

**Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers
Evaluated using Strain Energy Density**

Presented at the High Performance and Specialty Elastomers 2005

International Conference

Geneva, Switzerland

20-21st April, 2005

D. L. Hertz III

Seals Eastern Inc.

Red Bank, NJ, 07701

USA

ABSTRACT

Fluoroelastomers are characterized by excellent heat stability, thus suitable for sealing applications where high temperature performance is required. However, thermal excursions, defined as application temperatures in excess of normal operating temperatures, commonly occur. One example is an engine shutdown after extended operation at high load. Thermal excursions often exceed the normally prescribed thermal limits of a fluoroelastomer. Retention of viscoelastic properties subsequent to thermal excursions is crucial to an elastomer's viability.

The thermal stability of two classes of fluoroelastomers, FKM and FEPM, utilizing two popular cure systems, BPAF and TAIC, were tested and summarized. These four compositions were aged at 225C, 250C, and 275C, representative of such thermal excursions. The materials were aged in de-ionized water, mineral oil, and dry heat. Comparisons of tensile properties were made paying specific attention to strain energy density (SED) calculated at twenty percent strain. Strain energy density, calculated as the area under the stress strain curve up to twenty percent strain, reflects the stored mechanical energy per unit volume of an elastomer under strain. Strain energy density is a function of the polymeric structure, cross-link density, and filler interaction. This paper investigates the effect of extreme temperature, as might be seen during thermal excursions, on SED to determine the differences in behavior of these fluoroelastomer and cure system combinations.

INTRODUCTION

Background

Fluoroelastomers are typically specified for sealing applications requiring specific chemical resistance, thermal stability, or some combination thereof. Chemical resistance of the various fluoroelastomer families is widely documented and readily available.

Thermal stability, however, aside from generally prescribed operating guidelines, is not as thoroughly documented. Published thermal limits of fluoroelastomers are often contradictory and in some cases arguably misleading. For instance, Table X1.1¹ of ASTM D 2000 refers to “fluorinated elastomers (Viton®, Fluorel®, etc.)” as “H” type polymers whose testing yields prescribed results after 70 hours aging at 250°C².

Unfortunately, 70-hours is a grossly inadequate time frame to characterize the “heat resistance” of a material whose mechanical properties are distinctly time and temperature dependent. It is evident that significant changes in viscoelastic properties occur shortly after 70-hours at elevated temperatures.

While classifying elastomers remains desirable, end users should be aware that the steadily increasing variety of fluoroelastomers and their cure systems in conjunction with innumerable operating environments create distinctions that are more significant than often perceived. ASTM has defined three distinct classes of “fluoro rubber”, FEPDM, FKM, and FFKM. The FKM class embodies five types of molecular configuration³. The

¹ ASTM Standard D 2000 – 01, “Standard Classification System for Rubber Products in Automotive Applications”, “Table X1.1 Polymers Most Often Used In Meeting Material Requirements”, *Annu. Book ASTM Stand.* **09.02**, 103 (2001). “X1.1 This appendix is intended to assist the users of Classification System D 2000-SAE J200 and is not to be considered as part of the system.” (emphasis added), 102.

² ASTM Standard D 2000 – 01, “Standard Classification System for Rubber Products in Automotive Applications”, “Table 1 Basic Requirements for Establishing Type by Temperature”, *Annu. Book ASTM Stand.* **09.02**, 67 (2001).

³ ASTM Standard D 1418 – 01a, “Standard Practice for Rubber and Rubber Latices-Nomenclature”, “3. Class Designations”, *Annu. Book ASTM Stand.* **09.01**, 272-273 (2001).

actual number of fluoroelastomer configurations available within these three classes, taking into account cure site monomers and substituent groups, is staggering.

Consequently guidelines, including service parameters such as chemical compatibility and operating temperatures, are often general “rules of thumb”.

The ASTM D 2000 defines a framework for elastomers to be classified for automotive applications. Heat resistance, under this specification, is determined by change in (1) tensile strength (i.e. +/- 30% max), (2) change in elongation (i.e. -50% max), and (3) change in hardness (i.e. +/- 15 points max) at a given temperature after 70 hours of aging. These three attributes can be calculated by even the most uninitiated rubber laboratory. However, these attributes taken individually, do not necessarily reflect the mechanical properties that determine whether an elastomer will function properly within its application subsequent to thermal aging. Auda and Hazelton instead 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.

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

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

The author has taken liberty to apply this same framework to fluoroelastomers, but by examining the response of an elastomer within a more realistic design guideline, specifically strain energy at twenty percent strain.

Objectives

The first objective was to provide data regarding the effects of high temperature service, beyond that normally prescribed, upon fluoroelastomers. Invariably, users in the market place are inclined to “push” a widely used class of fluoroelastomer (FKM) to its thermal limit before paying the premium associated with using an alternative high-temperature variety of perfluoro-rubber (FFKM). Consequently, a primary issue becomes how hot and how long the elastomer can be operated while maintaining acceptable mechanical attributes.

Similarly, the market is often confronted with the issue of thermal excursions (excessive temperature) and their subsequent impact on material properties. Many applications are subject to short-term thermal excursions that expose the elastomer to higher heat than steady state testing assumes. One example would include an engine shutdown after extended operation at high load. Retention of viscoelastic properties in such applications, subsequent to thermal excursions, is the difference between success and failure. The issue of thermal degradation attributable to thermal excursions can sometimes be obviated with the application of a peroxide cured perfluoro rubber utilizing a thermally stable curesite monomer. However, the difference in cost, usually orders of magnitude, is often prohibitive.

