calculated percent change in volume of each specimen after a 24-hour soak under pressure. After the soaking period, pressure was released over a ten minute period to return to atmospheric pressure (sea level).

Test Group	Elastomers	Change in Length (mm)	Change in Volume (%)	Elastic Modulus (G') @ 22/23C (Pa)
Hydrocarbon	EPDM	3.0	9.3	1.204E+06
Hydrocarbon	HNBR	5.0	15.5	1.211E+06
Amine cure	FKM Type 1	9.0	29.5	2.167E+06
Amine cure	FKM Type 2	11.0	36.8	2.150E+06
Peroxy-TAIC cure	FEPM (Aflas 100H)	11.0	36.8	1.346E+06
Peroxy-TAIC cure	FEPM (ETP 600)	13.0	44.3	1.873E+06
Peroxy-TAIC cure	FKM Type 3	12.0	40.5	1.447E+06

Table 7 – Elastic Modulus and % change in volume

Figure **3** is a scatter plot of elastic modulus versus percent change in volume. The absence of any relationship between the two attributes confirms that other factors or interactions thereof are the primary determinants of swelling in CO_2 while under pressure. Hydrocarbon polymers clearly are less prone to swelling in CO_2 than the fluoroelastomer specimens. This observation stands in spite of the hydrocarbon elastomer specimens possessing a lower elastic modulus than the fluoroelastomer specimens. The non-polar EPDM exhibits the lowest swelling, a remarkable observation considering CO_2 is a linear, symmetrical molecule with no dipole moment. However, there is a transient dipole moment in CO_2 as discussed *supra*. In Figure 3, each elastomer group has a respective geometrical marker to facilitate analysis.

