

# **EFFECTS OF LOW TEMPERATURE ON THE CONTACT STRESS OF HIGH TEMPERATURE SERVICE ELASTOMERS**

Oilfield Engineering with Polymers  
7<sup>th</sup>-8<sup>th</sup> October 2008  
Cavendish Conference Centre  
London, England

**Hertz, D.L. III**  
Seals Eastern, Inc.

## **Abstract**

Operating temperature is an increasingly important factor in the selection of an elastomer for use in the oilfield. Most elastomer specifications are written to ensure preservation of mechanical properties after being subject to elevated temperature. However, the application engineer frequently finds himself with an elastomer selection that satisfies thermal stability, solubility, and modulus issues, but is poorly documented regarding suitability as a sealing material at cold temperature.

The viscoelastic response of a sealing material at low temperature is usually critical. The glass transition (“Tg”) attribute of elastomers is often used as a “rough” indicator of seal performance at lower temperatures. However, in the realm of “extreme” operating environments (e.g. aggressive chemicals, high temperature), using this attribute as a selection criteria may eliminate viable material alternatives from an already too short list of alternatives.

At low temperature, contact stress and the integrity of the sealing interface ultimately define whether a seal will work. The objective of this test program was to analyze the relationship of temperature and contact stress vis a vis the glass transition point of several materials. Empirical data was gathered using TMA, DSC, and DMRT to profile viscoelastic response and Tg of the elastomer. Contact stress data was obtained with the use of an environmental chamber utilizing pressurized air and pressure transducers to evaluate the rubber at specific low temperatures.

## **Table of Contents**

<b>SEALS EASTERN, INC.</b>	<b>1</b>
<b>ABSTRACT</b>	<b>1</b>
<b>INTRODUCTION</b>	<b>3</b>
<b>EXPERIMENTAL</b>	<b>4</b>
<b>A. Objectives</b>	<b>4</b>
<b>B. Experimental Method</b>	<b>4</b>
1. Scope	4
2. Subject Materials	4
3. Data Acquisition	5
i. TMA	6
Experimental	6
TMA Results Summary	6
ii. DSC	7
Experimental	7
DSC Results Summary	7
iii. DMRT	8
Experimental	8
DMRT Results Summary	8
iv. CONTACT STRESS	10
Experimental	11
Contact Stress Results Summary	11
<b>RESULTS</b>	<b>13</b>
<b>ELASTOMER SUMMARY</b>	<b>13</b>
<b>DISCUSSION</b>	<b>15</b>
<b>CONCLUSION</b>	<b>16</b>

## Introduction

In 1934, the Journal of Research, of the National Bureau of Standards published a paper that documented the change in volume of rubber with change of temperature. A smaller coefficient of expansion was observed below the phase transition temperature of amorphous polymers (aka rubber, elastomer) than was measurable above the same transition temperature. This phenomenon, previously documented, was measured using a mechanical apparatus designed to measure change in volume relative to temperature.<sup>i</sup> This measurable change in phase is now known as the glass transition phase (“Tg”).

This finding is relatively unremarkable in the context of our polymer knowledge base today. Treloar states

“The rubber-like state ... depends on the possibility of random thermal motion of chain elements by rotation about single bonds in the chain backbone. In any real material rotation cannot be completely free from restrictions imposed by the presence of neighboring groups of atoms .... The degree of freedom of rotation will be a function of the relative values of the thermal energy of the rotating group and the potential barrier that has to be overcome in order that rotation may occur. The probability that a given group will have sufficient energy to enable it to surmount a potential barrier  $\epsilon$  will be governed by a Boltzmann factor of the type  $\exp(-\epsilon/kT)$ , and will therefore increase rapidly with increase in temperature. Conversely, on lowering the temperature a point will be reached at which rotation will no longer take place at an appreciable rate.”<sup>ii</sup>

The physical result of colder temperatures is a dramatic increase in modulus and a reduction in thermal expansion. This phenomenon is easily measured using dynamic mechanical testing.

In the application of rubber to seals, the significance of Tg to seal performance has been generally recognized but not well understood. In the application of fluoroelastomers, interests have centered on high temperature characteristics and chemical compatibility. However, HTHP production in the oilfield can involve operation in cold deep waters or other cold operating environments. Thus, sometimes oil tools and apparatus using seals designed to handle 150C+ fluids must additionally be able to seal at sub zero temperatures.

