

EVALUATING THE RETENTION OF VISCOELASTIC PROPERTIES
FOR EXTREME AND LONG TERM SERVICE:
A CASE STUDY IN POTASSIUM FORMATE.

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ABSTRACT

The Costs associated with seal failure during hydrocarbon production have increased dramatically as environmental regulations become tougher and production zones become increasingly hot and deeper with associated high pressure. Oil companies are rightfully demanding more comprehensive proof that the elastomer components they require are capable of delivering leak-free performance for a specific service life. The requirement of accurately ascertaining and extending service life continues to increase as the costs associated with retrieving and redressing oil tools and other equipment increases.

The objective of this test program was to review the potential physical and chemical changes of three popular “high-performance” oilfield materials in potassium formate over a relatively short time period. Potassium formate is a popular completion fluid, on account of its benign environmental impact, high density, and its ability to retard corrosion. We reviewed physical aging using o-ring seals (ASTM D1414) and compressive stress relaxation. Chemical changes within the elastomers were monitored using Fourier Transform Infrared Spectroscopy (FTIR) with attenuated total reflectance (ATR). Bulk property changes were analyzed using conventional and dynamic mechanical rheological testing (DMRT) to further illuminate bulk property changes due to chemical attack. The test protocol utilized was designed to disclose otherwise latent aging phenomenon that might not be observed in similar aging periods. This same protocol was published in a SAE Paper in 2001¹.

INTRODUCTION

Testing to determine suitability for long-term sealing service should incorporate measurements of data meaningful to the application as well utilizing apparatus that represents a legitimate model of the application. Ascertaining long-term seal performance for applications under compression should start with an elastomer having a minimal potential for chemical change and/or long-term resistance to compression set and compressive stress relaxation. The test program and apparatus used for this paper were designed to provide data relevant to elastomer selection for oilfield logging equipment, completion equipment, and other applications involving seals under compression.

Premature failure can occur due to chemical attack on the base elastomer (a.k.a. backbone), the crosslink, or both. Physical relaxation (stress/strain relaxation) can lead to premature failure of seal contact stress and is typically accelerated by increasing temperature. The initial chemical changes on the elastomer’s surface can be monitored via Fourier Transform Infrared Spectroscopy (FT-IR) with the Attenuated Total Reflectance (ATR) technique.

Chemical stability of the base elastomer determines the retention of viscoelastic properties. However, the stability of the crosslink chemistry plays an equally important role in the retention of elastic properties. The bulk chemical changes are naturally time-temperature dependent. These changes can be monitored by dynamic mechanical and rheological thermal analysis (DMRT). DMRT testing is performed under shear (a linear elastic response). Shear modulus, G , of an elastomer is generally expressed as $G = \rho RT/M_c$, where ρ is density, R the universal gas constant, and T is temperature in Kelvin. M_c , a controversial term, is molecular weight between crosslinks. Considering M_c as the variable reflecting chemical changes that occur during the aging process we can now measure the elastomer’s bulk properties as they shift due to aging.

Maintenance of contact stress between elastomeric elements and mating surfaces is critical to proper sealing. The measurement of retained contact stress is a valuable method of determining compressive stress relaxation (CSR). This information offers valuable insight for prediction of long-term suitability of elastomers operating under compression at a fixed strain. A specimen geometry that reflects a typical o-ring cross section and realistic operating temperature were

used in this paper's test program to accurately model environmental conditions of seals (e.g. o-rings) in completion fluid service. Retention of contact stress will typically be determined by retention of viscoelastic properties under compression.

Strain Energy Density offers a unique means of evaluating the retention of viscoelastic properties under tension by simultaneously accounting for change in tensile strength (integrity) and change in elongation (extensibility). Auda and Hazelton² adopted Fractional Strain Energy at Break (Eq.1), simultaneously taking into account tensile and elongation, as a means of examining the thermal stability of EPDM compositions.

$$\text{Eq. (1) Fractional Strain Energy at Break} = (\text{TAB} \times \text{EAB})_{\text{aged}} / (\text{TAB} \times \text{EAB})_{\text{original}}$$

where TAB is tensile at break and EAB is elongation at break.

We incorporate an important distinction from the work of Auda and Hazelton. Specifically, we examine fractional strain energy as derived from an integration of the area under each specimen's stress strain curve up to 20% strain, whereas Auda and Hazelton examine the relative area under the stress-strain curve up to the point of the test specimen's breakage. Strain Energy calculated at 20% strain offers two distinct advantages. First, data is derived from the hyper-elastic region of the stress-strain curve offering better insight as to the integrity of the elastomer network as opposed to filler interactions. Second, 20% strain is a more realistic approximation of strain the elastomer will be subject to given generally accepted design guidelines³.

Formate fluids are commonly employed in the oilfield as an environmentally friendly fluid to control the density of either drilling or completion fluids. They are monovalent fluids as opposed to halide based brines. They utilize an alkali metal (e.g. Na, K, Cs) in conjunction with formate (HCOO). A major requirement for effective use of formate is pH maintenance to retard the formation of formic acid which is otherwise corrosive. This requires buffering the fluid to maintain an alkaline pH. For this reason, no FKM class polymers were examined. The phenomenon of dehydrohalogenation of vinylidene fluoride (a monomer in FKM elastomers) in alkaline environment is documented elsewhere.

EXPERIMENTAL

OBJECTIVES

The authors sought to compare and evaluate three "high-temperature" elastomers with respect to long-term sealing performance in a hot, high pH completion fluid- specifically potassium formate (K^+HCOO^-) at 150°C. This temperature was chosen so as not to exceed the capability of HNBR, but was sufficiently hot to accelerate any inevitable reactions. Test fixtures were used that closely simulate the conditions of an unrestrained o-ring under 25% compression.

Ideally, the elastic properties of an elastomeric material would remain unchanged after any amount of time in service. Obviously, exposure to working fluids and to higher than ambient temperatures causes some shift in mechanical properties. However, to be considered for long-term service, the change in properties should ideally reach desirable equilibrium values. In extreme environments, however, materials should ultimately be selected on the basis of greatest stability in molecular integrity as well as viscoelastic behavior under compression, tension, or shear.

EXPERIMENTAL METHOD

Table 1 below summarizes the test conditions, and Fig. 1 shows a cutaway view of the test fixture.

Variable	Description
3 "high temperature" down-hole compounds	TFE/P, HNBR, TFE/E/PMVE (See Table 2 for details)
1 Temperature	150°C
4 Test Times (In Addition to "Un-Aged" Samples)	336-hours (2-weeks), 672-hrs (4-weeks), 1008-hrs (6-weeks) and 1344-hrs (8-weeks)
1 Test Fluid	Potassium Formate
Samples per Set of Test Conditions	Size 214 O-Rings (3 per fixture) Under 25% Compression (ASTM D1414) Spherical Test Specimen Torsion Rectangular Sample

Table 1: Experimental Matrix

The aging vessel, Fig. 1 was designed to offer a bi-metallic environment capable of containing fluids at elevated temperature. The bi-metallic nature of the vessel introduces a small electric potential as one would encounter in a downhole environment. In the cylinder is a i) a stack of three dash number 214 o-rings, each under 25% compression., ii) a compressive stress relaxation (CSR) figure (2), and iii) a torsion rectangular sample. All rubber parts/samples in a given fixture were manufactured from the same rubber compound and fully submersed in the test media.

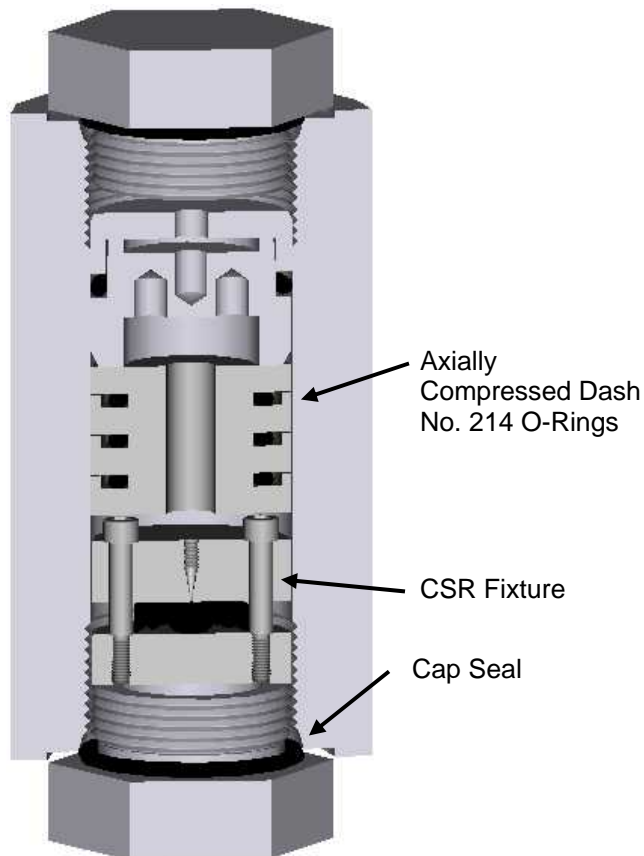


Figure 1: Test Cylinder Schematic

The assembled test cylinder is placed in an oven and aged for a specified amount of time at 150°C.

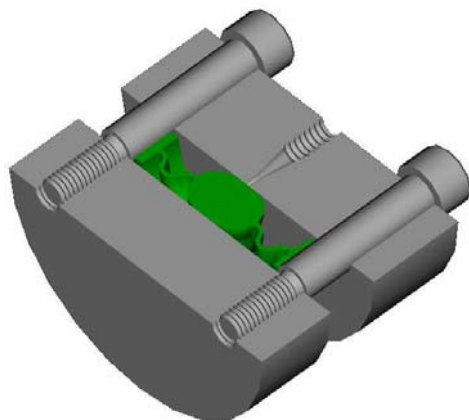


Figure 2: CSR Fixture Schematic

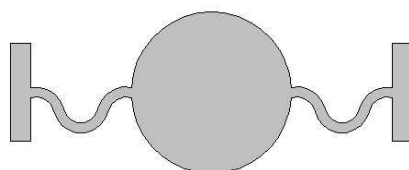


Figure 3: CSR Sample Cross Section

The base polymers of compounds tested are hereafter referenced as illustrated in Table 2.

Trade Name	Polymer	D1418 Designation	Referenced As
AFLAS®	TFE/P	FEPM	Aflas
Viton Extreme®	TFE/E/PMVE	FEPM	ETP
---	HNBR	HNBR	HNBR
7182DX	TFE/P	FEPM	7182DX*

*proprietary composition

Table 2: Material Designations

Aflas Formulation		ETP Formulation		HNBR Formulation	
Constituent	PHR	Constituent	PHR	Constituent	PHR
Aflas 100H	100	ETP 600S	100	Zetpol 2010	100
MT Black (N990)	30	MT Black (N990)	30	MT Black (N990)	30
TAIC	5	Zinc Oxide	3	Naugard 445	1.5
2,5-dimethyl 2,5-bis (t-butyl peroxy) hexane	1	DIAC 7	3	Vanox ZMT1	1.5
		Luperox 101XL45	3	Stearic Acid	0.5
				Vulcup 40 KE	6
				Sartomer SR 350	5

Table 3: Subject Formulations

RESULTS

Aging of all samples took place at 150°C, fully immersed in potassium formate.

AXIALLY COMPRESSED O-RINGS

COMPRESSION SET:

Size AS568-214 o-rings as shown in Fig. 1 were tested before and after aging. Experimentally derived values were based on three samples. All three o-rings, under 25% axial compression, were fully immersed in potassium formate. Test results include compression set, percent retained strain energy density, percent change in elongation, percent change in tensile at break (TAB), and change in durometer over aging time; these are shown in figures 4 through 8 below.

Compression set testing was conducted to ASTM D 1414 – 99⁴ and calculated per ASTM D 395 – 02 Test Method B⁵.