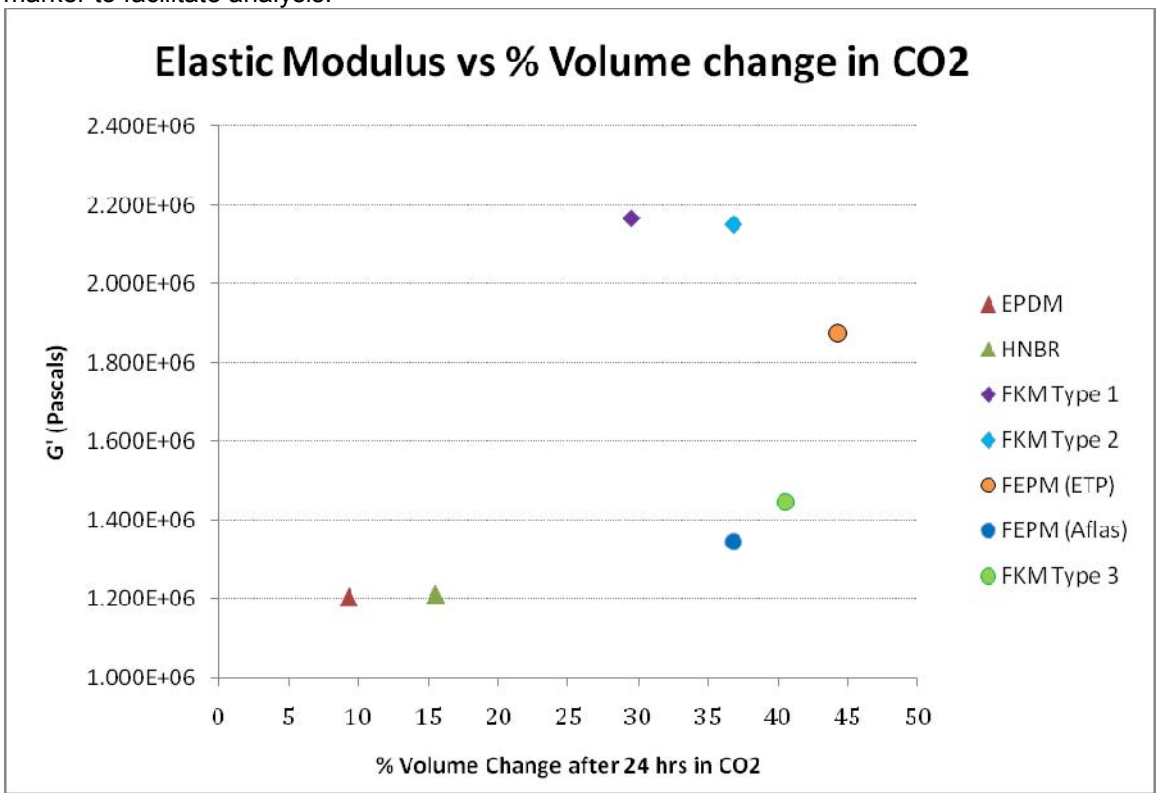

Figure 3 – Relationship of elastic modulus and volume change in CO_2

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. Due to a 30mm limitation in the test vials, linear change beyond 30% was recorded as 30%. Assuming elastomers to be isotropic materials, the % linear change in specimens reflects approximately a 3X change in volume. The changes in volume attributable to CO_2 absorption precedes seal failure modes. Although not within the scope of this study, RGD damage (e.g. blisters, fissures) was typically observed in the materials.

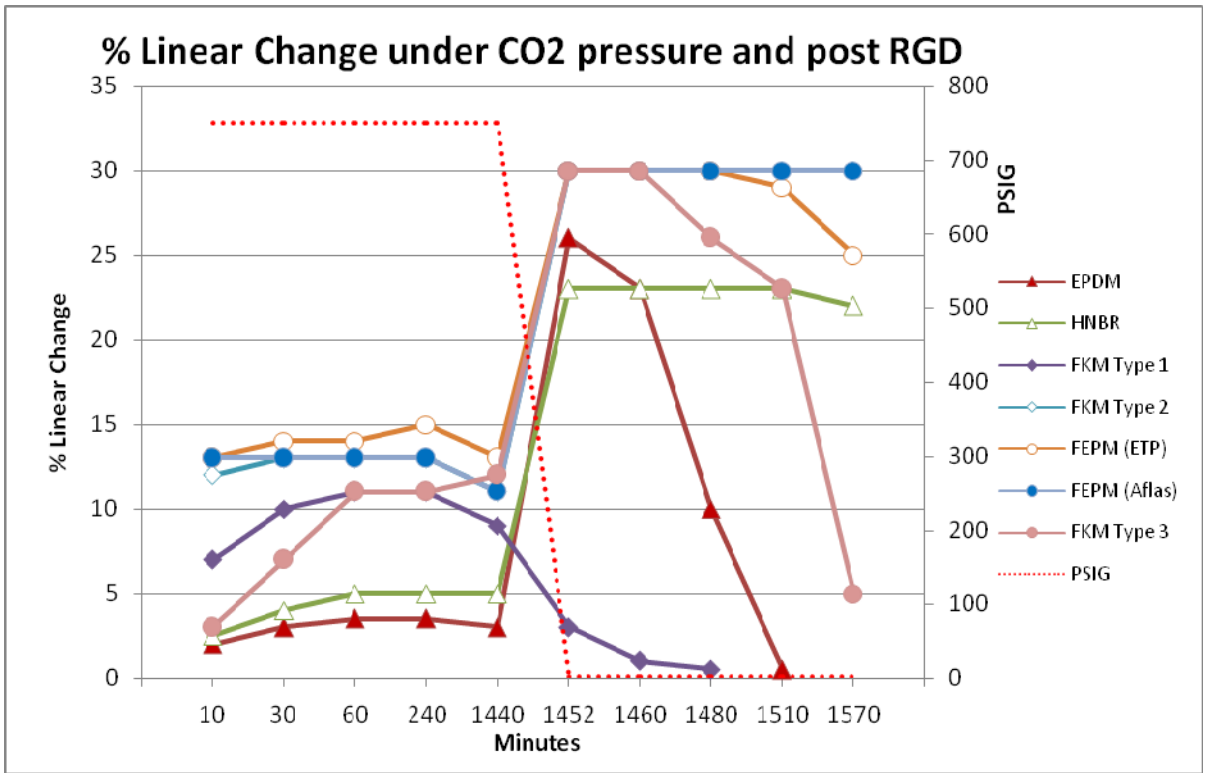

Figure 4 – Chronologic plot of swelling under pressure and subsequent to RGD

EXPERIMENT 1 - HYDROCARBON ELASTOMERS, REINFORCED

Evaluation of carbon black reinforced hydrocarbon elastomers lent itself to a Taguchi L_4 Orthogonal Array. The test matrix is documented in Table 8. There are significant differences between the two hydrocarbon elastomers tested. Specifically, the EPDM is non-polar while HNBR is polar. The HNBR analyzed has a 36% acrylonitrile content.