The second objective was to examine this data in the context of “Strain Energy” as introduced by R.S. Auda and D.R. Hazelton⁴ of the Elastomers Technology Division of Exxon Chemical Company. We have incorporated an important distinction from the

⁴ R.S. Auda, D.R. Hazelton, “Ethylene Propylene Elastomer technology for Improved High Temperature Serviceability”, Elastomers Technology Div., Exxon Chemical Co., Paper No. 750962

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 hyperelastic region of the stress-strain curve offering better insight as to the integrity of the elastomer network as opposed to filler interactions as discussed *infra*. Second, 20% strain is a more realistic approximation of strain the elastomer will be subject to given generally accepted design guidelines.

Scope

Elastomers:

Current high temperature elastomers fall into two categories, namely Fluoroelastomers and Silicones. We examined two classes of Fluoroelastomers, as defined by ASTM D1418-01a. Specifically,

FKM – “Fluoro rubber of the polymethylene type that utilizes vinylidene fluoride as a comonomer ... Type 2 – Terpolymer of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene”.

FEPM – “A fluoro rubber of the polymethylene type only containing one or more of the monomeric alkyl, perfluoroalkyl, and/or perfluoroalkoxy groups...”.

Crosslinks:

Bisphenols -

Schmiegel⁵ first elucidated the chemistry of the bisphenols (e.g. BPAF) and their use in crosslinking. Subsequent papers by Venkateswarlu et al⁶ and Arcella et al⁷ have shed further light on the subject.

Since the crosslinking mechanism of BPAF is ionic, the C-O-Ar linkage is likely vulnerable to cleavage. Ethers are comparatively unreactive compounds. However, the ether linkage itself is susceptible to cleavage by strong acids at high temperature. The mechanism is reportedly protonation of the ether, then nucleophilic attack (e.g. halide ion) on this protonated ether with the subsequent displacement of a weakly basic alcohol

⁵ Schmiegel, W.W. “Crosslinking of Elastomeric Vinylidene Fluoride Copolymers with Nucleophiles”, *Die Angewandte Makromolekulare Chemie* 76/77 (1979).

⁶ Venkateswarlu, P., et al., “Elucidation of Chemical Events Occurring in the Solid Phase During the Curing of Fluoroelastomers with Bisphenol AF”, Rubber Division, American Chemical Society, Paper No. 123 (October 1989).

⁷ Arcella, V., et al., “Cross-linking Chemistry of VF2 Fluorocarbon Elastomers by Bis-Nucleophiles”, Rubber Division, American Chemical Society, Paper No. 57 (October 1991).

molecule.ⁱ Thus, deionized distilled water was included as a pH neutral fluid, notwithstanding water's ability to act as either an acid or base.

Triazine:

The triazine curative, triallylisocyanurate (TAIC) is produced by cyclotrimerization of isoallyl alkoxy nitrile to create a ring structure with reactive allyl groups at the 1,3, and 5 sites⁸. These crosslinking sites are capable of crosslinking at any suitable reactive siteⁱⁱ, including homopolymerization. The triazine structure is thermally stable, but since it is a reaction product it is probably susceptible to cleavage by an acid, base or catalyst at elevated temperature.

Environment:

The thermal stability of these two categories of elastomers were examined in the context of three commonly encountered environments:

- 1) Aliphatic hydrocarbons (mineral oil),
- 2) Deionized water,
- 3) Dry heat.

The materials were aged at a temperature known to represent the outer thermal limit of this category of elastomer, specifically 225°C (437°F), as well as two additional temperatures exceeding the known thermal limit of these materials, specifically 250°C (482°F) and 275°C (527°F).

Evaluation:

At its simplest level, an elastomer ages individually or through some combination of three basic mechanisms: chain scission, crosslink scission, and/or crosslink addition.

⁸ Newkome, G.R., Paudler, W.W., "Contemporary Heterocyclic Chemistry", John Wiley & Sons (1982).

Kuhn developed an equation (Eq.2) for shear modulus that describes the effect of these mechanisms.⁹

$$(2) \quad G = NkT = \rho RT / M_c$$

Under this equation, shear modulus (G) is directly proportional to the number of polymer chains per unit volume (N) at a given temperature (T - Kelvin), where (k) equals Boltzmann's constant. Similarly, shear modulus is proportional to the material's density (ρ) at a given temperature and inversely proportional to the molecular weight between crosslinks (M_c) where (R) is the universal gas constant. One can quickly deduct that as crosslink density increases, modulus increases. Naturally, the molecular weight between crosslinks has decreased during crosslink addition.

Fractional strain energy (Eq.1) describes an aged vulcanizate in terms of both its integrity (retained tensile) and its extensibility (retained elongation). Use of fractional strain energy has been shown to be a reliable means of characterizing and projecting aging behavior of EP rubbers by Auda and Hazleton. We analyzed the mechanical properties of these elastomers using stress-strain tensile testing, specifically examining strain energy at twenty percent strain, first introduced by Peacock¹⁰, in order to illustrate their thermal limitations.