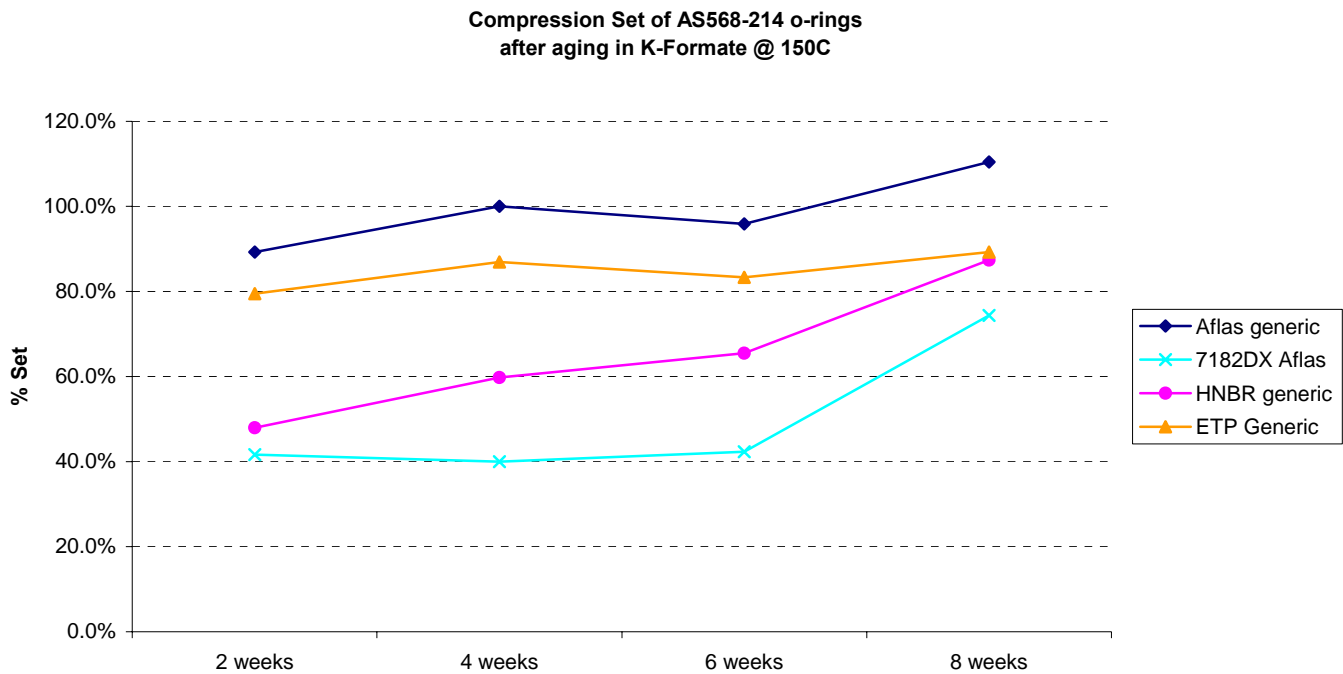


Figure 4: AS568-214 O-ring Compression Set vs. Aging Time

PERCENT RETAINED STRAIN ENERGY DENSITY:

Strain energy density was calculated as an integration of the area under the stress-strain curve, up to the point of 20% elongation, associated with AS568-214 o-rings drawn under tension using an Instron configured to ASTM D1414 – 99.

“Percent Retained Strain Energy Density” was calculated per Equation 2.

$$\text{Eq. (2) Percent Retained Strain Energy Density} = (\text{Strain Energy Density})_{\text{aged}} / (\text{Strain Energy Density})_{\text{unaged}}$$

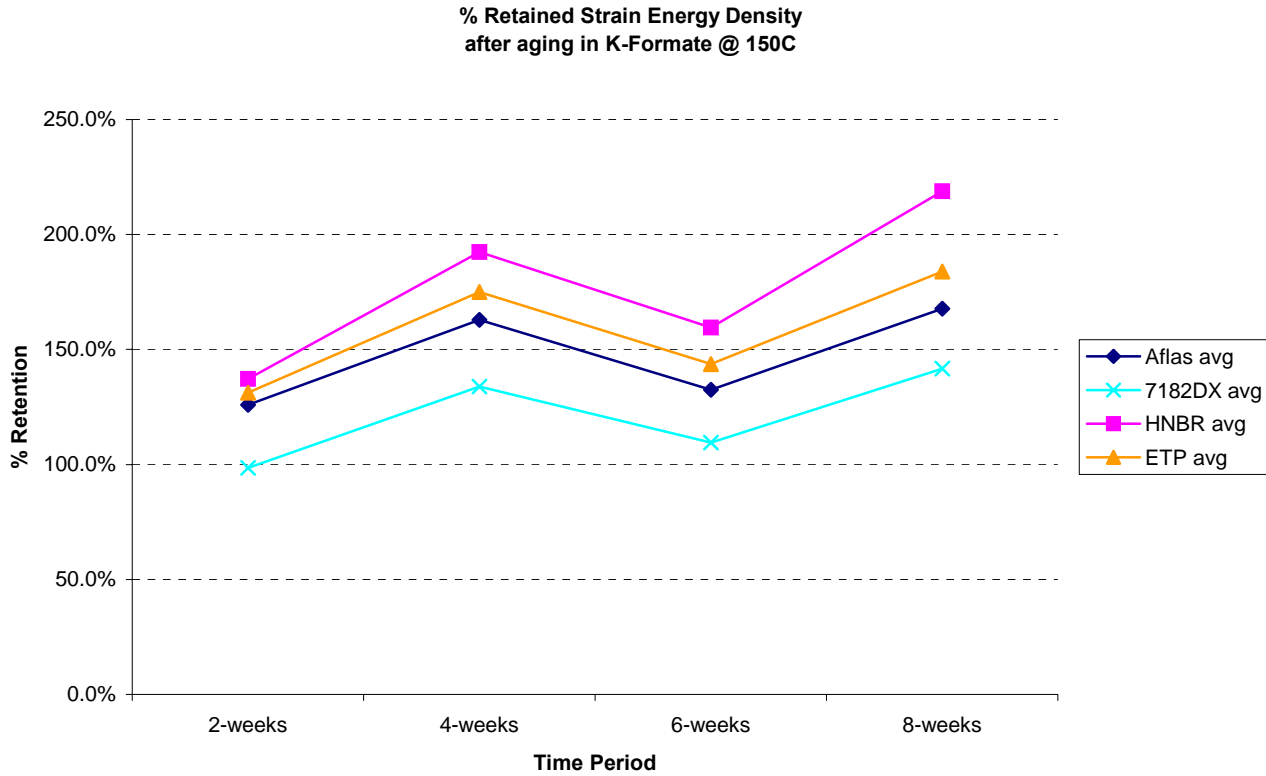


Figure 5: % Retained Strain Energy Density vs. Aging Time

PERCENT CHANGE IN ELONGATION

Elongation was determined from AS568-214 o-rings drawn under tension using an Instron configured to ASTM D1414 – 99.

“Percent Change in Elongation” was calculated per Equation 3.

$$\text{Eq. (3) Percent Change in Elongation} = (\text{Elongation}_{\text{aged}} - \text{Elongation}_{\text{unaged}}) / \text{Elongation}_{\text{unaged}}$$

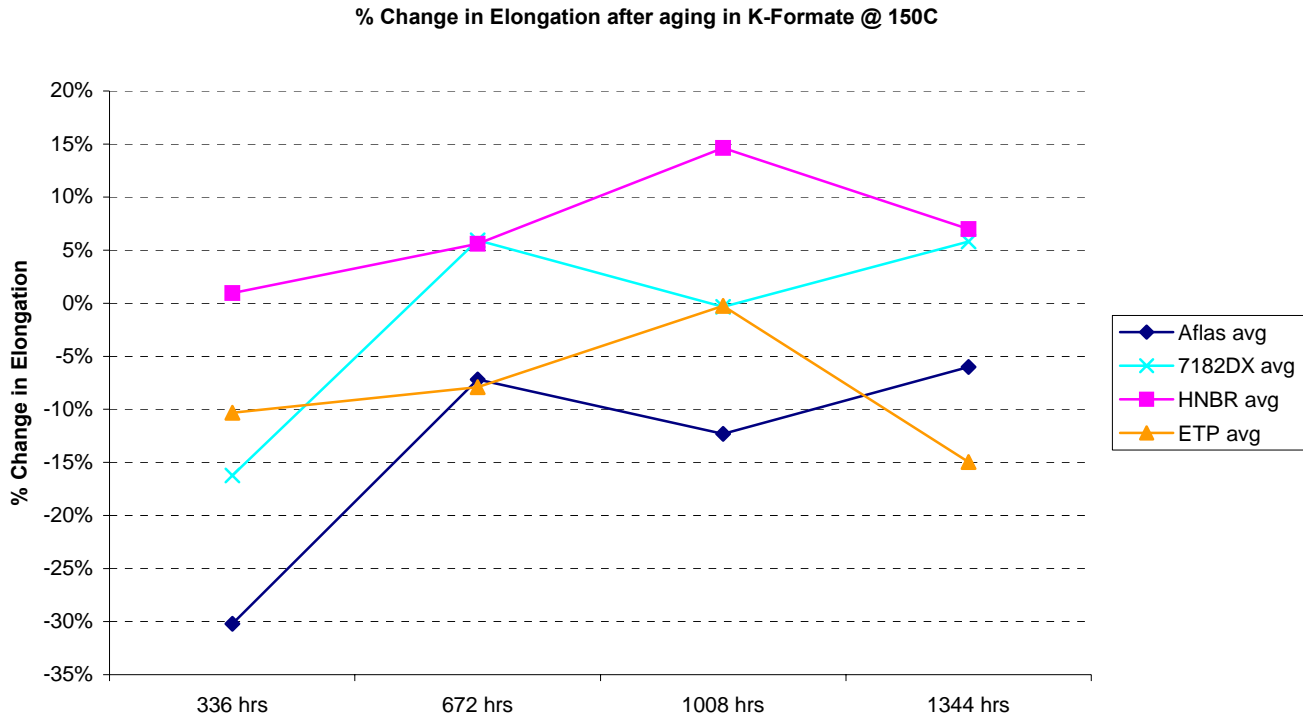


Figure 6: Percent Change in Elongation vs. Aging Time

PERCENT CHANGE IN TENSILE AT BREAK

Tensile at Break (TAB) was determined from AS568-214 o-rings drawn under tension using an Instron configured to ASTM D1414 – 99.

“Percent Change in TAB” was calculated per Equation 4.

$$\text{Eq. (4) Percent Change in TAB} = (\text{TAB}_{\text{aged}} - \text{TAB}_{\text{unaged}}) / \text{TAB}_{\text{unaged}}$$

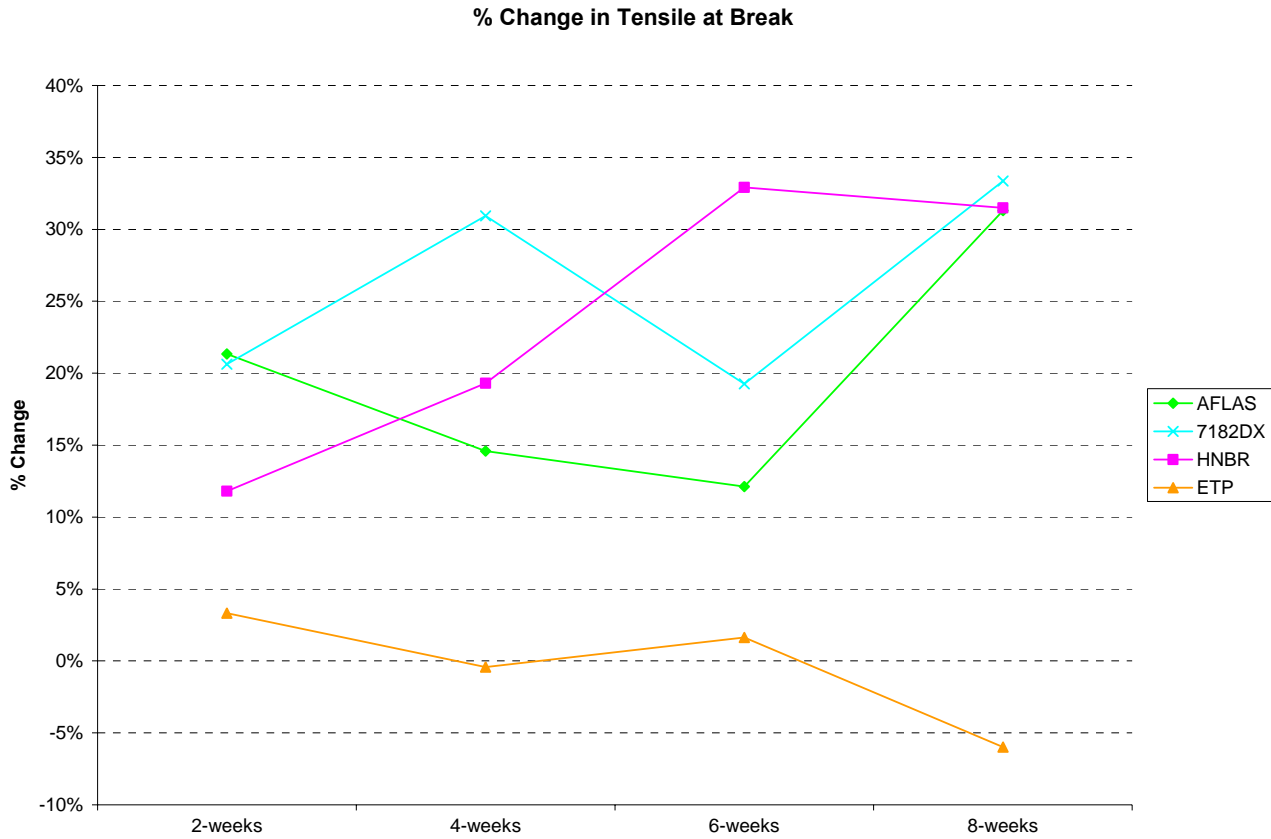


Figure 7: Percent Change in Tensile vs. Aging Time

DUROMETER

Durometer was measured from AS568-214 o-rings according to ASTM D2240 – 02b using a Shore-M gage.