FACTORS		LEVELS 1	2
A	POLYMER	EPDM	HNBR
B	CURE PPH	5	6
C	FILLER TYPE	N990	N330
uncontrolled	FILLER PPH	30	30

Table 8 – Factors and associated levels for reinforced hydrocarbon elastomer study

Rather than full factorial testing, requiring 2^3 or eight (8) conditions, the following orthogonal array in Table 9 was evaluated.

Condition	Polymer	Cure pph	Filler Type
#1	EPDM (A1)	5 (B1)	N990 (C1)
#2	EPDM (A1)	6 (B2)	N330 (C2)
#3	HNBR (A2)	5 (B1)	N330 (C2)
#4	HNBR (A2)	6 (B2)	N990 (C1)

Table 9 – Taguchi L_4 Orthogonal Array for reinforced hydrocarbon elastomer study

RESULTS AND DISCUSSION:

Swelling at the end of a 24-hour soak is recorded in Table 10. Swelling 2 minutes subsequent to the 10 minute RGD is recorded in Table 11.

EPDM presented less swelling under pressure than HNBR. EPDM also exhibited less swelling 2 minutes subsequent to RGD. Filler particle size had no effect on swelling under pressure but had significant impact subsequent to RGD, with the smaller particle size mitigating swelling.

PHR of cure had no effect on swelling under pressure. On the hand, an increase in curative corresponded with an increase in swelling subsequent to RGD in HNBR. A full factorial examination of this relationship within HNBR revealed an interaction of particle size and increased curative subsequent to RGD. Specifically, the study (Table 9A) revealed that increasing curative with an N990 increased swelling subsequent to RGD while increasing curative with an N330 decreased swelling subsequent to RGD.

HNBR w/ 30 phr black	5 phr Cure	6 phr Cure
N330	56.1%	40.5%
N990	64.3%	104.8%

Table 9A – Post RGD % Volume Change study of particle size to cure phr

The swelling response of EPDM is somewhat counter intuitive given its non-polar composition and CO_2's non-polar configuration. However, when consideration is given to the doubly degenerate bending of the CO_2 molecule, the polarity is in fact different. Thus, we also observed a

greater absorption of CO_2 by HNBR, a non-polar elastomer. Results are depicted graphically in Figure 5.

	A	B	C	% Vol Δ	EPDM A1	HNBR A2	5 phr B1	6 phr B2	N990 C1	N330 C2
#1	1	1	1	6.1%	6.1%		6.1%		6.1%	
#2	1	2	2	6.1%	6.1%			6.1%		6.1%
#3	2	1	2	15.8%		15.8%	15.8%			15.8%
#4	2	2	1	15.8%		15.8%		15.8%	15.8%	
				Total	0.122	0.315	0.219	0.219	0.219	0.219
				Average	0.061	0.158	0.109	0.109	0.109	0.109

Table 10 - % Volume Change after 24 hours in CO_2

	A	B	C	% Vol Δ	EPDM A1	HNBR A2	5 phr B1	6 phr B2	N990 C1	N330 C2
#1	1	1	1	6.1%	6.1%		6.1%		6.1%	
#2	1	2	2	6.1%	6.1%			6.1%		6.1%
#3	2	1	2	56.1%		56.1%	56.1%			56.1%
#4	2	2	1	104.8%		104.8%		104.8%	104.8%	
				Total	0.122	1.609	0.622	1.110	1.110	0.622
				Average	0.061	0.805	0.311	0.555	0.555	0.311