Over time, Tg has come to be viewed as the lower limit below which a sealing material can no longer successfully operate. However, in system qualification testing, we often witness seals performing successfully at or below their Tg temperature. **Thus, the oxymoronic question invariably becomes “at how cold a temperature can my high**

**temperature sealing material operate?”** This paper explores empirical data that was compiled to either help answer or provide insight to this question.

## **EXPERIMENTAL**

### ***A. Objectives***

This study sought to determine the relationship, if any, of readily obtained phase transition data to a “high temperature” sealing material’s suitability at specific low temperatures of operation.

Furthermore, this study sought to quantify whether the glass transition temperature is a practical guide to a high temperature oilfield elastomers’s efficacy for operation at or below the determined glass transition temperature.

### ***B. Experimental Method***

#### **1. Scope**

This study involved the widely accepted, commercially available, high temperature sealing materials utilized in oil & gas operations. HNBR was included although its continuous high temperature service limit should not much exceed 150°C.

Fluoroelastomers specifically designed for cold temperature operation were not included in the study.

A material’s ability to maintain contact stress at a given temperature was observed only in the energized state. Contact stress was initiated at room temperature in all instances with the operating temperature subsequently decreased.

Contact stress was evaluated using air (atmospheric) only.

#### **2. Subject Materials**

Table 1 details the materials studied.

<b>Trade Name</b>	<b>Polymer</b>	<b>D1418 Designation</b>	<b>Referenced As</b>
AFLAS® 100H	TFE/P	FEPM	Aflas
Viton® Extreme	TFE/E/PMVE	FEPM	ETP
Zetpol® 2010	HNBR (36%ACN)	HNBR	HNBR
Viton® A	HFP/VDF	FKM Type 1	FKM-1
Viton® B	HFP/VDF/TFE	FKM Type 2	FKM-2

Table 1: Material Designations

The materials were uniformly compounded, as exhibited in Table 2, to the extent they could be practically cured, to best enhance differences associated with the polymer backbones. Molding was conducted at 165C with a cure cycle of 8 minutes. The Aflas was molded for 12 minutes. The manufacturers' recommended post cures were used.

<b>Aflas Formulation</b>		<b>ETP Formulation</b>		<b>HNBR Formulation</b>	
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	DIAK 7	3	Vanox ZMTI	1.5
		Luperox 101XL45	3	Stearic Acid	0.5
				Vulcup 40 KE	6
				Sartomer SR 350	5

<b>FKM Type 1</b>		<b>FKM Type 2</b>	
Constituent	PHR	Constituent	PHR
Viton A	100	Viton B	100
MT Black (N990)	30	MT Black (N990)	30
Bisphenol Onium	2.5	Bisphenol Onium	2.5
High Activity Magnesium Dioxide	3	High Activity Magnesium Dioxide	3
Calcium Hydroxide	6	Calcium Hydroxide	6
VPA No. 3	1	VPA No. 3	1

Table 2: Subject Formulations

### 3. Data Acquisition

Attribute data was derived from the following instruments for the evaluation *infra*.

Test	Instrument / Device	Attribute
TMA	TA Instruments	Rate of Expansion
DMRT	Rheometrics Scientific ARES	Elastic Modulus, Loss Modulus, Tan-Delta, Glass Transition ("Tg")
DSC	TA Instruments DSC Q1000	Glass Transition
Contact Stress	Proprietary Apparatus	Contact Stress

Table 3: Instruments, Devices

### **i. TMA**

Thermal Mechanical Analysis (“TMA”) is frequently used to evaluate a material’s coefficient of linear thermal expansion. A change in the rate of expansion is usually observed at or near the glass transition of the material.

Molded rubber specimens based on AFLAS®, EPT, HNBR, Type 1 FKM and Type 2 FKM were submitted to AGC Americas for evaluation using TMA. The specimens used were 12.7 mm (½ inch) cubes cut from the center of post cured compression set buttons. Orientation of the specimen in the test fixture was through the thickness (molded surfaces).

### ***Experimental***

Each sample was tested in duplicate. The instrument used was a TA Instruments Q400 V7.4 TMA with a TA Instruments Mechanical Cooling Accessory. The following method sequence was used:

1. Rapid cool to -50°C
2. Equilibrate @ -50°C
3. Isotherm @-50°C for 10 minutes
4. Heat @ 5°C/minute to 210°C

Data was collected at the beginning of the 5°C/minute ramp from -50°C to 210°C.