“Change in Durometer” was calculated per Equation 5.

$$\text{Eq. (5) Change in Durometer} = (\text{Durometer}_{\text{aged}} - \text{Durometer}_{\text{unaged}})$$

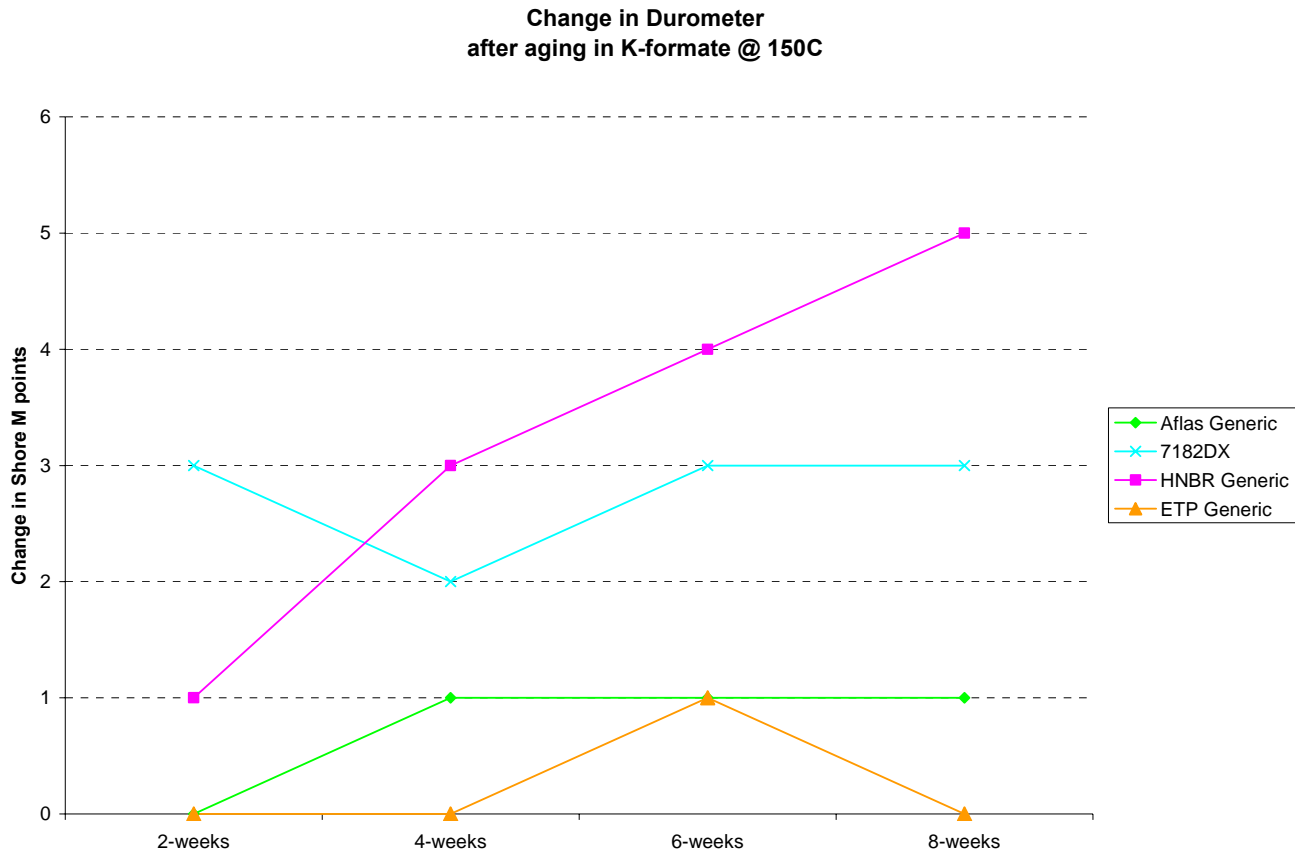


Figure 8: Change in Shore M Durometer vs. Aging Time

PERCENT RETAINED CONTACT STRESS

Contact stress was evaluated by measuring the amount of air pressure that can be sealed at a .032 inch orifice by a 0.25 inch molded sphere that has been “compressed” upon the orifice by 25%. The premise is that the rubber sphere can only contain an air pressure less than or equal to the contact stress. After an aging period, CSR fixtures were removed from their aging bomb and cooled at room temperature for twenty-four hours. Air pressure, regulated to 500 PSI max was applied and then allowed two (2) minutes to equilibrate. At the end of two minutes, a reading of the “remaining pressure” was taken. By measuring sealing pressure (contact stress) and its decline over time subject to an environment, we gain insight into “compressive stress relaxation” which is a function of crosslink density, polymer architecture, and the integrity of the network. A decline in percent retention of contact stress reflects compressive stress relaxation attributable to network damage and/or rearrangement.

The compressive stress relaxation sample and fixture (as shown in Fig. 3 and Fig. 4) yielded results of actual sealing pressure (contact stress) versus aging time. Our interest was not so much the absolute value of the contact stress, but the percent retention of contact stress to disclose compressive stress relaxation. Percent retention was calculated per equation 6. The data plotted in figure 5 represents the average of three distinct sample readings.

$$\text{Eq. (6) Percent Retained Contact Stress} = (\text{Contact Stress})_{\text{aged}} / (\text{Contact Stress})_{\text{unaged}}$$

These results are plotted in figure 8.

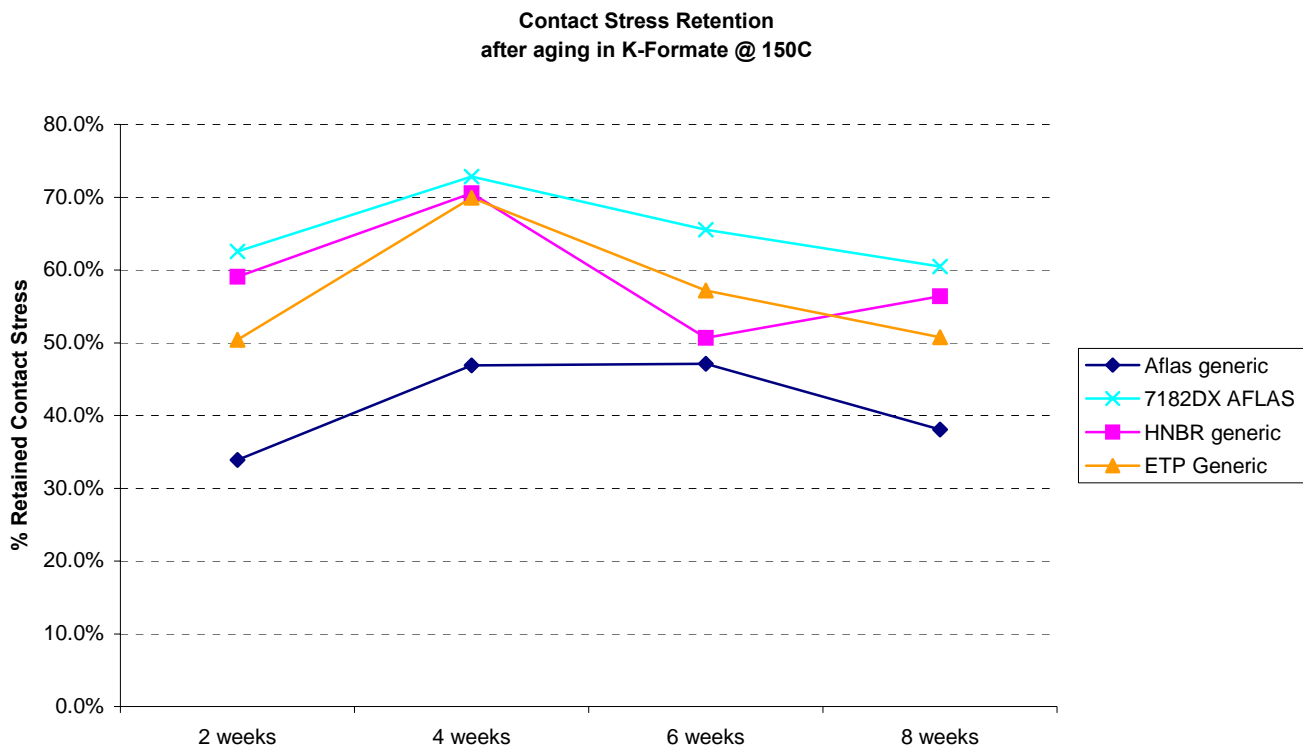


Figure 9: Retained Contact Stress vs. Aging Time

GLASS TRANSITION TEMPERATURE

Glass transition temperature, T_g , was calculated from plots of $\tan \delta$ versus temperature. During the tests, temperature was increased at a rate of 5°C per minute; data was collected between -20°C and 150°C. Frequency of oscillation was 0.1 Hz. Amplitude of oscillation was chosen to be within the linear viscoelastic region (LVR) for each compound. The LVR was reevaluated after each aging time. Glass transition temperature versus aging time is plotted in Figure 10.

Significant changes in glass transition are particularly useful in evaluating the stability of HNBR compositions. Any degradation of the acrylonitrile segments tends to decrease the glass transition temperature as observed by Hertz and Farinella⁶.