Table 11 - % Volume Change 2 minutes subsequent to RGD

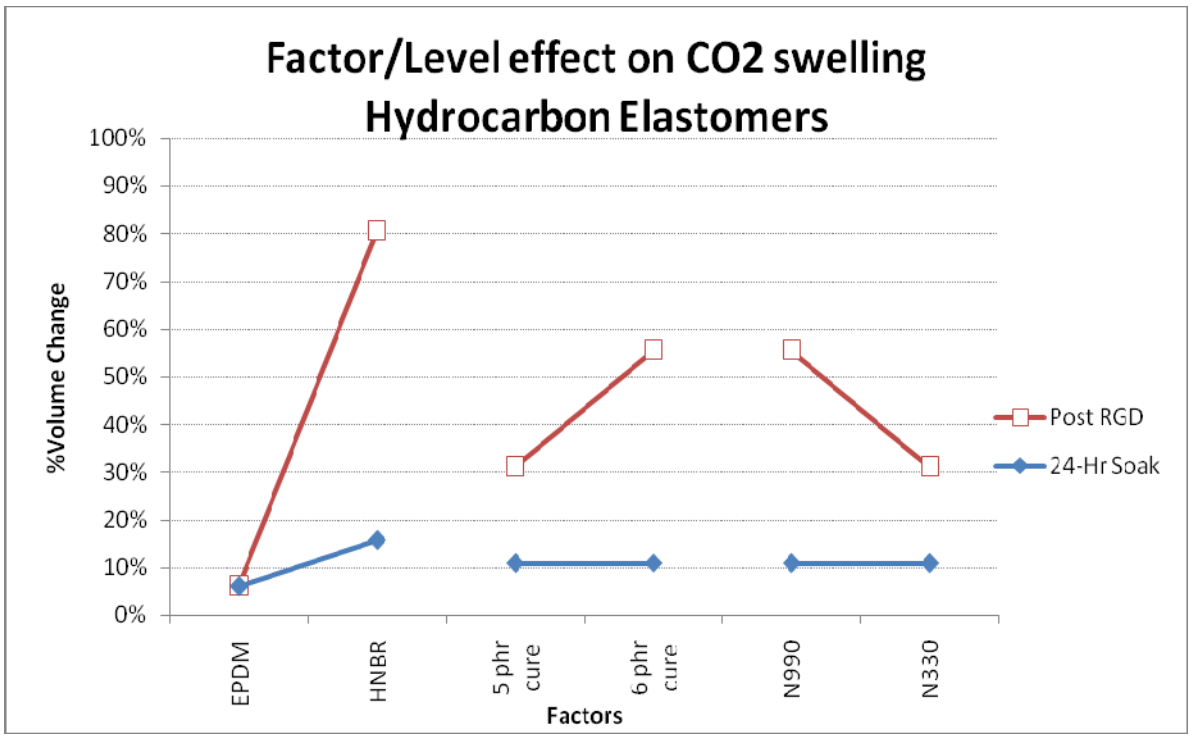

Figure 5 – Factor/Level effects on swelling in CO2.

EXPERIMENT 2 - AMINE CURED FKM ELASTOMERS, REINFORCED

Evaluation of carbon black reinforced amine cured FKM elastomers lent itself to a Taguchi L_4 orthogonal array. The test matrix is documented in Table 12. The FKM I and FKM II studied do not utilize any coagent. Cure is accomplished via amine induced dehydrohalogenation. Due to the brand nature of the FKM Type 1 and FKM Type 2 studied, the amine initiators are specific to the polymer and are thus chemically different. An assumption has been made that the differences in chemical structure of the amine compounds will participate nominally, if at all, in the results whereas the differences in respective quantity of curative will be a more significant factor. Carbon black grade and magnesium oxide loadings were constant and uncontrolled in this study.

FACTORS		LEVELS 1	2
A	POLYMER	FKM-I	FKM-II
B	AMINE PHR	2	3
C	FILLER PHR	30	70
Uncontrolled	FILLER TYPE	N990	N990
Uncontrolled	MgO PPH	15	15

Table 12 – Factors and associated levels for reinforced amine cure FKM study

The following Taguchi L_4 Orthogonal array per Table 13 was evaluated.

Condition	Polymer	Cure pph	Filler Type
#1	FKM-I (A1)	2 (B1)	30 (C1)
#2	FKM-I (A1)	3 (B2)	70 (C2)
#3	FKM-II (A2)	2 (B1)	70 (C2)
#4	FKM-II (A2)	3 (B2)	30 (C1)

Table 13 – Taguchi L_4 Orthogonal Array for reinforced amine cure FKM elastomer study

RESULTS AND DISCUSSION:

FKM Type 1 exhibited less swelling than the FKM Type 2 both under pressure and after RGD. Increasing the particle black loading decreased swelling both under pressure and after RGD. The premise that carbon black does not absorb CO_2 renders this observation unremarkable. Incremental change in curative had no effect on swelling under pressure but an increase in curative appears to have increased swelling subsequent to RGD. As discussed in the results of Experiment 1, there is an interaction between curative phr and large particle blacks. The FKM data suggests this same interaction is present in the amine cured FKM I and FKM II.
Results are depicted graphically in Figure 6.