We have defined fractional strain energy (Eq.3) as the ratio of strain energy density of the aged material to the strain energy density of the un-aged material at 20% strain.

$$(3) \quad SED_f = (SED)_{aged} / (SED)_{original}$$

⁹ Hertz, Jr., Daniel, "Sealing Technology", Rubber Products Manufacturing Technology, p.790, Marcel Dekker, Inc. (1994).

Logically, the energy potential of an elastomer is better evaluated at low strains, staying within the hyperelastic region of the stress-strain curve. On a basic level, the modulus of a formulated elastomer will be a function of the elastomer's molecular constitution, the cross-link density, and the elastomer's interaction with a reinforcing filler. A reinforcing filler, such as carbon black, will effect an elastomer's modulus as a function of the filler's particle size, surface energy, and loading. Generally speaking, the smaller the particle size, holding all else constant (including particle structure), the higher the modulus.

Hertz, in his chapter on Sealing Technology¹¹, observed this logical increase in modulus as particle size decreased when evaluated using strain energy calculated at twenty percent strain. This relationship, however, failed when stress was examined at strains in excess of 100% presumably due to rupture at the polymer-filler interface. Arguably, at high strain, polymer-filler interactions become increasingly complex and unpredictable as reflected in the broad range of stress values. For instance, the standard deviation of stress data points is increasingly larger as strain increases. Thus, the author's opinion is that chemically and thermally induced changes to the vulcanizate's structure will be best reflected by changes in strain energy at 20% strain.

¹⁰ Peacock, Christopher, Quality Control testing of Rubber Shear Modulus, "Elastomerics", (May 1992).

¹¹ Hertz, Jr., Daniel, "Sealing Technology", Rubber Products Manufacturing Technology, p.781, Marcel Dekker, Inc. (1994).

EXPERIMENTAL

Four commercially available fluoroelastomer base polymers were selected, based upon their class and recommended cure systems. The first class of elastomers was a Type 2, FKM. The two samples of this class were further differentiated from one another by their cure system. The first elastomer is especially suited to curing with a bisphenol-AF in combination with an “onium” salt. This material, which we will refer to as FKM-BPAF, was formulated per Table 1.

Constituent	PHR
TFE/VDF/HFP terpolymer	100
MT Black (N990)	30
Bisphenol / Onium	2.5
High Activity Magnesium Oxide	3
Calcium Hydroxide	6
VPA® No. 3	1

Table 1

The second material is an elastomer designed with a cure-site monomer (CSM) susceptible to a peroxide and crosslinked with TAIC as a coagent. This material, which we will refer to as FKM-TAIC, was formulated per Table 2.

Constituent	PHR
TFE/VDF/HFP terpolymer w/ CSM	100
MT Black (N990)	30
Zinc Oxide	3
Triallyl isocyanurate (TAIC)	3
2,5-dimethyl 2,5-bis (t-butyl peroxy) hexane	3

Table 2

The second class of elastomers was FEPM. The two samples of this class of elastomer were differentiated by their cure systems. The first elastomer possesses a cure-site monomer that is especially suited to curing with a bisphenol-AF in combination with an “onium” salt. This material, which we will refer to as FEPM-BPAF, was formulated per Table 3.

Constituent	PHR
TFE/P w/CSM	100
MT Black (N990)	30
Bisphenol Onium (incorporated)	--
Calcium Hydroxide	2
VPA No. 2	0.5

Table 3

The second material is an elastomer activated by a peroxide and crosslinked with TAIC as a coagent. This material, which we will refer to as FEPM-TAIC, was formulated per Table 4.

Constituent	PHR
TFE/P	100
MT Black (N990)	30
Triallyl isocyanurate (TAIC)	5
2,5-dimethyl 2,5-bis (t-butyl peroxy) hexane	1

Table 4

Variables such as sample size, test conditions, temperatures, aging period and specimens tested are presented in Table 1.

Aging period	<ul style="list-style-type: none"> • 24 hours • 70 hours • 168 hours • 336 hours
Test Specimen	<ul style="list-style-type: none"> • ASTM D412 dumbbells, n = 3
Test media	<ul style="list-style-type: none"> • Mineral Oil (with mixed Tocopherols added as a stabilizer), • Deionized Ultra Filtered water • Dry heat
Test Temperature	<ul style="list-style-type: none"> • 225C • 250C • 275C

Table 5: Experiment test matrix

Methodology

Our experiment was geared towards understanding the difference, if any, in the relative thermal stability of BPAF and TAIC in a particular media at short or long-term excessive temperature. A fundamental premise is that the thermal stability of the cure system and/or elastomer will be reflected by changes in the stress-strain characteristics of the vulcanizate as molecular weight between crosslinks either increases or decreases. We specifically are interested in fractional retention of the vulcanizate's energy potential as defined by its stress-strain curve up to twenty percent strain.