### ***TMA Results Summary***

TA Instruments Universal Analysis software was used to analyze the data for rate of expansion and transition temperature inflection point. Results are tabulated in Table 4.

Base Elastomer of Compound	Rate of expansion below transition [ $\mu\text{m}/(\text{m}\cdot^\circ\text{C})$ ]	Transition temperature [ $^\circ\text{C}$ ]	Rate of expansion above transition [ $\mu\text{m}/(\text{m}\cdot^\circ\text{C})$ ]
AFLAS®	78.8	2.2	274.2
ETP	91.3	-8.7	341.5
FKM Type 1	53.3	-10.1	233.8
FKM Type 2	66.8	-3.4	262.9
HNBR	79.0	-22.4	201.4

Table 4: TMA Results Summary

The rate of expansion above the transition temperature is 2.5 to 4.5 times that observed below the transition temperature. Thus, as a material is cooling, at some point approximating the glass transition temperature, the rate of contraction will be considerably less than that observed prior.

## ii. DSC

A Differential Scanning Calorimeter (“DSC”) is frequently used to evaluate a material’s thermal properties including melt point and glass transition (“Tg”). The instrument measures heat flow to a sample and the sample’s temperature. One can then observe the absorption (endotherm) or release (exotherm) of energy in the form of heat flow. As the temperature moves above the phase transition of an elastomer, the rate of change in heat flow decreases. In this instance, DSC was used to ascertain the Tg independent of a frequency.

The subject materials were submitted to AGC for evaluation using DSC. Ten (10) mg specimens were cut from compression set buttons.

### *Experimental*

The instrument used was a TA Instruments DSC Q1000 with TA Instruments DSC Refrigerated Cooling System. The following method sequence was used:

1. Equilibrate @ -45°C
2. Isotherm @ -45°C for 2 minutes
3. Heat @ 10°C/minute to 200°C.

Data was collected at the beginning of the 10°C/minute ramp from -45°C to 200°C.

### *DSC Results Summary*

TA Instruments Universal Analysis software was used to analyze the data for the glass transition temperature as tabulated in Table 5 below.

Base Elastomer	Tg (D°C)
AFLAS	2.27
ETP	-10.03
FKM Type 1	-17.50
FKM Type 2	-8.71
HNBR	-24.99

Table 5: Tg per DSC

### iii. DMRT

“If a body is subjected to a forced sinusoidal oscillation of small amplitude, viscoelastic information may be obtained simultaneously. It is possible to deform the sample at a controlled stress and measure the strain, or the sample can be subjected to a controlled strain and the resulting stress measured.”<sup>iii</sup>

DMRT is a convenient and accurate way of measuring the viscoelastic response of an elastomer to changes. By examining  $G'$  (elastic modulus),  $G''$  (loss modulus), and  $\tan \delta$ , we gain valuable insight to an elastomer's response over time and temperature.  $T_g$  is considered that point at which a distinct peak in  $\tan \delta$  is observed.

#### ***Experimental***

Three (3) thermal sweeps were run from  $-15^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  at a frequency of 0.05 Hz. A 0.1% strain was applied. Temperature was reduced  $5^{\circ}\text{C}/\text{min}$ . Cylindrical specimens measuring 3.52 mm in diameter by  $\sim 30$  mm long were used.

#### ***DMRT Results Summary***

Base Elastomer	$T_g$ (C)
AFLAS	3.6
ETP	-3.2
FKM Type 1	-10.1
FKM Type 2	-3.7
HNBR	-19.2