	A	B	C	% Vol Δ	FKM-I A1	FKM-II A2	2 phr cure B1	3 phr cure B2	30 phr N990 C1	70 phr N990 C2
#1	1	1	1	29.5%	29.5%		29.5%		29.5%	
#2	1	2	2	22.5%	22.5%			22.5%		22.5%
#3	2	1	2	26.0%		26.0%	26.0%			26.0%
#4	2	2	1	33.1%		33.1%		33.1%	33.1%	
				Total	0.520	0.591	0.555	0.556	0.626	0.485
				Average	0.260	0.295	0.277	0.278	0.313	0.242

Table 14 - % Volume Change of amine cure FKM elastomers in CO_2

	A	B	C	% Vol Δ	FKM-I A1	FKM-II A2	2 phr cure B1	3 phr cure B2	30 phr N990 C1	70 phr N990 C2
#1	1	1	1	19.1%	19.1%		19.1%		19.1%	
#2	1	2	2	15.8%	15.8%			15.8%		15.8%
#3	2	1	2	15.8%		15.8%	15.8%			15.8%
#4	2	2	1	33.1%		33.1%		33.1%	33.1%	
				Total	0.349	0.489	0.349	0.489	0.522	0.315
				Average	0.174	0.244	0.174	0.244	0.261	0.158

Table 15 - % Volume Change 2 minutes subsequent to RGD

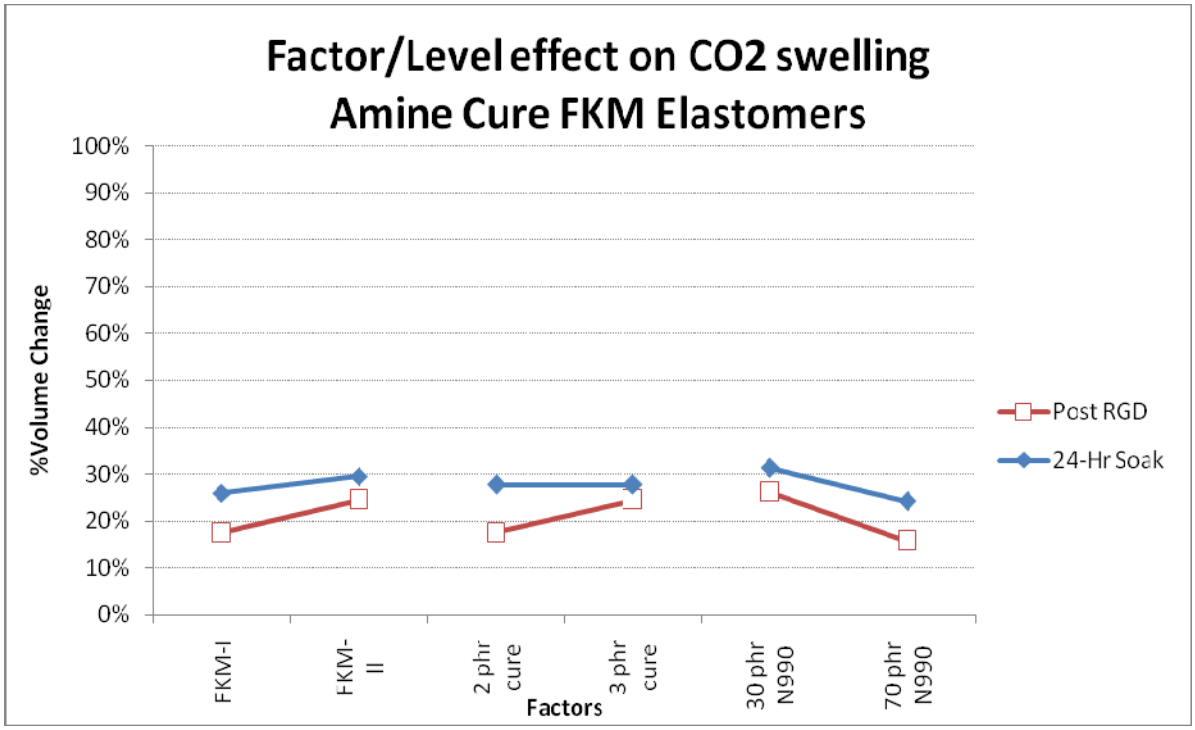

Figure 6- Factor/Level effects on swelling of amine cure FKM in CO2.

EXPERIMENT 3 - PEROXIDE-TAIC CURED FLUOROELASTOMERS, REINFORCED

Evaluation of reinforced peroxide-TAIC cured fluoroelastomers required a Taguchi L_9 Orthogonal Array. The test matrix is documented in Table 16. TAIC loading was constant and uncontrolled in this study.

FACTORS		LEVELS		
		1	2	3
A	POLYMER	Aflas	ETP	FKM-III
B	CURE PHR	2	3	4
C	FILLER TYPE	N330	N550	N990
D	FILLER PHR	10	30	50
uncontrolled	TAIC PHR	5	5	5

Table 16 – Factors and associated levels for reinforced peroxide-TAIC cure study

The following Taguchi L_9 Orthogonal Array, per Table 17, was evaluated. Results are documented in Tables 17 thru 19.