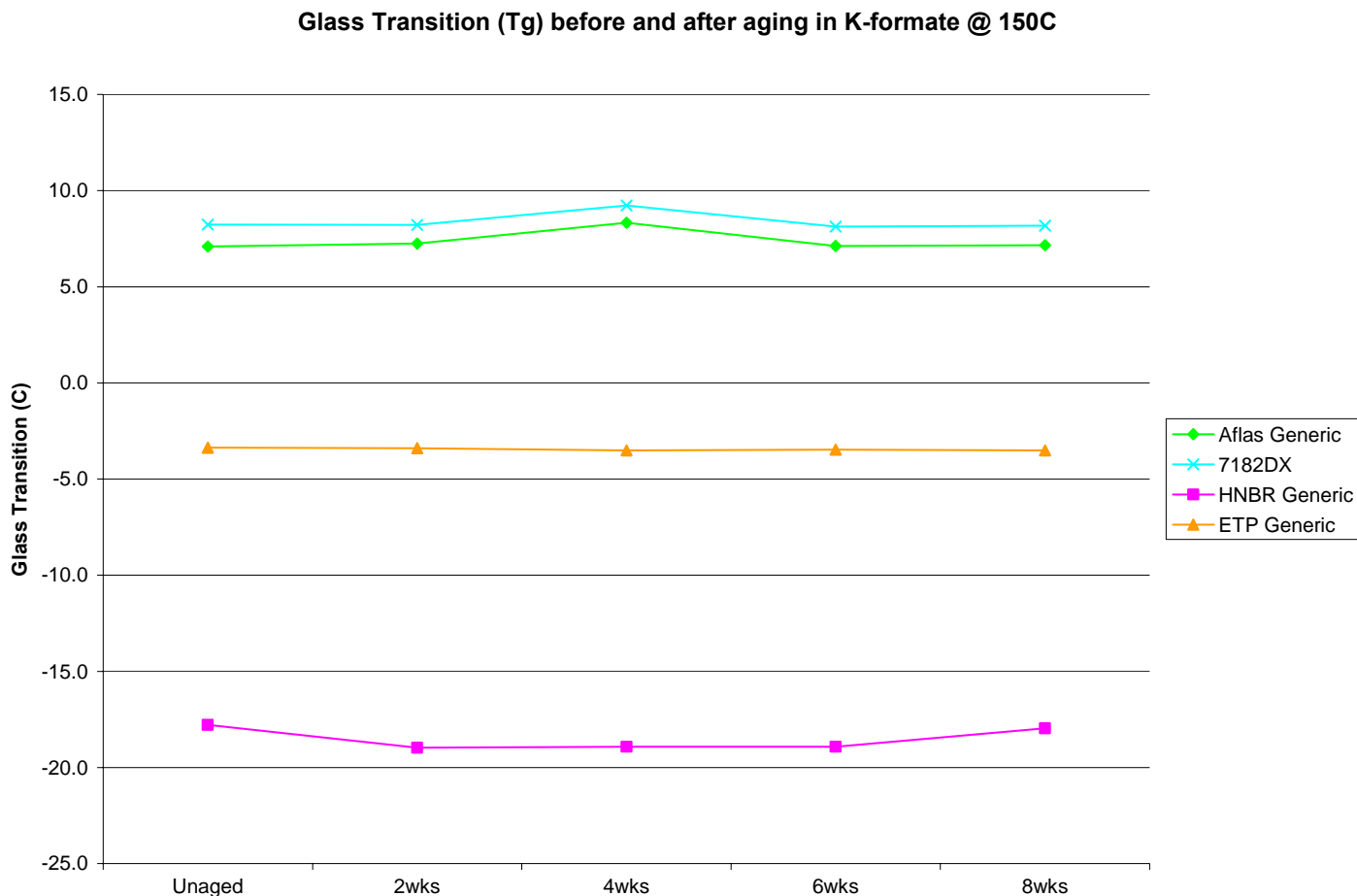


Figure 10: Glass Transition Temperature, T_g vs. Aging Time

FTIR ANALYSIS

Infrared spectra were collected from samples of the axially compressed test o-rings. Scans are included of the surface (exterior) of the seal (exposed to potassium formate) as well as the interior of the sample after slicing with a clean razor blade. Surface scans may include residue of the test fluid from direct contact. Spectra associated with the interior are due to chemical change of the elastomer and/or diffusion of the fluid through the surface into the bulk material. Only one material, HNBR, exhibited significant changes in spectra obtained from the interior. Interior spectra of the other materials are thus omitted.

Multiple spectra included on a single chart are shown on an offset scale. In other words, they share the same relative scale for absorbance, but not a common origin. Spectra from unaged samples are plotted at the bottom of the y-axis. As the aging period increases, spectra are presented further up the y-axis such that spectra from unaged material are at the bottom, then 2-weeks, 4-weeks, 6-weeks, and finally spectra from material aged 8-weeks is at the top.

Data shown are for spectra collected using the Attenuated Total Reflectance (ATR) method. Axes are percent absorbance versus wave length (cm^{-1}). Exterior / interior scans are shown for each material in figures 11 through 14 below.

Aflas:

No remarkable changes in FTIR spectra were observed on scans of the interior of Aflas specimens. Thus, the spectrum was not included.

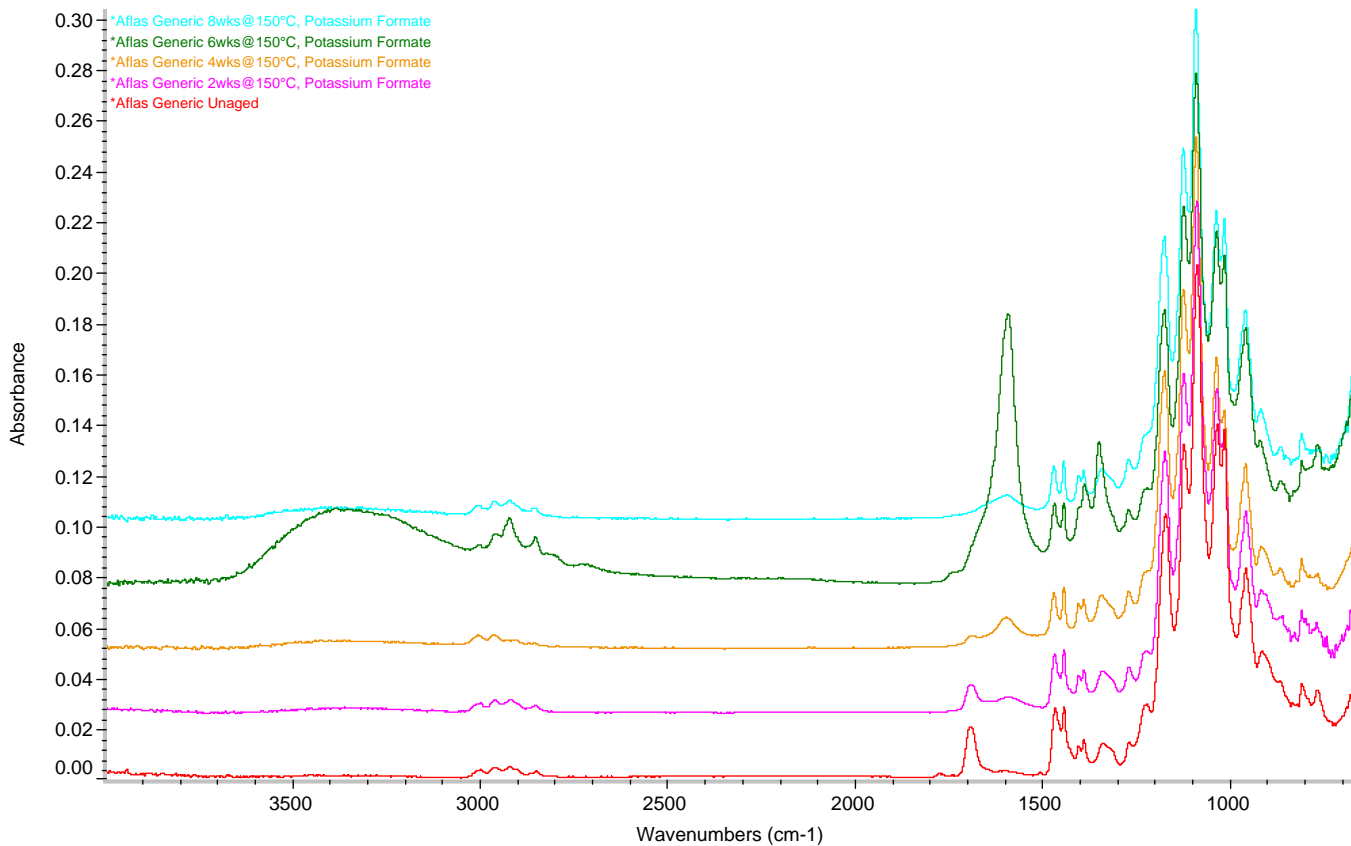


Figure 11: Exterior Infrared Spectra for Aflas aged 0, 336, 672, 1008, 1344 Hours

On the exterior of Aflas specimens, carboxylic acid (R-COOH) presence was indicated after 6-weeks aging by absorbance associated with the hydroxyl ($-\text{OH}$) in a broad band around 3300 cm^{-1} and pronounced absorbance around 1590 cm^{-1} , indicative of carboxylate ions ($-\text{COO}^-$). Absorbance at 1390 and 1350 is indicative of carbonyl (CO^-) ions.

The reduction of absorbance at and $1690 \pm 5 \text{ cm}^{-1}$ (unsaturated rings containing C=O groups) reflects the decrease of the cyclic feature, which indicates a degradation of the TAIC structure.

7182DX Aflas:

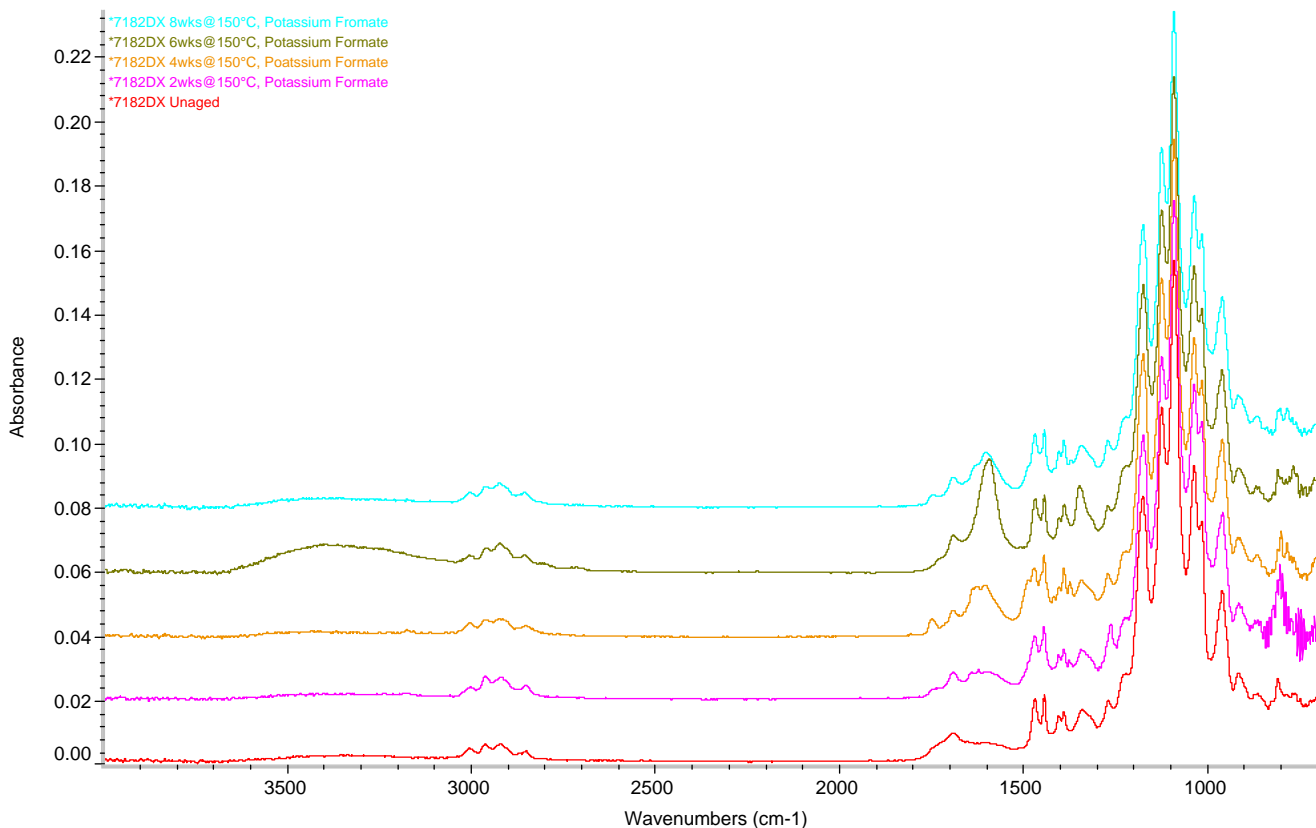


Figure 12: Exterior Infrared Spectra for 7182DX Aflas aged 0, 336, 672, 1008, 1344 Hours

Spectra associated with 7182DX (a proprietary aflas compound) is similar to that observed in the generic Aflas but with less intensity. At 6-weeks aging, carboxylic acid (R-COOH) presence was indicated by absorbance associated with the hydroxyl (-OH) in a broad band around 3300 cm⁻¹ and absorbance around 1590 cm⁻¹, indicative of carboxylate ions (-COO⁻). Absorbance at 1350 is indicative of carbonyl (CO⁼) ions.

ETP:

No remarkable changes in FTIR spectra were observed on scans of the interior of ETP specimens. Thus, the spectrum was not included.