Table 6:  $T_g$  per DMRT  $\tan \delta$

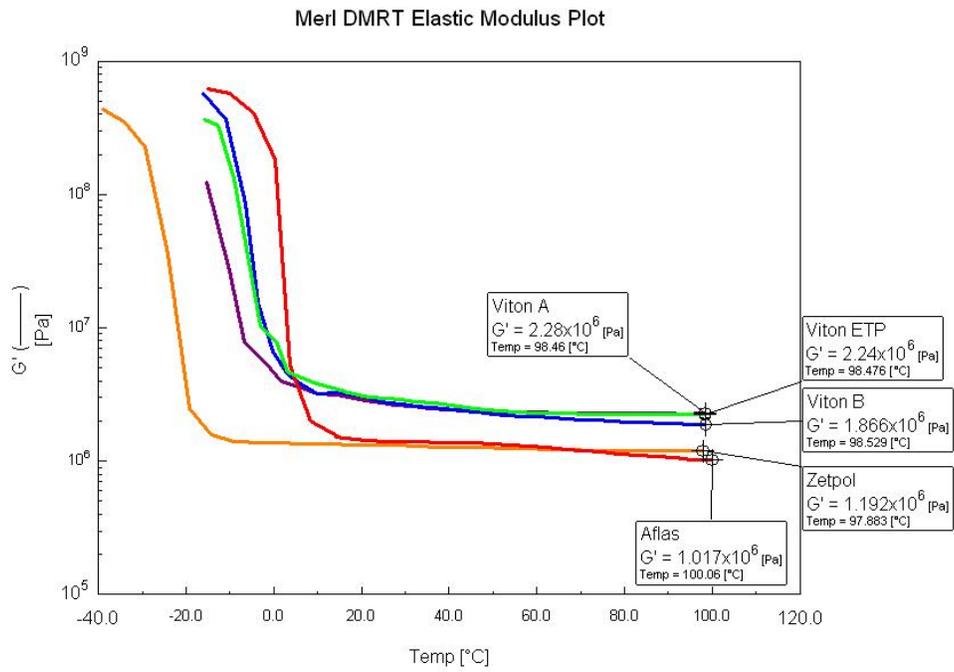


Figure 1: Elastic Modulus ( $G'$ ) per ARES DMRT  
.1 Hz, .01% Strain

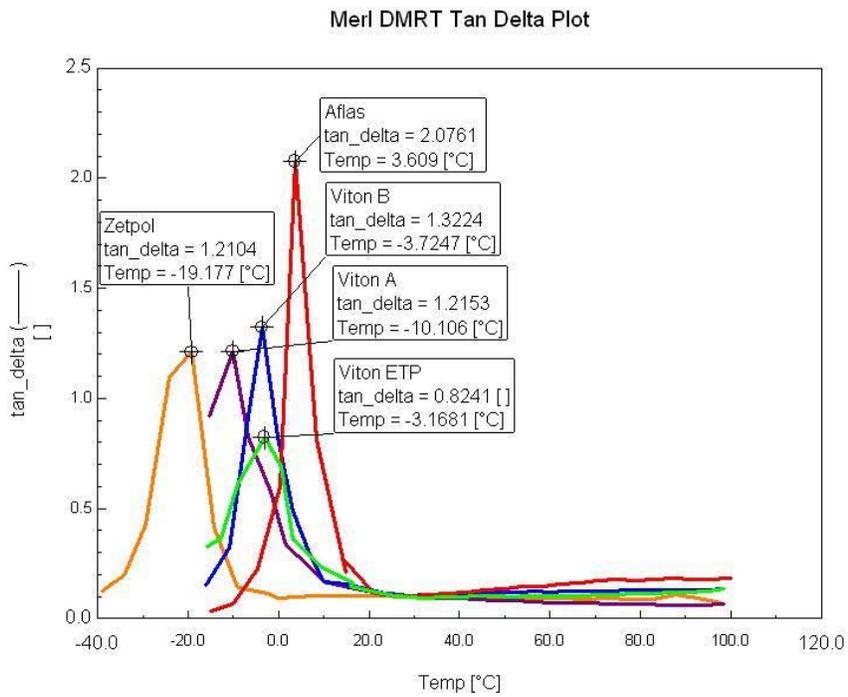


Figure2: Tan Delta per ARES DMRT.

#### iv. CONTACT STRESS

Contact stress was evaluated by measuring the amount of air pressure that can be sealed at a 0.8 mm (0.032 inch) orifice by a 6.35 mm (0.25 inch) cross-section molded sphere (see figure 3) that has been “compressed” upon the orifice by 25%. The premise is that the rubber sphere can only contain an air pressure equal to or less than to the contact stress.

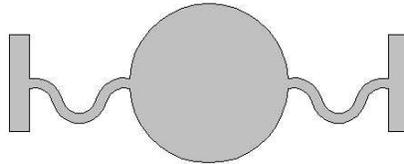


Figure 3: CSR Sample Cross Section

The contact stress fixture (figure 4) is screwed onto a manifold inside an environmental test chamber. The ports on the manifold are individually pressurized using 3.2 mm (1/8 inch) copper tubes of approximately equal length. The temperature is regulated, and air pressure monitored through a PLC. Air pressure, regulated to 3.45 MPa (500 PSI) max was applied and then allowed to bleed off until equilibrium with contact stress was attained. By measuring sealing pressure (contact stress) and its decline over time subject to a temperature, we could evaluate the response of a material and its ability to effectively seal gas at lower temperatures.