ConditIon	Polymer	Cure PHR	Filler type	Filler PHR	24hr Soak % Vol Δ	Post RGD % Vol Δ
#1	Aflas (A1)	2 (B1)	N330 (C1)	10 (D1)	36.8%	119.7%
#2	Aflas (A1)	3 (B2)	N550 (C2)	30 (D2)	12.5%	72.8%
#3	Aflas (A1)	4 (B3)	N990 (C3)	50 (D3)	26.0%	12.5%
#4	ETP (A2)	2 (B1)	N550 (C2)	50 (D3)	29.5%	6.1%
#5	ETP (A2)	3 (B2)	N990 (C3)	10 (D1)	40.5%	29.5%
#6	ETP (A2)	4 (B3)	N330 (C1)	30 (D2)	36.8%	6.1%
#7	FKM-III (A3)	2 (B1)	N990 (C3)	30 (D2)	33.1%	19.1%
#8	FKM-III (A3)	3 (B2)	N330 (C1)	50 (D3)	26.0%	6.1%
#9	FKM-III (A3)	4 (B3)	N550 (C2)	10 (D1)	36.8%	15.8%

Table 17 – Taguchi L_9 Orthogonal Array for reinforced peroxide-TAIC cured fluoroelastomer study

	Aflas	ETP	FKM III	2phr cure	3phr cure	4phr cure	N330	N550	N990	10phr black	30phr black	50phr black
	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
#1	37%			37%			37%			37%		
#2	12%				12%			12%			12%	
#3	26%					26%			26%			26%
#4		30%		30%				30%				30%
#5		40%			40%				40%	40%		
#6		37%				37%	37%				37%	
#7			33%	33%					33%		33%	
#8			26%		26%		26%					26%
#9			37%			37%		37%		37%		
Total	0.75	1.07	0.96	0.99	0.79	0.99	0.99	0.79	1.00	1.14	0.82	0.81
Avg	0.25	0.36	0.32	0.33	0.26	0.33	0.33	0.26	0.33	0.38	0.27	0.27

Table 18 - % Volume Change after2 minutes subsequent to RGD

	Aflas	ETP	FKM III	2phr cure	3phr cure	4phr cure	N330	N550	N990	10phr black	30phr black	50 phr black
	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
#1	120%			120%			120%			120%		
#2	73%				73%			73%			73%	
#3	12%					12%			12%			12%
#4		6%		6%				6%				6%
#5		30%			30%				30%	30%		
#6		6%				6%	6%				6%	
#7			19%	19%					19%		19%	
#8			6%		6%		6%					6%
#9			16%			16%		16%		16%		
Total	2.05	0.42	0.41	1.45	1.08	0.34	1.32	0.95	0.61	1.65	0.98	0.25
Avg	0.68	0.14	0.14	0.48	0.36	0.11	0.44	0.32	0.20	0.55	0.33	0.08

Table 19 - % Volume Change 2 minutes subsequent to RGD

RESULTS AND DISCUSSION:

Figure 8 offers a graphic presentation of the data. The three peroxide-TAIC cured polymers exhibited mostly the same swelling under pressure. Increasing cure phr produced no appreciable trend in volume change. Particle size had no effect on swelling under pressure. Finally, there is a trend of decreasing swelling as the phr of particle black increased.

Contrary to the prior two experiments, an increase in peroxide corresponds to a decrease in swelling subsequent to RGD. It should be noted that this group of polymers contains a coagent (i.e. TAIC) whereas the preceding two groups bond through unsaturated sites in the polymer backbone. The constitution of their respective crosslink networks is substantially different.

Contrary to the prior two experiments, an increase in particle size corresponded with a reduction in swelling subsequent to RGD. This is a remarkable but suspect observation given the premise of increased surface area and associated increased strength with smaller particle size black.

It is probable that the effects of particle black loading and peroxide loading are overshadowing this factor. Additional study in this regard would be warranted.

Similar to the results of the FKM study, increasing the phr loading of particle black decreased swelling subsequent to RGD.