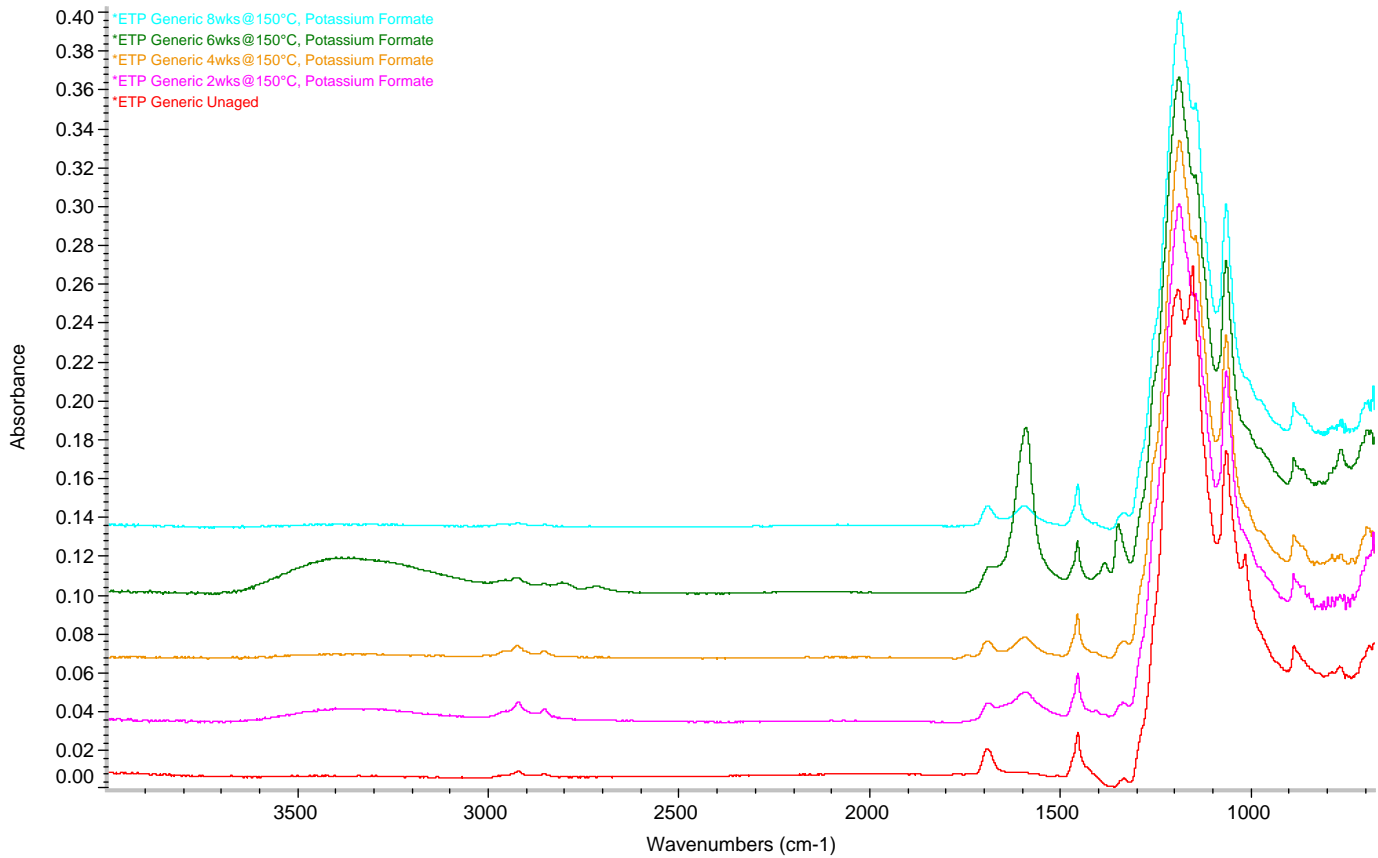


Figure 13: Exterior Infrared Spectra for ETP aged 0, 336, 672, 1008, 1344 Hours

Absorbance at 1590 cm⁻¹ is indicative of a carboxylate ion (-COO⁻). Absorbance at 1350 is indicative of carbonyl (CO⁼) ions.

HNBR:

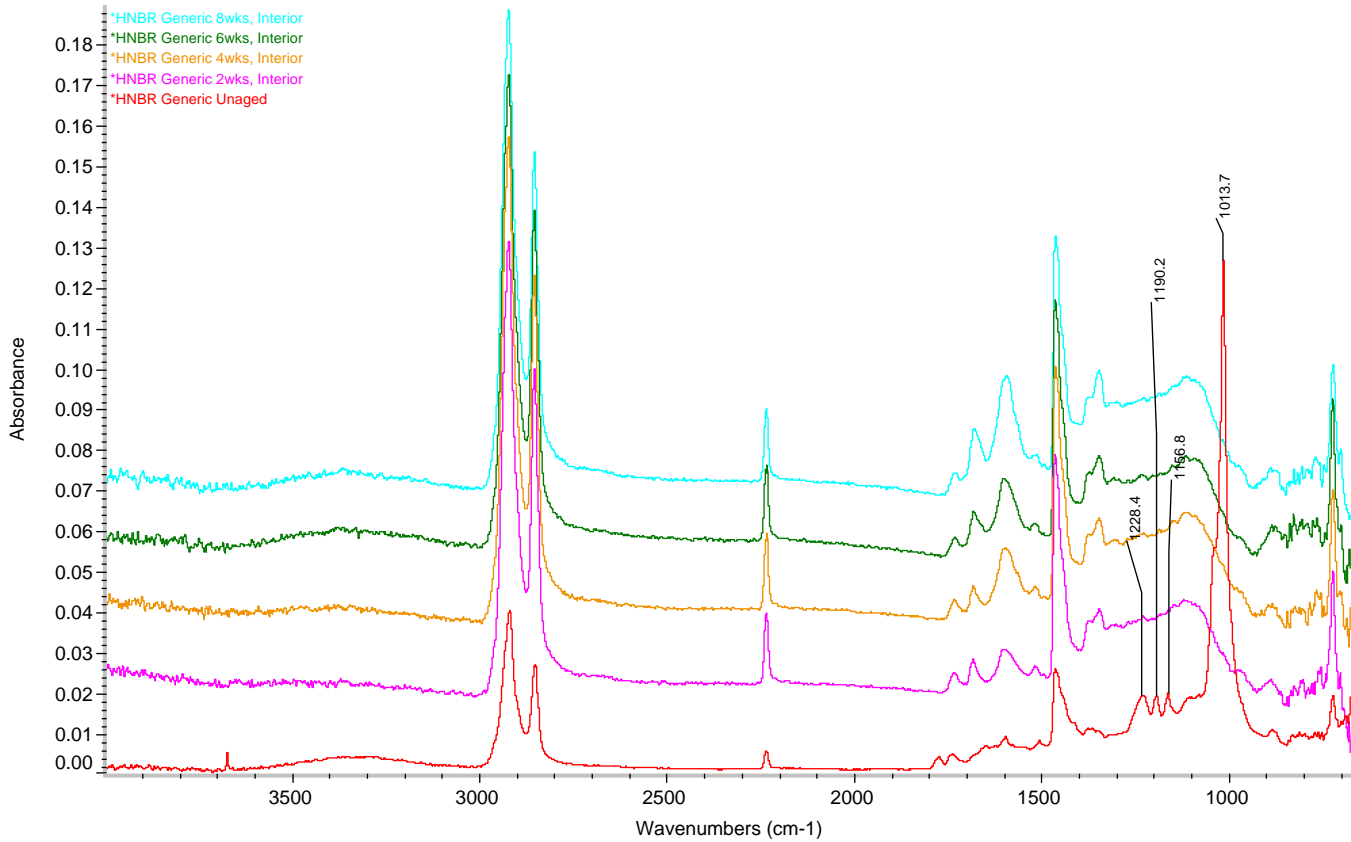


Figure 14: Interior Infrared Spectra for HNBR aged 0, 336, 672, 1008, 1344 Hours

Cursory review of spectra obtained from the interior of HNBR samples indicates that potassium formate readily permeates an HNBR composition. Increased absorbance in the region of $2850-2915\text{ cm}^{-1}$ indicates an increase in CH_2 and CH_3 groups possibly attributable to protonation of unsaturated sites and chain scission. Pronounced absorbance in the region $1560-1590\text{ cm}^{-1}$ ($-\text{COO}^-$, triazine) could be attributable to presence of formate. Absorbance at 1470 cm^{-1} ($-\text{CH}_2$) offers additional confirmation of an increase in methylene groups. Absorbance in the region of $1400 - 1440\text{ cm}^{-1}$ ($-\text{COOH}$) could be attributable to hydrolysis of nitrile groups to carboxylic acid. A pronounced reduction in absorbance at 1014 cm^{-1} (ether). This could be attributed to a breakdown of the acrylate (SR 350) used to cure the material. Significant instability observed by 2-weeks.

Spectra obtained from the exterior was not included since it is readily apparent that potassium formate both soluble within and reactive with HNBR.

DYNAMIC MECHANICAL AND RHEOLOGICAL THERMAL ANALYSIS (DMRT) INTERPRETATION

Chemical attack by the fluids will logically take place at exposed surfaces of a seal and propagate through to the bulk of the material as diffusion and/or conversion of chemical species progresses. We thus assumed that the FT-IR surface changes would ultimately be representative of the elastomeric bulk phase. DMRT is a convenient and accurate way of measuring the viscoelastic response to these changes. By examining G' (elastic modulus), G'' (loss modulus), and $\tan \delta$, we gain insight on the elastomer's network changes such as an increase or decrease in crosslink density or chain scission.

Aflas:

**Aflas G' , G'' , Tan-delta
Unaged and after aging 8-weeks in K Formate @ 150C**

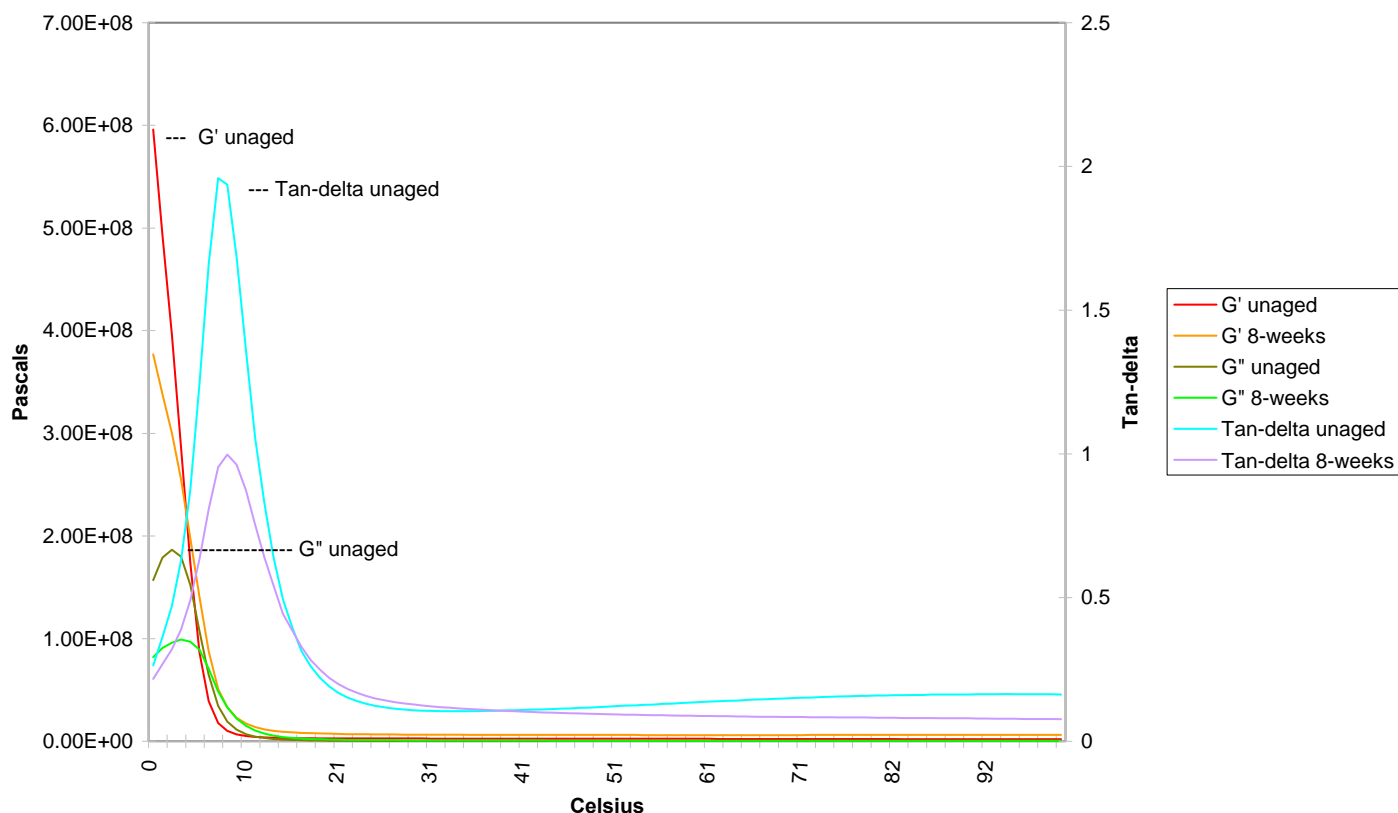


Figure 15: Aflas DMRT temp sweep, G' , G'' , Tan-delta

There appears to be significant reduction in storage modulus (G') and loss modulus (G'') at temperatures below the glass transition of Aflas or approximately 7°C. The glass transition remained un-changed at approximately -5°C. It is unlikely that this reduction in modulus can be attributable to solubility of the formate since no detection of such was found in interior FTIR spectra of aged samples. On the other hand, an increase in storage modulus of 150 to 300% is observed at temperatures above the T_g of Aflas (See Figure 16). The DMRT data confirms observed increase in strain energy density as well as the increase in tensile at break.