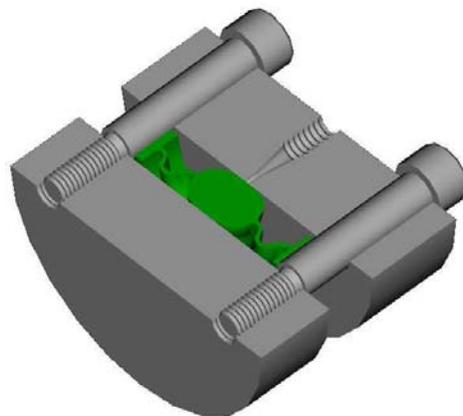


Figure 4: Contact Stress Fixture

The contact stress sample and fixture (Figures 3 and 4) provided results of actual sealing pressure (contact stress) over time at a specified temperature. Because of deliberate changes in temperature and the consequent changes in pressure, our interest was not

so much the absolute value of the contact stress, but the change in contact stress per incremental change in temperature over time (dP/dt) per equation 1.

$$\text{Eq. 1: } dP/dt = \sum ( P - P_i ) / \sum ( t - t_i )$$

Sudden increases in dP/dt were indicative of leaking more so than the thermal contraction of the gas or stress relaxation of the elastomer.

### ***Experimental***

Two separate experiments were run: one isothermal and the other involving a thermal decline. Three (3) data points per material were obtained over a 24 hour period. Each experiment involved pressurizing the pneumatic port behind the molded sphere until the pressure would exceed the capability of the seal, generally around 2.07 MPa (300 PSI). At that point, no more pressurized air was applied and the air pressure was allowed to equilibrate with the contact stress of the sphere. Each experiment allowed a one hour period at room temperature to allow for initial stress relaxation.

The thermal decline was run according to the tabulated schedule.

Temperature	Time (hrs)	Cum. Time (hrs)	Description
20C	1.0	1.0	Allow initial stress relaxation
20C -> 10C	0.5	1.5	Thermal decline
10C	4.3	5.8	Soak
10C -> 0C	0.5	6.3	Thermal decline
0C	4.3	10.6	Soak
0C -> -10C	0.5	11.1	Thermal decline
-10C	4.3	15.4	Soak
-10C -> -20C	0.5	15.9	Thermal decline
-20C	4.3	20.2	Soak
-20C -> -30C	0.5	20.7	Thermal decline
-30C	4.3	25.0	Soak

Table 7: Contact Stress thermal decline.

### ***Contact Stress Results Summary***

#### **Contact Stress Thermal Decline**

The derivative of the pressure verse time/temperature was chosen to help overcome a bias in the data associated with the gradual cooling of pressurized air and the consequent decrease in air pressure otherwise described by the ideal gas law. The derived data highlighted sudden reductions in contact stress (retained air pressure) attributable to a reduction in temperature beyond the materials' ability to respond (see figure 5).