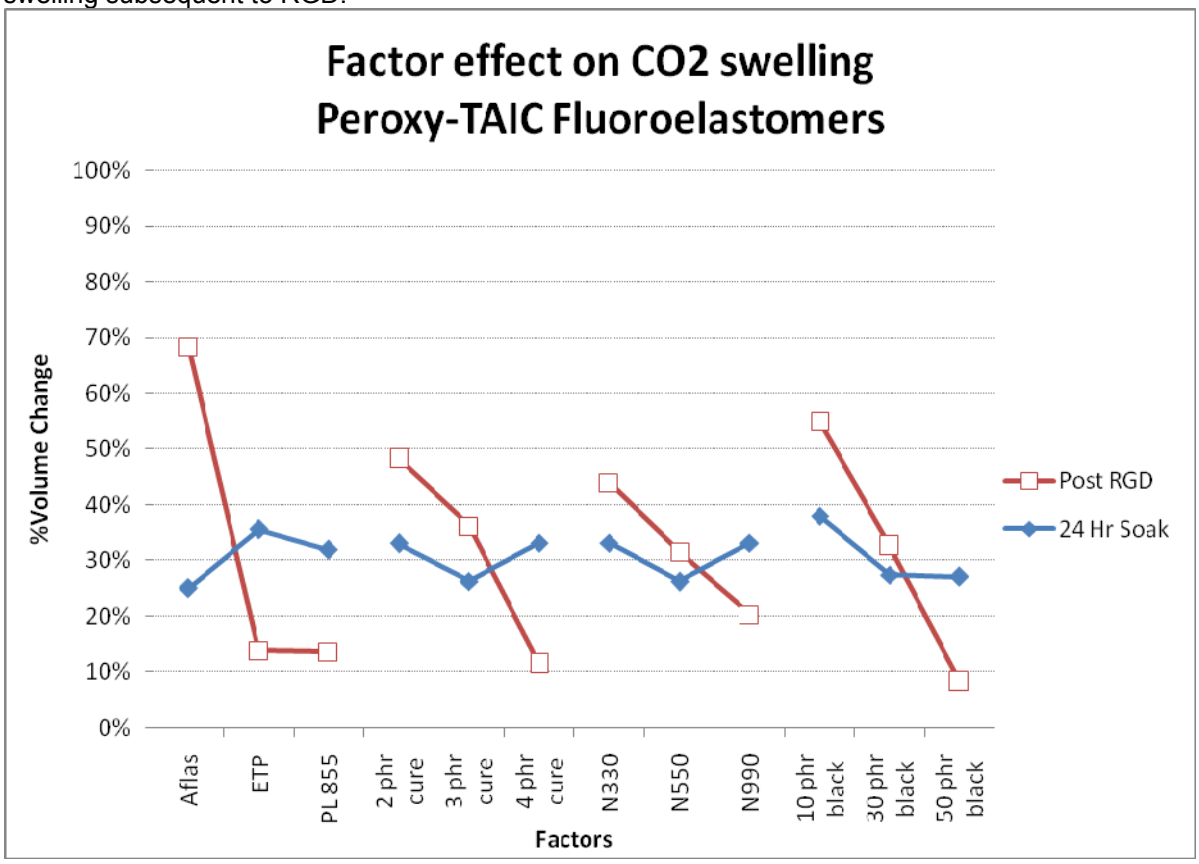

Figure 8- Factor/Level effects on peroxide - TAIC cured fluoroelastomer swelling in CO2.

SOURCES OF ERROR

Changes in specimen length were recorded by visual examination. As such, a significant source of error could be introduced. Figure 8 plots the percent change to be added or subtracted to calculated volume changes in the event of 1mm error in observing the length of a specimen. The error associated with ±1 mm change in length is calculated per Equations 4 and 5.

Eq.4 : +Tolerance = +tol = $[(1 + \Delta Len\% + .01)^3 - 1] /1 - [(1 + \Delta Len\%)^3 - 1] /1$

Eq.5 : -Tolerance = -tol = $[(1 + \Delta Len\%)^3 - 1] /1 - [(1 + \Delta Len\% - .01)^3 - 1] /1$

In evaluating data, the reader may want to consider volume change within a range rather than as a single point.