While the FTIR spectra suggest the TAIC ring structure has been compromised, it is clear that an alternative crosslink network has developed causing an increase in modulus.

Aflas G' and G'' Unaged and after aging in K Formate @ 150C

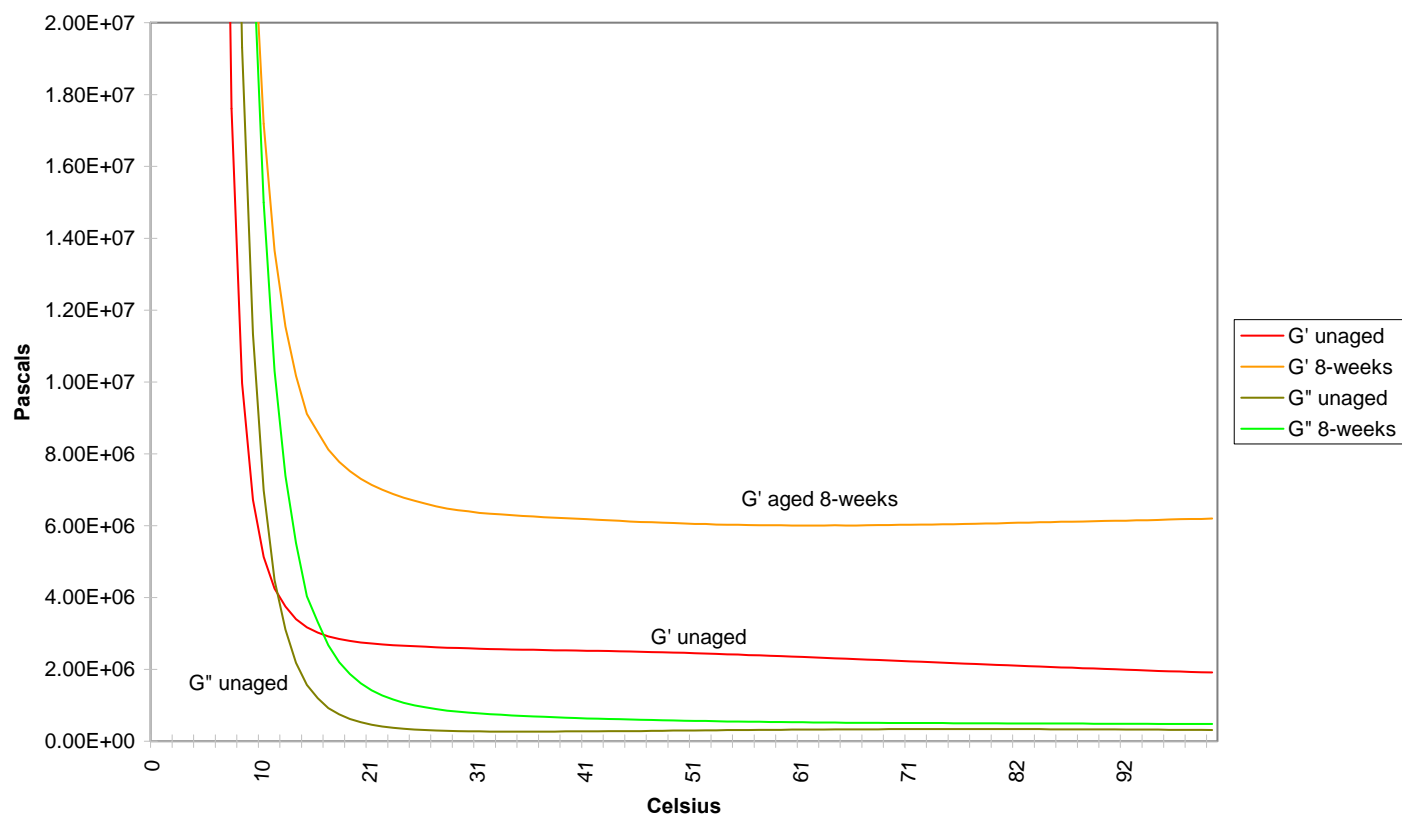


Figure 16: Aflas DMRT temp sweep, G', G''

7182DX:

7182DX: G', G'', and Tan-delta
Unaged and aged 8-weeks in K formate @ 150C

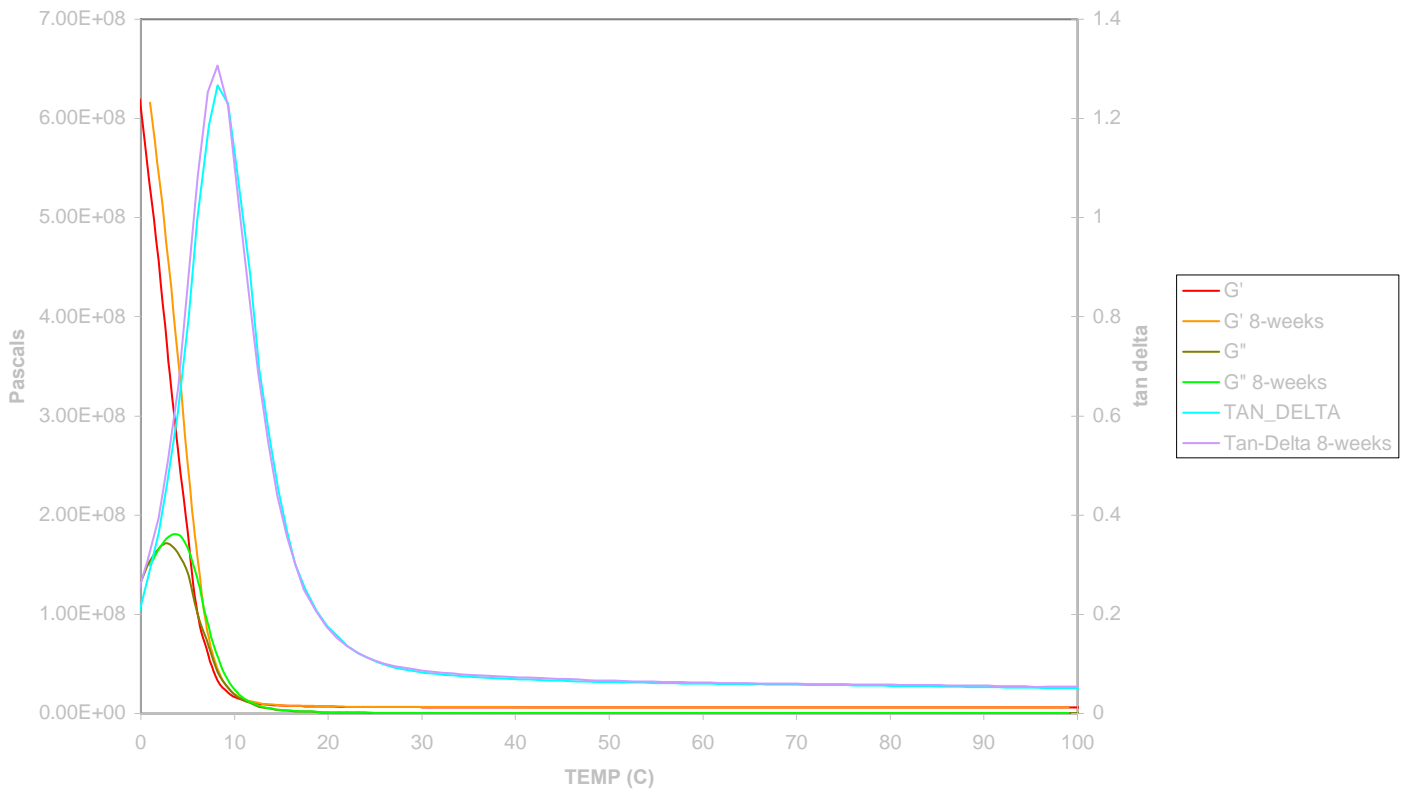


Figure 17: 7182DX Afas DMRT temp sweep, G', G'', Tan-delta

There are no remarkable differences observed in the DMRT analysis of aged and unaged 7182DX Afas. It can be concluded that the difference in cure network and saturation of the polymer play a significant role in retarding residual cure in the presence of formate. Further confirmation can be observed in the strain energy density data as well as a closer examination of G' and G'' in Figure 18.

The remarkable observation of this data is the difference it represents vis a vis a standard Afas composition.

7182DX G' & G''
unaged and after aging 8-weeks in K formate @ 150C

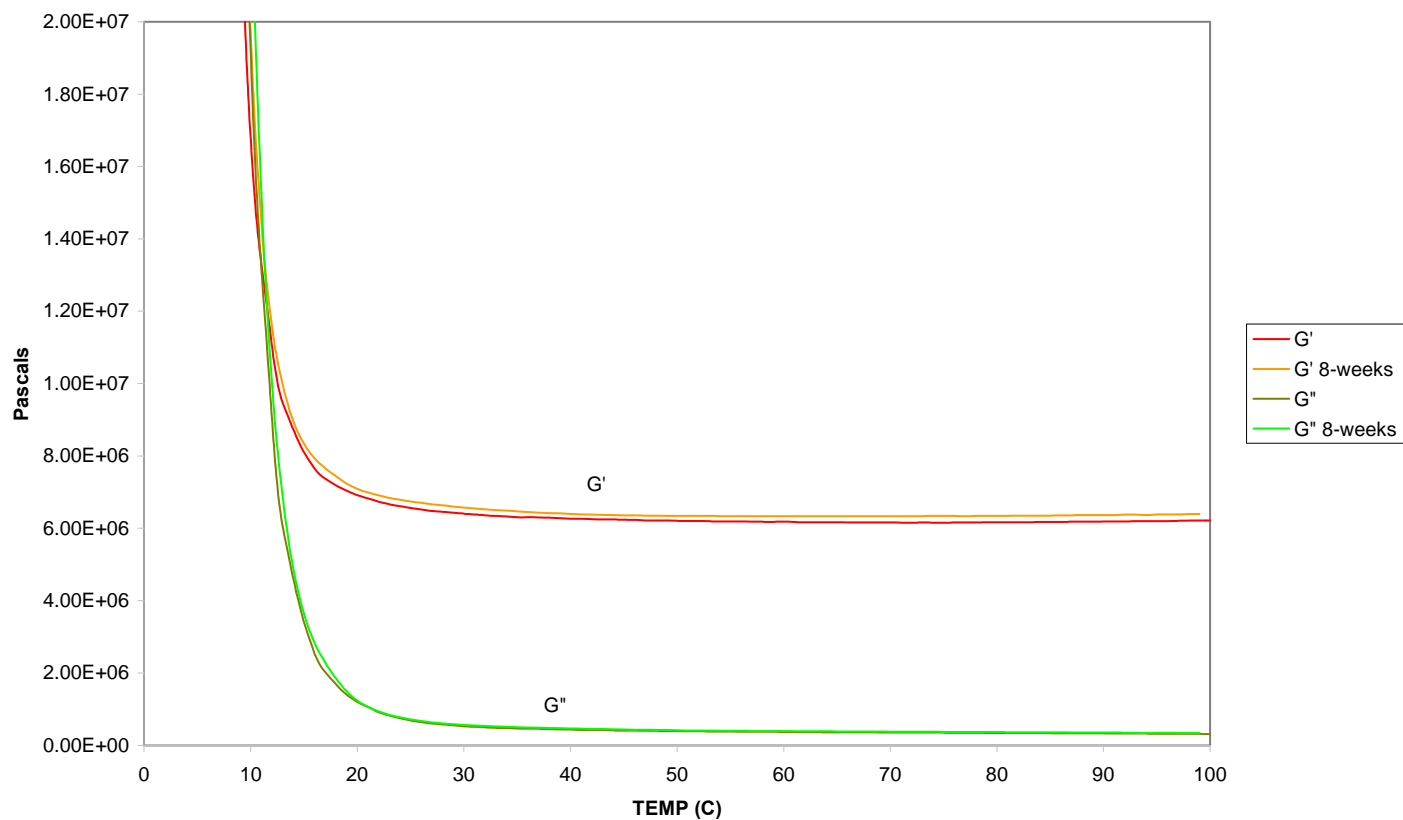


Figure 18: 7182DX Afas DMRT temp sweep, G', G''