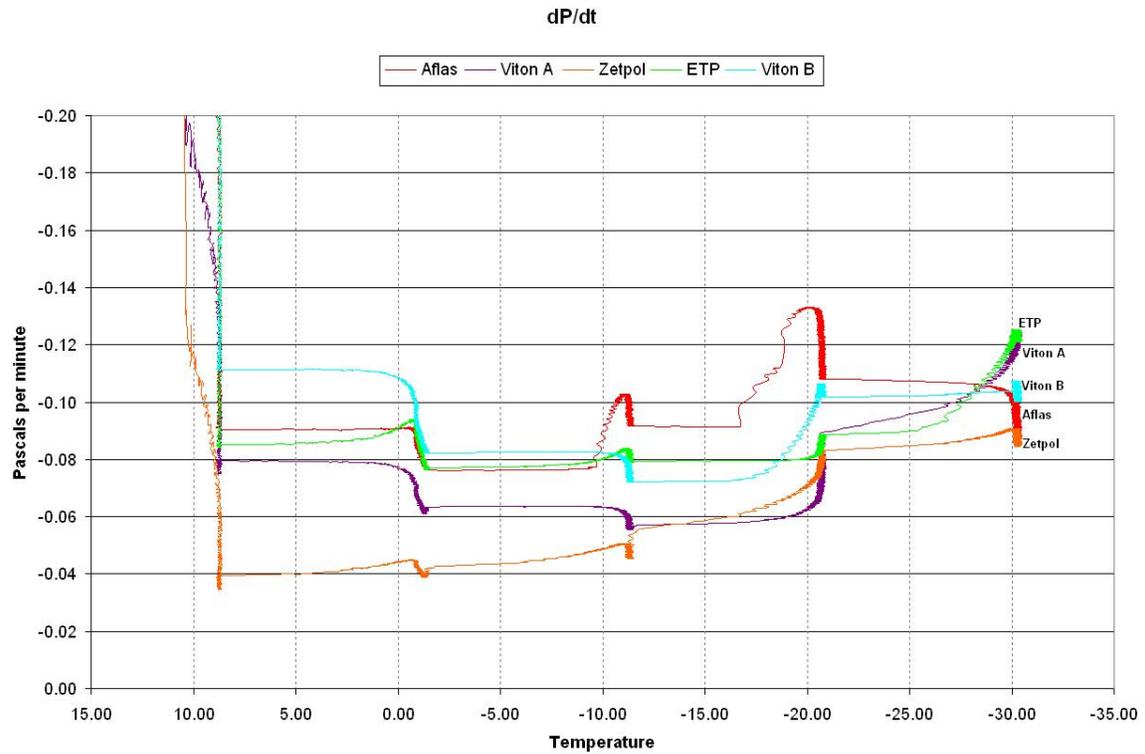


Figure 5: dP/dt of Contact Stress

The temperature at which the first appreciable increase in dP/dt was observed is noted in table 8 (hereinafter “dP/dt Increase Temp”).

Base Elastomer	dP/dt Increase Temp (°C)
AFLAS	-9
ETP	-23
FKM Type 1	-17
FKM Type 2	-16
HNBR	na

Table 8: dP/dt – Temperature at which first appreciable increase in the rate of pressure loss observed.

### **Isothermal Results –**

Twenty-four long hour isothermal tests were run at 0 °C, -10 °C, and -20 °C. After 24 hours of retaining a pressure differential, or attempting to, the number of ports retaining pressure and those having failed were recorded (see table 9). The HNBR material was the only material, of those tested, able to retain pressure at -20°C.

Base Elastomer	0 (°C)	-10 (°C)	-20 (°C)
AFLAS	3:0	0:3	na
ETP	3:0	3:0	0:3
FKM Type 1	3:0	3:0	1:2
FKM Type 2	3:0	3:0	0:3
HNBR	na	2:1	3:0

Table 9: (#Pass : #Fail) - Isothermal results.

## **RESULTS**

### ***ELASTOMER SUMMARY***

Table 10 provides a summary of the compiled data.

Base Elastomer	TMA Transition (°C)	DSC Tg (°C)	DMRT Tg (C)	dP/dt Increase Temp (°C)
AFLAS®	2.2	2.3	3.6	-9
ETP	-8.7	-10.0	-3.2	-23
FKM Type 1	-10.1	-17.5	-10.1	-17
FKM Type 2	-3.4	-8.7	-3.7	-16
HNBR	-22.4	-25.0	-19.2	na

Table 10: Data Summary

One concern was that the contact stress results were simply a reflection of each material's modulus. Although compression modulus was not available, shear modulus ( $G'$ ) was obtained through DMRT analysis. The scatter plot shown below in Figure 6 reveals no statistically significant correlation although it can be inferred that modulus is a factor.