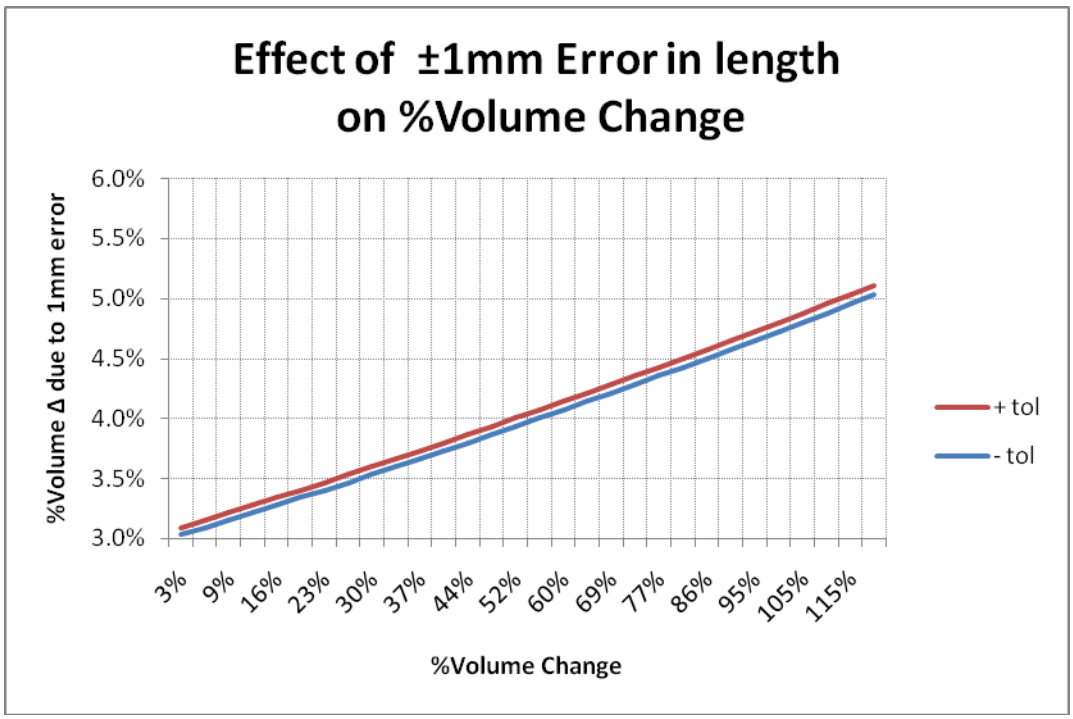

Figure 8 - %Change in Volume tolerance attributable to ±1 mm

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. An error of .5 grams corresponds to an error of 0.1 PHR. With curatives weighed as low as 2 phr, a 0.5 gram error would amount to a 5% deviation from the test formula.

CO_2 Pressure was regulated for the soak. However, pressure release was unregulated over a 10 minute period. Some test specimens may have experienced faster or slower decompression rates, but all decompression from 750 PSI to atmospheric occurred within 9 to 10 minutes. Swelling subsequent to RGD was taken 2 minutes after reaching atmospheric pressure. It is reasonable to assume a specimen length tolerance of ±1mm for the post RGD data.

SUMMARY

1) Choice of Elastomer is the primary determinant of swelling in CO_2.
    a) EPDM possesses the least amount of swelling under pressurized CO_2. Particle black reinforced EPDM exhibits the least amount of swelling subsequent to RGD.
    b) ETP and FKM Type 3 gum possess the greatest amount of swelling under pressurized CO_2.
    c) FKM Type 1 gum possesses the least amount of swell subsequent to RGD and exhibits the most rapid out-gassing subsequent to RGD.
2) Carbon black is a significant if not overshadowing factor in swelling subsequent to RGD.
    a) Increasing PHR of carbon black decreases swelling under CO_2 pressure and post RGD.
    b) Carbon black particle size has no effect on swelling under pressure.
    c) Decreasing particle size reduces swelling subsequent to RGD (Note conflicting data in Experiment 3).
3) Curative loading has an effect on post RGD swelling and can interact with carbon black reinforcement.
    a) Increasing PHR of curative has no effect on swelling under pressure for all the elastomers studied.
    b) For the peroxide cure and amine cure compounds not utilizing a coagent (i.e. HNBR, FKM I, FKM II), there is an interaction between carbon black particle size and curative loading on swelling subsequent to RGD. Specifically, as studied in HNBR, increasing curative while using N990 black coincides with an increase in swelling subsequent to RGD while increasing curative with N330 reduces swelling subsequent to RGD.
    c) Increasing PHR of curative in peroxide TAIC cured fluoroelastomers has no effect on swelling under pressure but coincides with a reduction in swelling subsequent to RGD.

ACKNOWLEDGEMENTS

The author would like to thank Kris Solaas for his diligent work in Seals Eastern's laboratory: both being the *sine qua non* of this paper. Additional gratitude is extended to Harold Cook for his DMRT work and Dan Hertz, Jr for his prior works and "hands-off" guidance.

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[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).