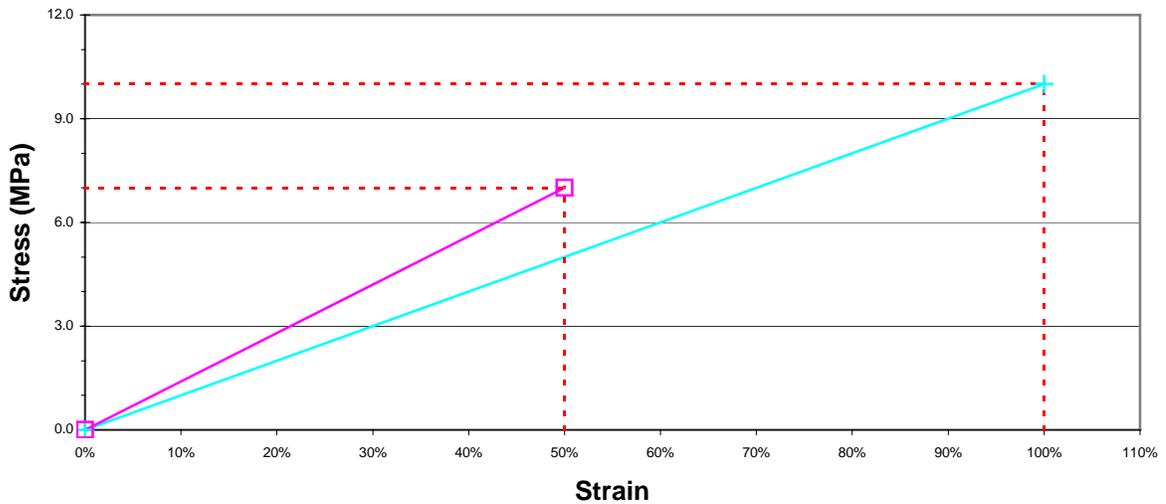
The same filler was used in the four formulations and a best effort made to develop an approximately equal crosslink density with the objective of isolating the constitution of the crosslink as one variable of these two materials and the elastomer backbone as the other variable. Obviously, the differences in molecular constitution of BPAF and TAIC, respectively bi-functional and tri-functional, will tend to deliver different properties, thus we focused on relative changes in strain energy to make our inferences.

Aging in DI water and mineral oil was achieved by immersing test specimens in steel cylindrical test vessels, containing the test media, which could be sealed for thermal aging. Dry heat aging was achieved by placing specimens in a conventional convection oven.

RESULTS AND DISCUSSION

Proper evaluation of the data required that we be able, at some point, to determine when a material composition had effectively failed. ASTM D2000 prescribes that a “type” designation, for service temperature, is determined by “changes in tensile strength of not more than +/- 30%, elongation of not more than -50%, and hardness of not more than +/- 15 points after heat aging for 70 hours at an appropriate temperature.”¹² Obviously, any material not conforming to these limits at a specific temperature cannot be identified as the corresponding “type”. That is, the material has effectively failed under the logic of D2000. Accepting ASTM’s methodology in this regard, we can establish an upper and lower fractional strain energy value that considers such change in the area defined under a stress-strain curve.

Figure 1 - Stress-Strain Curves



To calculate a failure point, we simplified the area under the stress strain curve as a rectangle with two transverse corners defined at the origin and at the point of breakage as

¹² ASTM Standard D 2000 – 01, “Standard Classification System for Rubber Products in Automotive Applications”, Section 4.2, *Annu. Book ASTM Stand.* **09.02**, 67 (2001).

in Figure 1. This area can be subsequently defined as percent strain at break multiplied by the stress at break. First we assumed an unaged material having a stress at break of 10MPa (1,450 psi) and an elongation at break of 100%. The area under the stress-strain curve would be 10MPa (1,450 psi). Next we assumed that stress and elongation declined to the extent permissible in ASTM D2000 for establishing “type”. Specifically, stress at break declined 30 percent to 7MPa (1015 psi) and elongation declined 50 percent to 50% at break. The area is now 3.5MPa (507.5 psi). The fractional value is 3.5MPa over 10MPa or 0.35. Thus we assigned .35 as our lower fractional strain energy failure point. Using the same logic, we derived 1.3 as our upper fractional strain energy failure point.

Deionized Water

Table 6 contains the tabulated results of aging in deionized water. Exhibited is the approximate number of hours to failure at the respective aging temperature.

The symbol “~” indicates +/- 24-hours; “<” indicates “less than”; and “+” indicates an un-quantified “greater than”.

Deionized Water @ 225C			Deionized Water @ 250C			Deionized Water @ 275C		
	BPAF	TAIC		BPAF	TAIC		BPAF	TAIC
FKM	< 168	168+	FKM	~70	70 - 168	FKM	~70	~24
FEPM	~24	168+	FEPM	~70	168+	FEPM	~70	168+

Table 6 – Hours to failure in Deionized Water

The BPAF cure system is characteristically unstable in deionized water at temperatures of 225C and above. Time to failure of the BPAF cure is generally about 70 hours, except at 225C where time to failure is slightly more. Likewise, the FKM elastomer is less stable than the FEPM-TAIC formulation irrespective of its cure system, with the exception of aging at 225C. The FKM compositions as well as the FEPM-BPAF composition exhibit

rapid decreases in fractional strain energy within 168 hours. The greatest stability at excessive temperatures in deionized water was exhibited by the FEPM-TAIC composition, which consistently operated in excess of 168 hours at temperatures of 225C to 275C. However, the FEPM-TAIC composition failed by 336-hours at 275C.