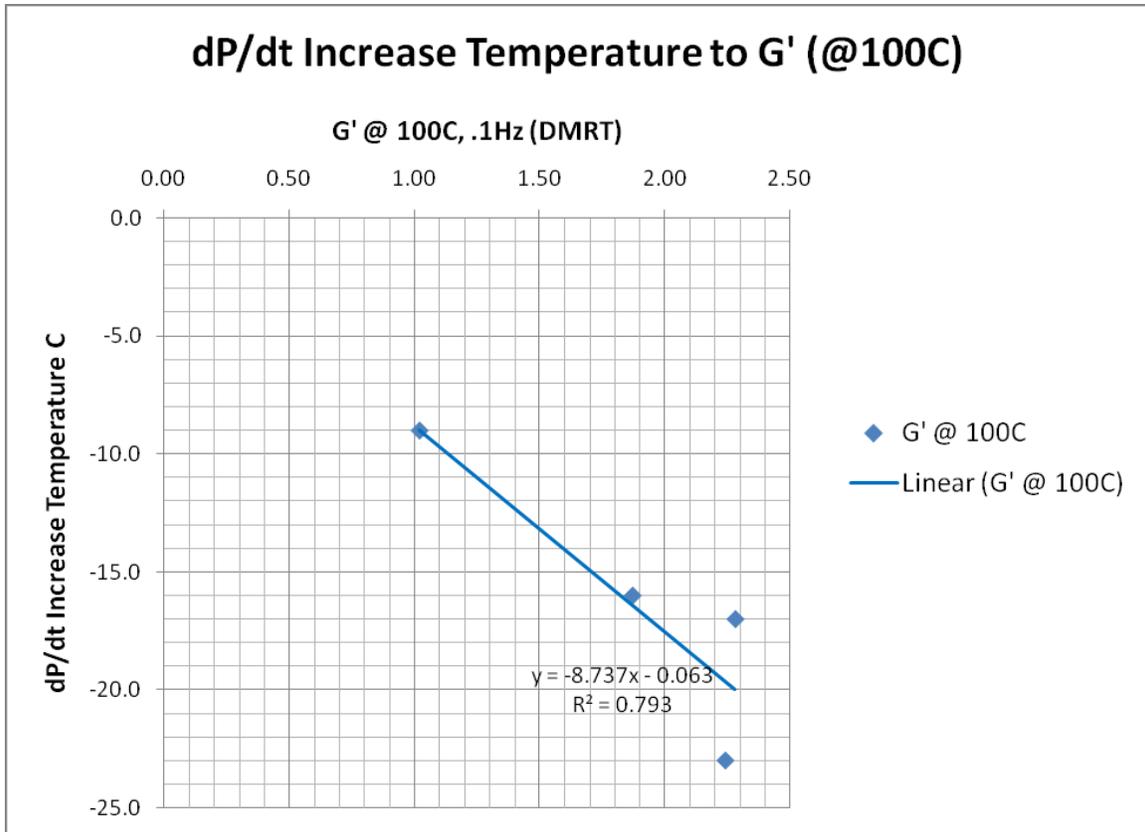


Figure 6: dP/dt Increase Temperature to Shear modulus measured at 100°C.

Figure 7 provides a scatter plot of the results comparing the Tg, as measured by either TMA, DSC, or DMRT to that temperature at which a notable increase in dP/dt of contact stress was observed.

HNBR data is not included in figure 6 or figure 7 because there was no “failure point” observed above -30°C.