ETP:

**ETP: G', G'', and Tan-delta
Unaged and after aging 8-weeks in K Formate @ 150C**

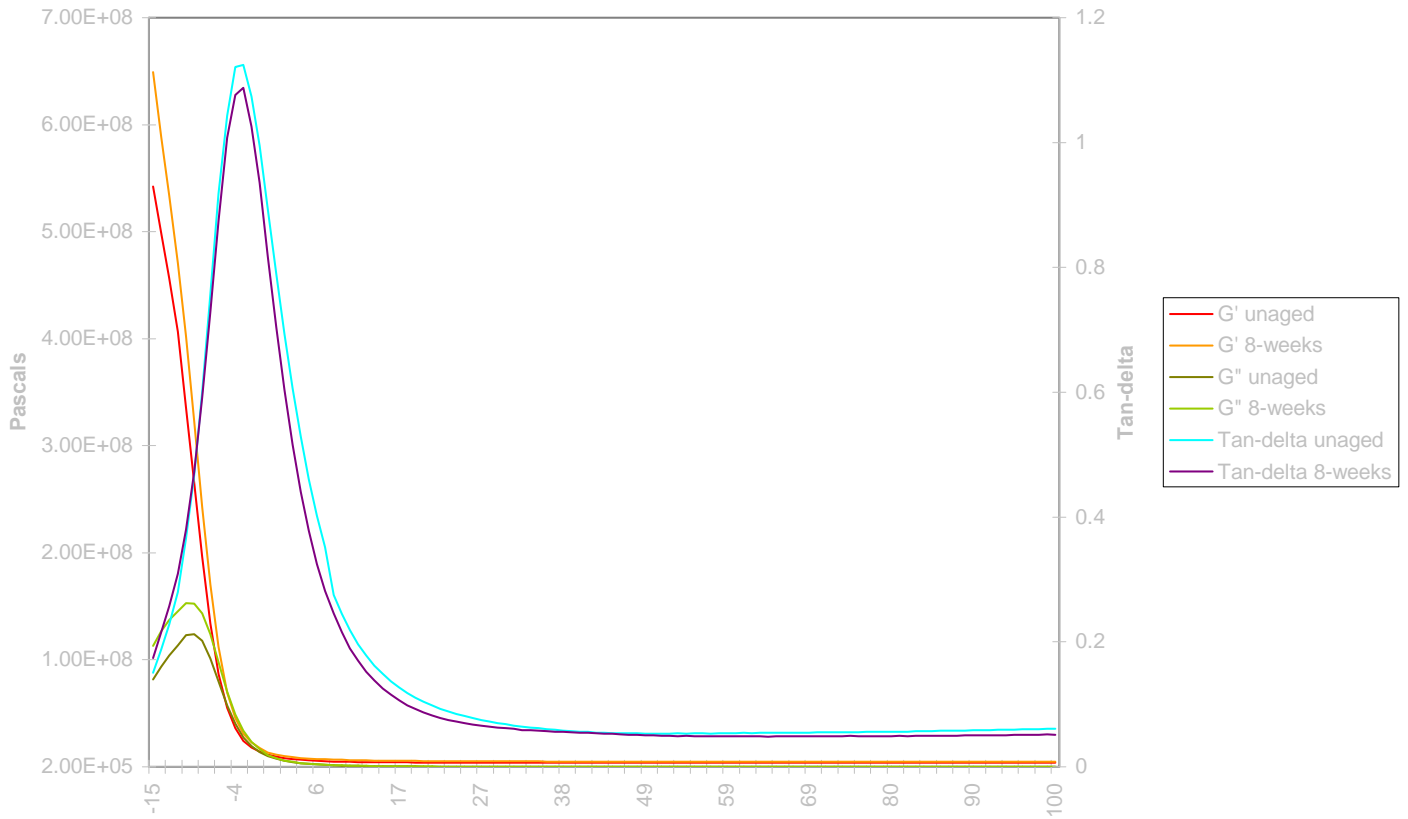


Figure 19: ETP DMRT temp sweep, G', G'', Tan-delta

There are few remarkable differences observed in a comparative temperature sweep between the unaged ETP and that aged 8-weeks in potassium formate. Storage modulus (G') Increased for the aged material both below and above the glass transition of this material (-4°C). The glass transition remained un-changed and no meaningful change in loss modulus (G'') was discernible. Similar to Aflas, there was an observed increase in storage modulus at temperatures above the material's glass transition point. However, only a 25% increase was observed as compared to the 150% – 300% increase observed with Aflas. The DMRT data indicates ETP as a mostly stable material in this environment.

ETP: G' & G''
Unaged and after aging 8-weeks in K Formate @ 150C

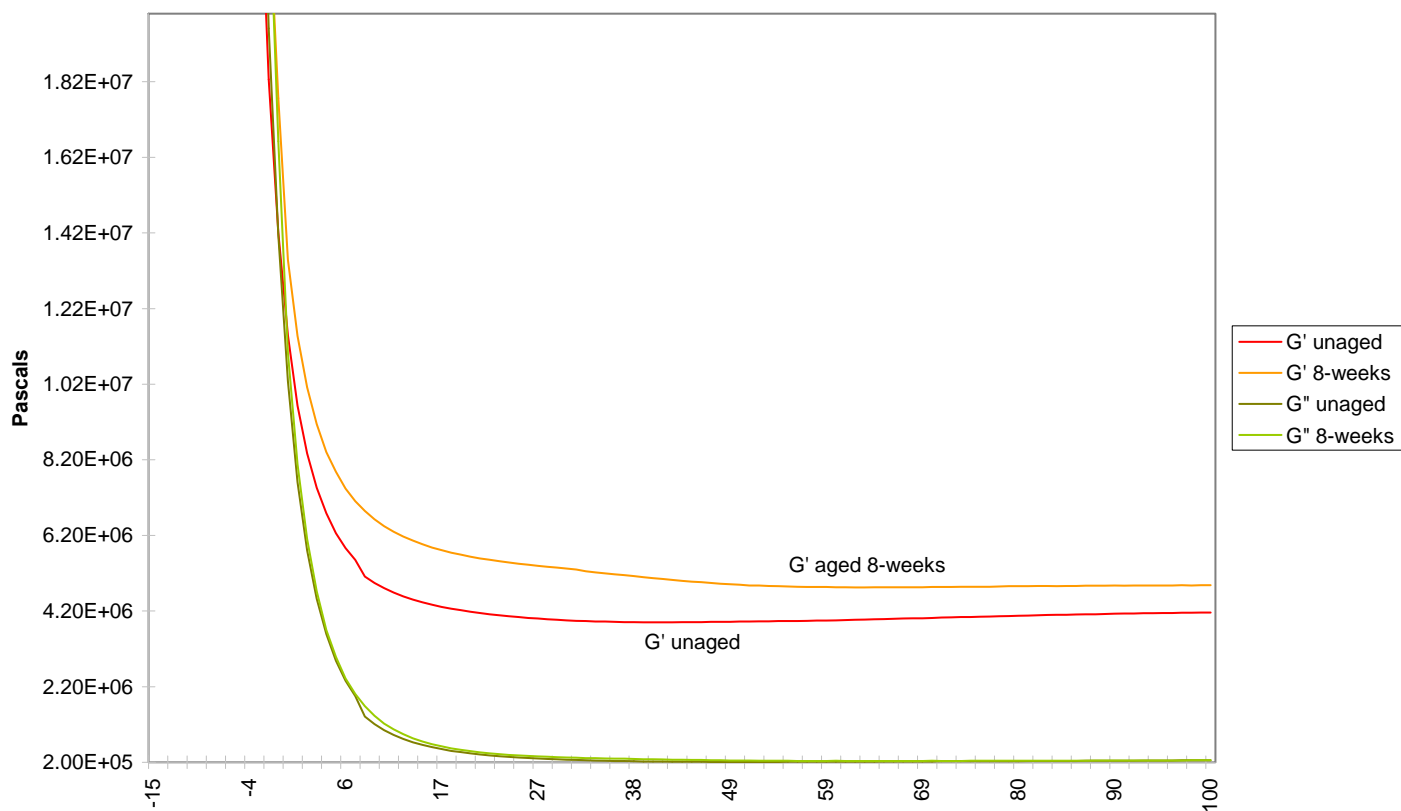


Figure 20: ETP DMRT temp sweep, G', G''

HNBR:

HNBR: G', G'', Tan-delta
Unaged and after aging 8-weeks in K Formate @ 150C

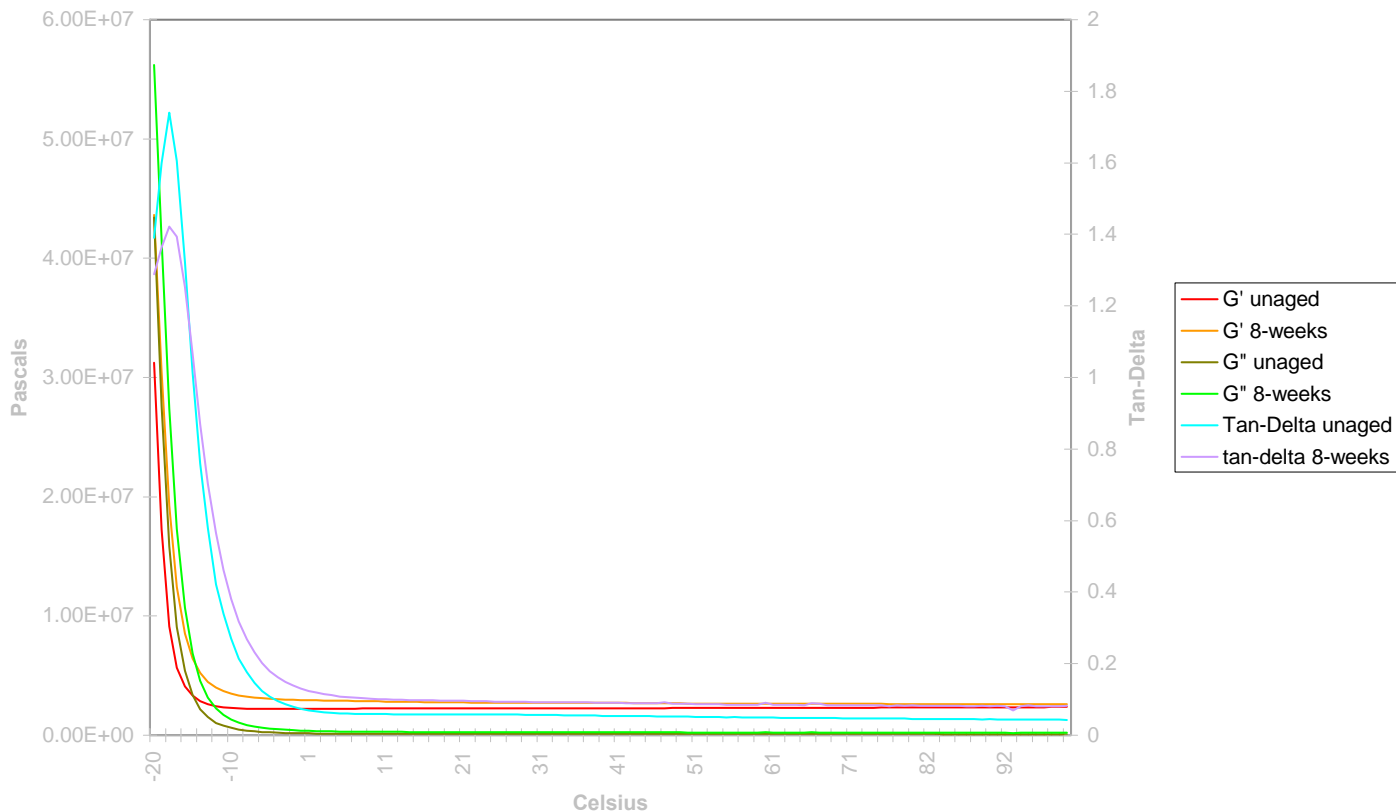


Figure 21: HNBR DMRT temp sweep, G', G'', and Tan-delta

The storage and loss modulus of HNBR after aging in potassium formate by 8 weeks exhibited a distinct increase in modulus. The increase was most pronounced at lower temperatures and tended to diminish as temperature increased. This viscoelastic behavior suggests that additional intra-molecular attraction may have developed via protonation of unsaturated sites and hydrolysis of acrylonitrile segments⁷.