Figure 2 - Aging in 225C De-Ionized Water

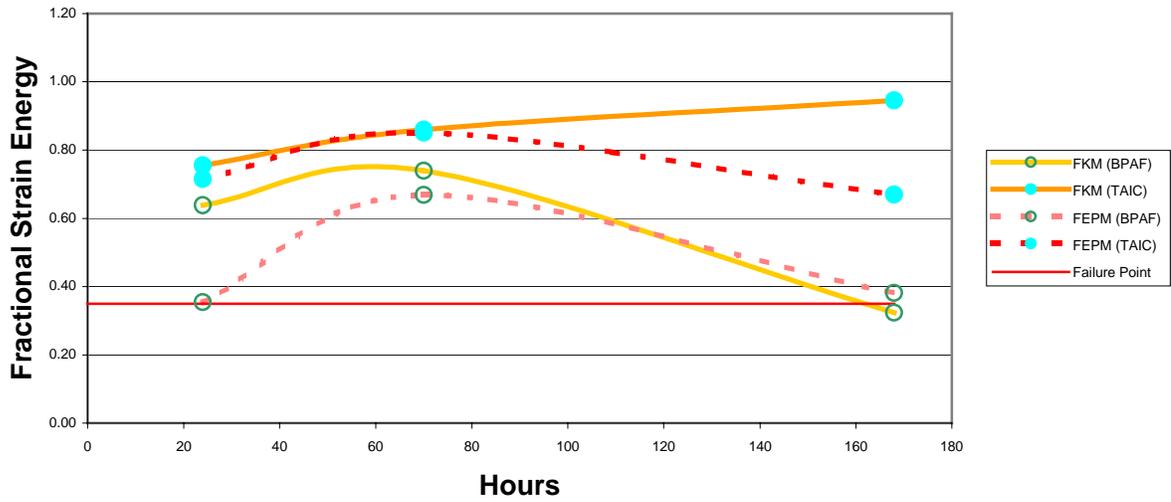


Figure 3 - Aging in 250C De-Ionized Water

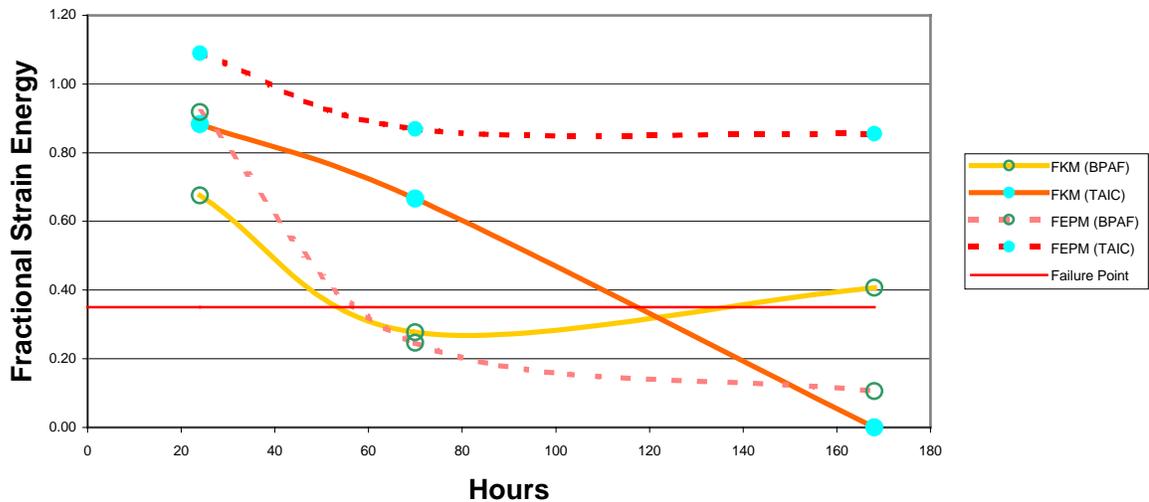
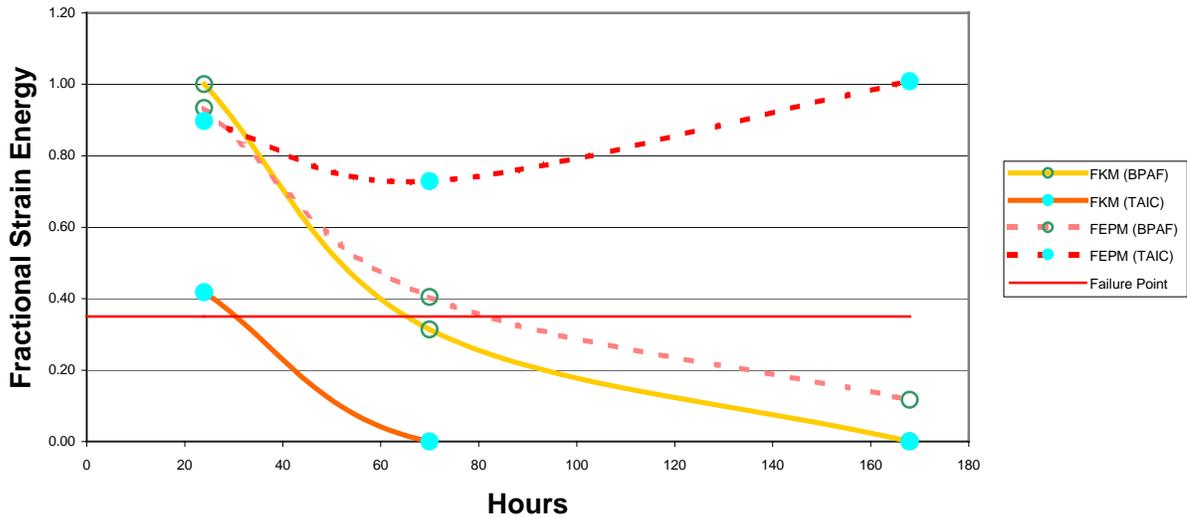


Figure 4 - Aging in 275C De-ionized water



Mineral Oil

Table 7 contains the tabulated results of aging in mineral oil. Exhibited is the approximate number of hours to failure at the respective aging temperature.