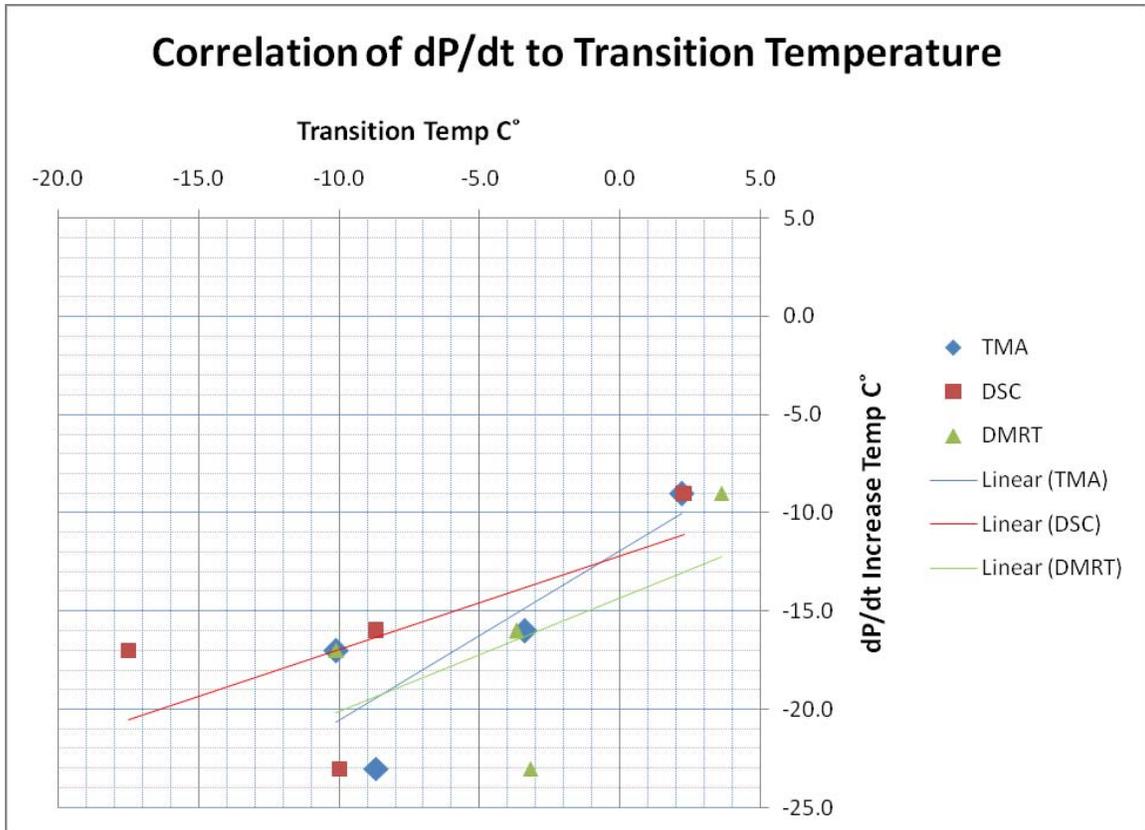


Figure 7: Graphical Data Summary

## DISCUSSION

HNBR presented an anomaly in the study. Unlike the fluoroelastomers examined, the HNBR exhibited a small but steady increase in dP/dt. The fluoroelastomers, on the other hand, exhibited a constant dP/dt with the exception of thermal decreases when dP/dt would decline or when the seal began to fail at which point dP/dt would rapidly increase (see figure 5).

DSC recorded a lower transition temperature for the five materials examined with the exception of Aflas. This may be attributable to the heating rate. Hertz & Farinella report that a higher heating rate utilized in DSC analysis, will result in a lower Tg value.<sup>iv</sup> It can also be observed in their work that DSC does not correlate with DMRT data.

In all instances, an unconstrained, energized rubber sphere was able to hold pressure at temperatures below their respective Tg. On average, the materials would seal roughly 10°C below their Tg temperatures (see figure 7). However, there is no statistical correlation to this finding.

Changes in measured contact stress (retained air pressure) attributable to changes in system pressure were measured on average at 0.15%/1°C over the temperature range

of 20°C to -30°C. Other loss in contact stress is attributable to stress relaxation of the rubber spheres being evaluated and impaired ability to seal as pressure was reduced.

A tendency of higher shear modulus materials to retain contact stress at lower temperatures was observed (see figure 6), but with no statistical significance.

Finally, this study confirms the Hertz & Farinella observation that there is no single definitive Tg temperature for an elastomer<sup>v</sup>. If Tg is ever referenced within a specification, it would be prudent to specify the device used to measure the Tg and where relevant, either the frequency, strain, or rate of cooling/heating.

## Conclusion

There is no statistical correlation of the “Tg”<sup>vi</sup> of an unconstrained elastomer in the energized state to the temperature at which it can no longer seal a gas. However, using Tg as a rough guide for lower temperature suitability, of the elastomers studied, does provide some guidance with a margin of safety.

## ACKNOWLEDGEMENTS

The author would like to thank the AGC Chemicals Americas, Inc. for their assistance in running the TMA and DSC analysis.

The author also expresses gratitude to Tim Matlock for his valuable assistance in preparing and compiling the DMRT and contact stress data.

## CONTACT

Daniel L. Hertz, III, VP Sales & Market Development, Seals Eastern, Inc.; 134 Pearl Street, Red Bank, NJ 07701, USA (732) 747-9200 [dhertziii@sealseastern.com](mailto:dhertziii@sealseastern.com)

## TRADEMARKS

AFLAS® is the registered trademark of Asahi Glass Co.

Viton® is the registered trademark of Dupont Performance Elastomers.

Zetpol® is the registered trademark of Zeon Chemicals.

Rev. 9/5/2008 5:02:10 PM

## References

---

<sup>i</sup> Bekkedahl, Norman, “Forms of Rubber as Indicated by Temperature-Volume Relationship”, Rubber Chemistry and Technology, Volume VIII, No.1, ACS (Jan. 1935).

<sup>ii</sup> Treloar, L.R.G., “The Physics of Rubber Elasticity”, p.13, Oxford (1975).

<sup>iii</sup> Rohn, Charles, L., “Analytical Polymer Rheology”, p.218, Hanser (1995).

<sup>iv</sup> Hertz, D., Jr., Farinella, A., “Low Temperature Testing of Elastomers”, Spring Technical Meeting NY Rubber Group (Mar. 1999).

<sup>v</sup> Id.

<sup>vi</sup> Tg obtained using either DMRT at low frequency or TMA. DSC presents too much variability.