HNBR: G', G"
Unaged and after aging 8-weeks in K Formate @ 150C

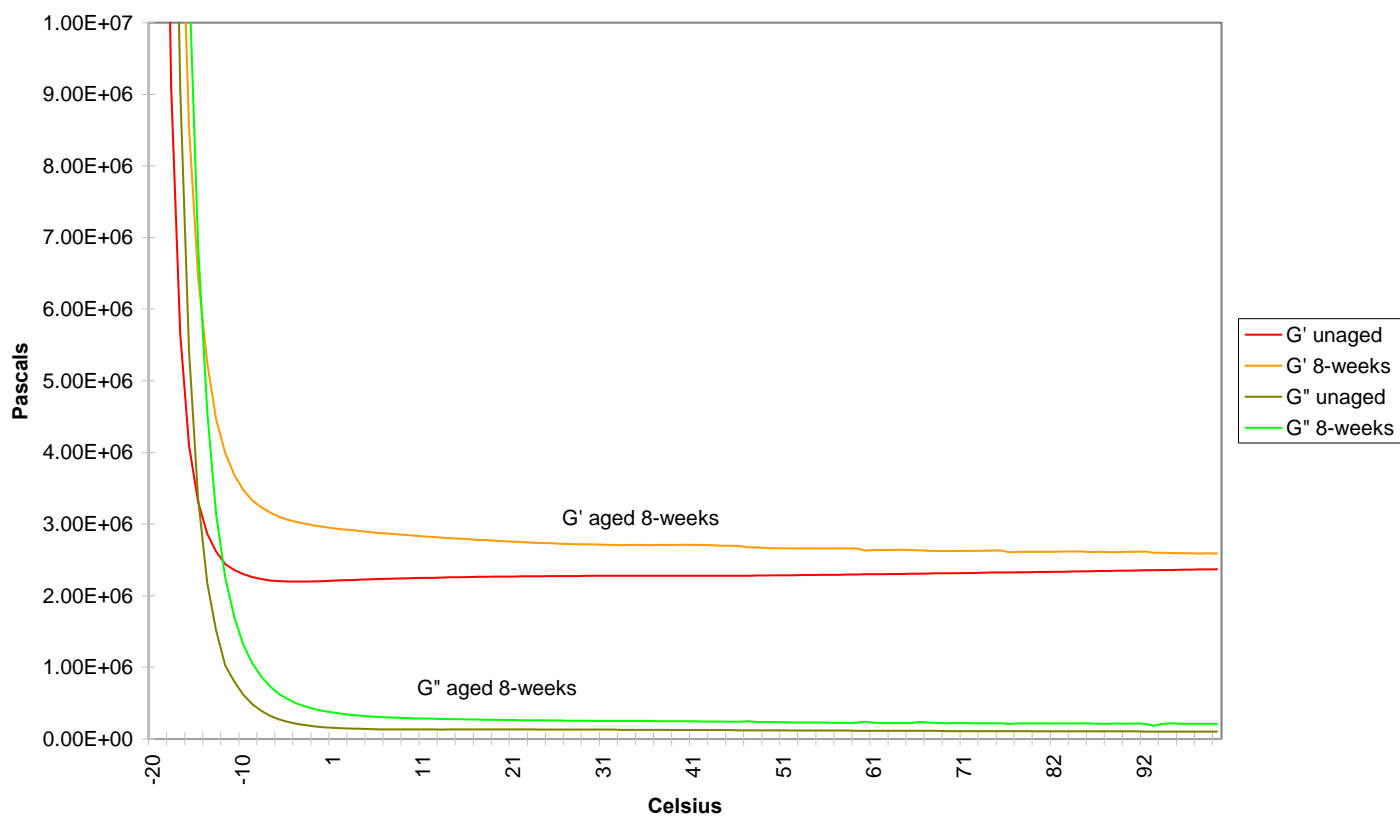


Figure 22: HNBR DMRT temp sweep, G', G''

ELASTOMER SUMMARY

Aflas

Test Type	Comments – observation over an 8-week (1,344-hour) period	8-week rating 1- best 4-worst
Tensile at Break (TAB)	12% to 31% change	2
Elongation	-30% to -5% loss in elongation.	4
Durometer	0 to +1 point gain in Shore-M hardness	2
Strain Energy Density (SED)	50% increase in SED.	2
Compression Set	Highest compression set, exceeding 100% by end of study.	4
Contact Stress	35% to 45% retention of contact stress. Lowest retained contact stress.	4
Glass Transition Point	7 to 8°C	-
FTIR	Interior: stable; Exterior: 1590 cm ⁻¹ (-COO ⁻), 1390 & 1350 cm ⁻¹ (CO ⁻). Interaction observed by 6 weeks.	3
DMRT	Significant change in storage modulus	4

Table 4: Aflas Results

7182DX Aflas

Test Type	Comments – observation over an 8-week (1,344-hour) period	8-week rating 1- best 4-worst
TAB	19% to 33% change	4
Elongation	-15% to +5% change in elongation over 8-weeks.	3
Durometer	+2 to +3 point gain in Shore-M hardness	3
Strain Energy Density (SED)	40% increase in SED. The most stable SED reading of the 4 tested materials.	1
Compression Set	Stable at 40% up to 6 weeks; subsequent increase to 75%. Lowest compression set of 4 tested materials.	1
Contact Stress	60% to 73% retention of contact stress. Highest retained contact stress.	1
Glass Transition Point	8 to 9°C	-
FTIR	Interior: stable; Exterior: 1590 cm ⁻¹ (-COO ⁻), 1390 & 1350 cm ⁻¹ (CO ⁻). Interaction observed by 6 weeks.	2
DMRT	Nominal changes in modulus	1

Table 5: 7182DX Aflas Results

HNBR

Test Type	Comments – observation over an 8-week (1,344-hour) period	8-week rating 1- best 4-worst
TAB	12% to 33% change	3
Elongation	2% to 15% increase in elongation over 8-weeks.	1
Durometer	+1 to +5 point gain	4
Strain Energy Density	50% to 100% increase in SED. Largest change of 4 materials.	3
Compression Set	Steady increase in compression set exceeding 80% by 8 weeks.	2
Contact Stress	50% to 70% retention of contact stress	2
Glass Transition Point	-18 to -19°C	-
FTIR	Interior & Exterior: increased absorbance 2850-2915 cm ⁻¹ (CH ₂ , CH ₃), 1560-1590 cm ⁻¹ (-COO ⁻ , triazine), 1470 cm ⁻¹ (-CH ₂), 1350 cm ⁻¹ (CO ⁼), Reduced absorbance at 1014 cm ⁻¹ (ether). Instability observed by 2-weeks.	4
DMRT	Increase in storage modulus that decreases as temperature rises.	3

Table 6: HNBR Results

ETP

Test Type	Comments	8-week rating 1- best 4-worst
TAB	3% to -6% change	1
Elongation	0% to 15% loss in elongation.	2
Durometer	0 to +1 point gain	1
Strain Energy Density	50% increase in strain energy density.	3
Compression Set	Relatively stable between 80% to 90% compression set.	3
Contact Stress	50% to 70% retention of contact stress.	3
Glass Transition Point	-3.5°C	-
FTIR	Interior: stable; Exterior: 1590 cm ⁻¹ (-COO ⁻), 1350 cm ⁻¹ (CO ⁼). Interaction observed at 6 weeks.	1
DMRT	Minor increase in storage modulus observed.	2

Table 7: ETP Results

DISCUSSION

Table 8 offers a comparative view of the elastomers studied. The ratings are relative from best to worst. Two observations are immediately apparent.

First, there is a remarkable difference in performance between a “standard” Aflas and one utilizing a more sophisticated cure, particularly when evaluated under compression or at low to moderate strain. Thus, considerable care should be taken categorizing elastomers by brand polymer alone.

Second, traditional evaluations such as change in durometer, change in tensile, and change in elongation can suggest selection of a particular material. Two of these three attributes are derived under tension and extreme strain. These attributes do not reflect product performance within reasonable design considerations unless the engineered component is in fact serving under sever tension. Consequently, a product’s performance, if selected using these evaluations, may not be consistent with material evaluation results.

Rating for Attribute Retention 1-best ... 4-worst					
Mode	Attribute	Aflas	7182DX	HNBR	ETP
Shear/Compression					
	Durometer - Δ	2	3	4	1
Tension					
	Tensile at Break - % Δ	2	4	3	1
	Elongation at Break - % Δ	4	3	1	2
	Strain Energy Density - %Retained	2	1	4	3
Compression					
	Compression Set	4	1	2	3
	Contact Stress - % Retained	4	1	2	3
Shear					
	DMRT – Stability	4	1	3	2
Molecular					
	FTIR - Stability	3	2	4	1

Table 8: Comparative Results

CONCLUSION

Evaluating elastomers for long term service in aggressive media, such as formates, requires appropriate performance measurements. For instance, traditional criteria such as change in tensile, elongation, and durometer will suggest the use of one material while evaluating criteria more closely focused on retention of viscoelastic behavior, compression set, and relative stability of the molecular network suggests the selection of an alternative material. Unfortunately, basing an elastomer selection on traditional criteria can deliver an inferior material for long term service.

For example, in evaluating elastomers for use potassium formate on the basis of changes in durometer, tensile, and elongation, an ETP composition is clearly a superior selection. If the application is one primarily operating under tension, there is no issue. However, if the application involves a design under compression, and if retention of viscoelastic characteristics within typical design guidelines is important, a “high-performance” Aflas composition would be an appropriate selection.

Care should be taken not to make sweeping generalizations regarding a particular class of polymer. For instance, a general Aflas composition was perhaps the worst elastomer evaluated in this study. However, that same base polymer, with modifications in its ultimate composition and manufacture, delivered a “best-in-class” performance when evaluated upon the criteria of resistance to compression set, compressive stress relaxation, and retention of viscoelastic characteristics within typical design guidelines.

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REFERENCES

¹ Hertz, D.L. Jr., Farinella, A.C., and Bussem, H., "Elastomer Service Life Prediction in Organic Acid Coolants", Paper 2001-01-1179, (SAE 2001)

² R.S. Auda, D.R. Hazelton, "Ethylene Propylene Elastomer technology for Improved High Temperature Serviceability", Elastomers Technology Div., Exxon Chemical Co., Paper No. 750962.

³ Hertz III, D. L. "Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density", Rubber Division, American Chemical Society, Paper No. 28 (May 2005).

⁴ ASTM Standard D 1414 – 94 (Reapproved 1999), "Standard Test Methods for Rubber O-rings", *Annu. Book ASTM Stand.* **09.02**, 53 (2003).

⁵ ASTM Standard D 395 – 02, "Standard Test Methods for Rubber Property – Compression Set", *Annu. Book ASTM Stand.* **09.01**, 42 (2003).

⁶ Hertz, D.L. Jr., Bussem, H., and Farinella, A.C., "Long-Term Testing of Base Resistant Elastomers (BRE) Suitable for Power Cylinder Systems", Paper 2000-01-0923, (SAE 2000).

⁷ Jones, M., "Organic Chemistry", W.W. Norton & Company, 1032-34 (1997).