	Mineral oil @ 225C		Mineral oil @ 250C		Mineral oil @ 275C	
	BPAF	TAIC	BPAF	TAIC	BPAF	TAIC
FKM	168+	168+	168+	168+	336+	70 - 168
FEPM	~168	168+	168+	*168+	336+	~168

Table 7 – Hours to failure in Mineral Oil

The TAIC cure is characteristically unstable in mineral oil at temperatures of 250C and above. At 275C, a rapid increase in fractional strain energy of the TAIC compositions is observable shortly after 70-hours of aging. The greatest thermal stability in mineral oil at elevated temperatures was exhibited by the FKM-BPAF composition.

Figure 5 - Aging in 225C Mineral Oil

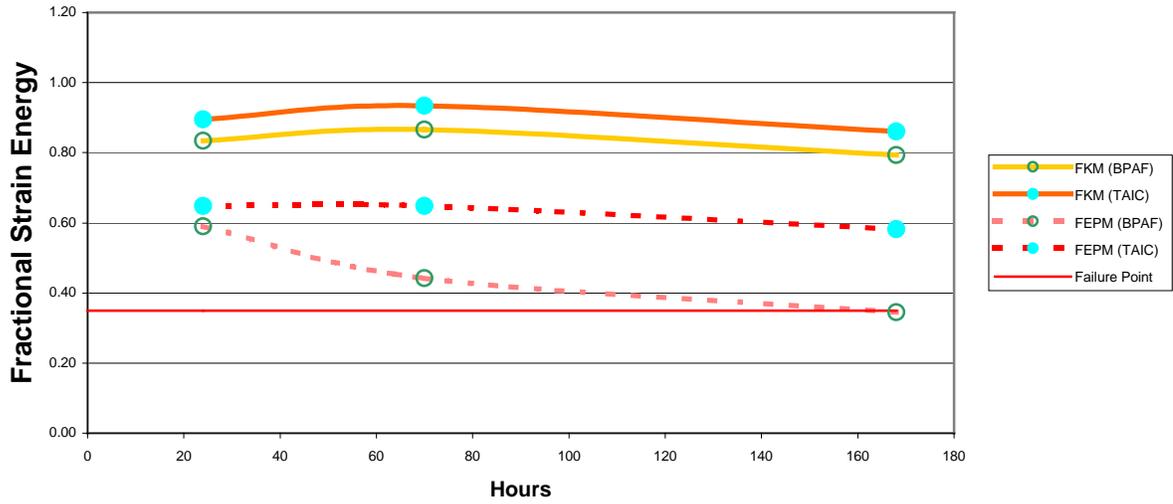


Figure 6 - Aging in 250C Mineral Oil

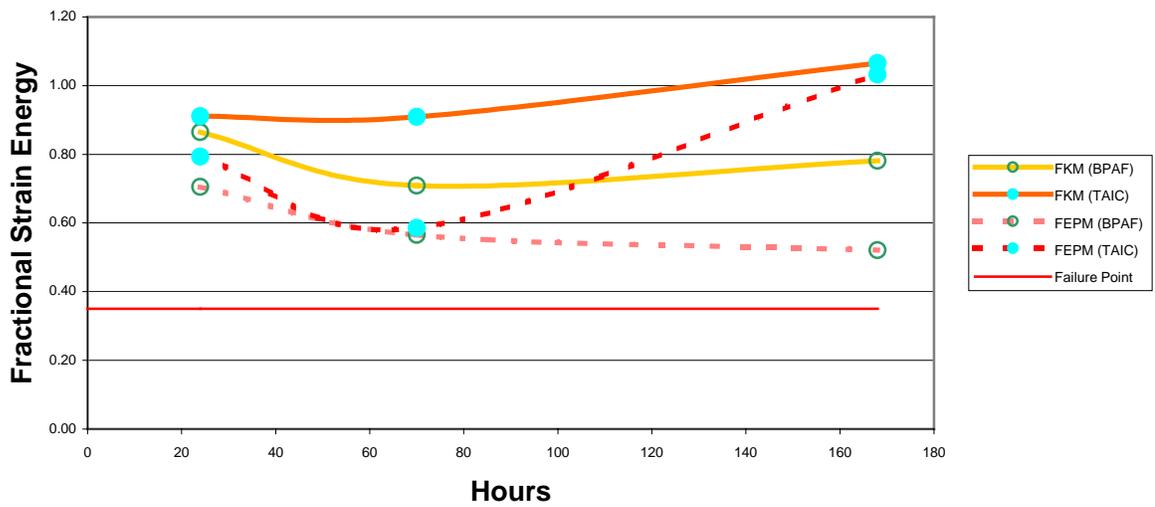
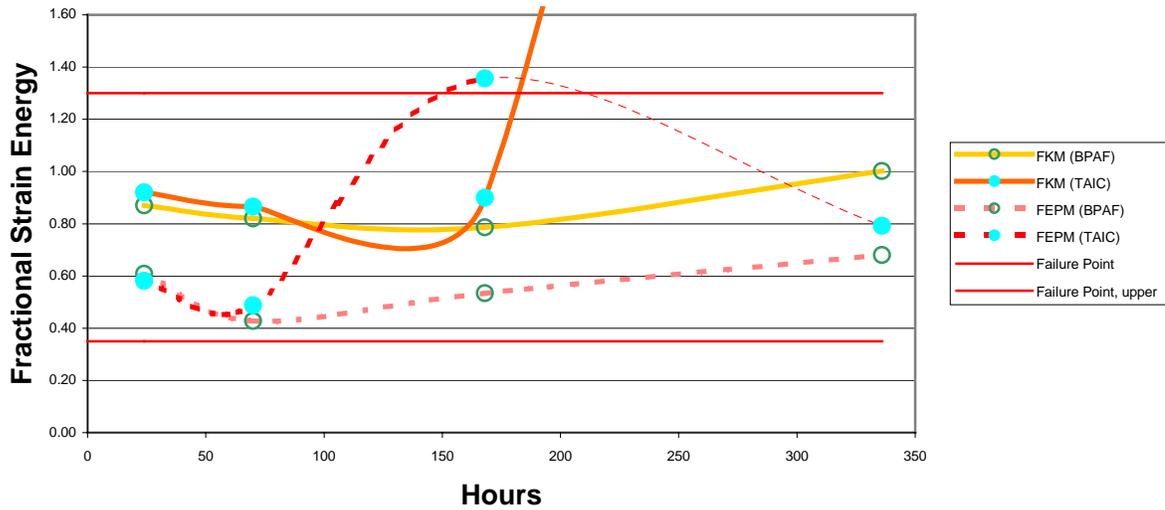


Figure 7 - Aging in 275C Mineral Oil



Dry Heat

Table 8 contains the tabulated results of dry heat aging. Exhibited is the approximate number of hours to failure at the respective aging temperature.

Dry Heat @ 225C			Dry Heat @ 250C			Dry Heat @ 275C		
	BPAF	TAIC		BPAF	TAIC		BPAF	TAIC
FKM	168+	168+	FKM	168+	168+	FKM	336+	< 336
FEPM	168+	168+	FEPM	168+	< 168	FEPM	< 336	< 168

Table 8 – Hours to failure in Dry Heat

The BPAF cure is characteristically more stable than the TAIC cure at dry heat temperatures of 225C and higher. The FKM elastomer appears to offer greater stability than the FEPM elastomer up to 168 hours at temperatures from 225C to 275C. The composition offering the greatest thermal stability up to 336 hours in dry heat at temperatures up to 275C is the FKM-BPAF composition.

Figure 8 - Aging in 225C Dry Heat

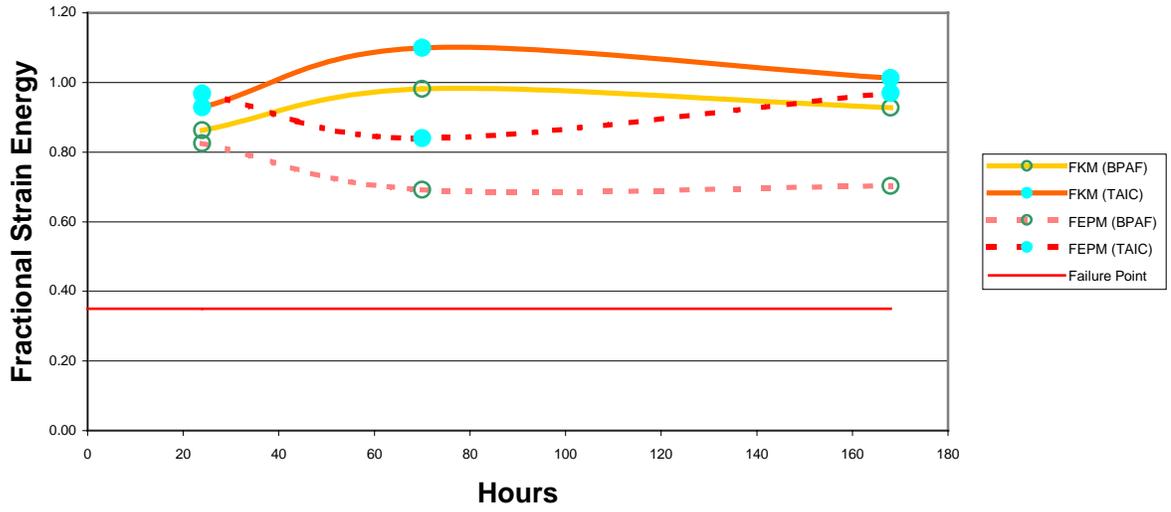


Figure 9 - Aging in 250C Dry Heat

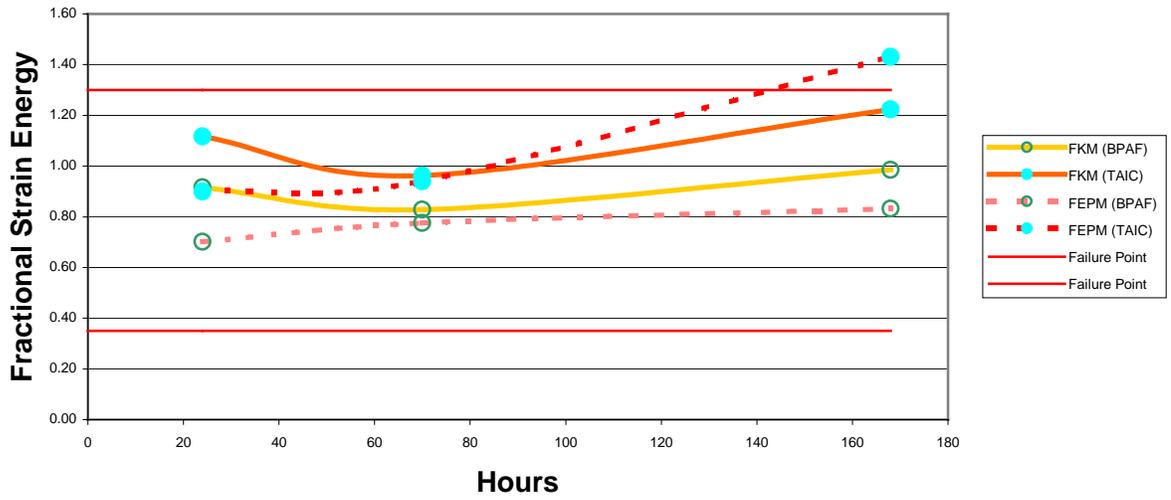
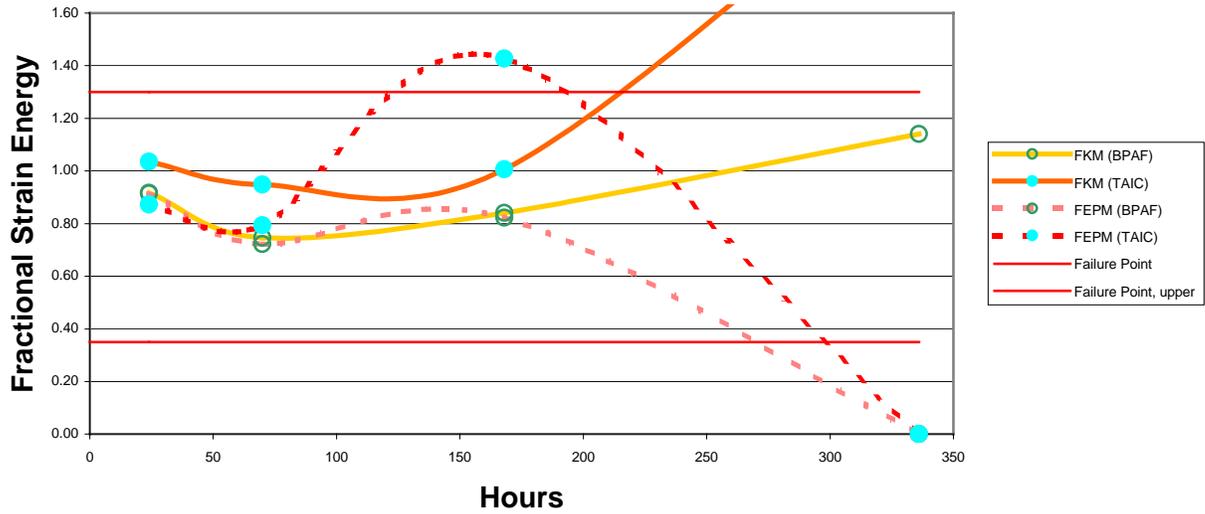


Figure 10 - Aging in 275C Dry Heat



SUMMARY

- 1) Given the large number of fluoroelastomer options today, careful consideration should be given to both elastomer selection and the cure system for applications requiring continuous high temperature service, as well as those subject to extreme thermal excursions. Temperature, duration of thermal excursions if any, and the operating medium are critical factors to consider at temperatures in excess of 200C.
 - a) The BPAF cure system is characteristically unstable in deionized water at temperatures of 225C and above. The greatest stability at excessive temperatures in deionized water was exhibited by the FEPM-TAIC composition, which consistently operated in excess of 168 hours at temperatures of 225C to 275C.

- b) The TAIC cure is characteristically unstable in mineral oil at temperatures of 250C and above. The greatest thermal stability in mineral oil at elevated temperatures was exhibited by the FKM-BPAF composition.
 - c) The BPAF cure is characteristically more stable than the TAIC cure at dry heat temperatures of 225C and higher. The composition offering the greatest thermal stability up to 336 hours in dry heat at temperatures up to 275C is the FKM-BPAF composition.
- 2) When relying upon ASTM D2000 “Type” (i.e. heat resistance) designations, materials should be considered in context of the testing period. Careful examination should be made of the “Heat Resistance” suffix since material properties can change dramatically within short periods of time at elevated temperatures.
- 3) Strain energy density, when calculated at low strains, offers consistent data for evaluating the extent of thermal aging in elastomeric compositions.

Viton® is a registered trademark of DuPont Dow Elastomers.

Fluorel® is a registered trademark of Dyneon.

VPA® No. 3 is a registered trademark of DuPont Dow Elastomers.