

## Poly(fluoroalkoxyphosphazenes)—Versatile Seal Materials

JOHN C. VICIC and KENNARD A. REYNARD, *Horizons Incorporated, Division of Horizons Research Incorporated, Cleveland, Ohio 44122*

### Synopsis

Poly(fluoroalkoxyphosphazene) fluoroelastomers are members of a new family of polymers based on a phosphorous-nitrogen backbone. Physical property evaluation tests have demonstrated that these fluoroelastomers possess excellent stress-strain properties, low-temperature flexibility, thermal stability, and resistance to a variety of demanding environments including synthetic lubricants, hydrocarbon fuels, and aqueous caustics. Their service temperature range is about  $-60^{\circ}$ – $200^{\circ}$ C. Poly(fluoroalkoxyphosphazene) fluoroelastomers have shown the capability to function in severe dynamic applications; i.e., lip seals (1 $\frac{1}{8}$  in. I.D.) performed for >1000 hr at 5500 rpm in MIL L-7808G lubricant at  $115^{\circ}$ C. Also, O-ring seals successfully completed a 1000-hr dynamic qualification test over a temperature range of  $-54^{\circ}$ – $163^{\circ}$ C in a rod seal test apparatus. These elastomers can be used for seals, O-rings, gaskets, diaphragms, hose, and protective coatings.

### INTRODUCTION

Extreme service applications for fluoroelastomers have grown steadily as a result of new developments in military and civilian requirements. These applications demand strong, solvent-resistant materials which are capable of service over wide temperature extremes in a variety of fluids and air.

Poly(fluoroalkoxyphosphazene) elastomers, developed by Horizons Incorporated, have demonstrated the potential to meet the requirements of new and existing extreme service applications. Poly(fluoroalkoxyphosphazene) elastomers are members of the polyphosphazenes, a series of polymers based on an alternating phosphorous-nitrogen backbone. Peroxide-cured poly(fluoroalkoxyphosphazenes) display excellent fluid resistance, good mechanical properties, low-temperature flexibility, and thermal stability. Their service temperature range is  $-60^{\circ}$  to about  $200^{\circ}$ C.

The technology and commercial development of poly(fluoroalkoxyphosphazene) elastomers have been licensed to the Firestone Tire and Rubber Company. These polymers are now being marketed in pilot plant quantities under the trade name phosphonitrilic fluoroelastomers and the trademark PNF.

### EXPERIMENTAL

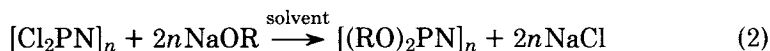
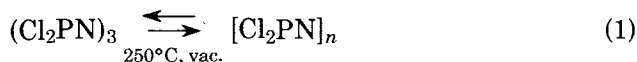
**Synthesis.** Synthesis of the poly(fluoroalkoxyphosphazene) elastomers used in our studies followed procedures described previously.<sup>1,2</sup>

**Compounding.** Compounding of poly(fluoroalkoxyphosphazene) elastomers was carried out in an Atlantic Research Helicone Mixer Model 2CV, a C. W. Brabender Prep. Center Mixer Model C.E. 0.6, and on a P. E. Albert 6 × 12 in. two-roll rubber mill. Test specimens were compression molded and vulcanized under pressure in a heated, hydraulically operated press. Process and vulcanization conditions varied according to compound characteristics.

**Physical Testing.** Test procedures for characterization and evaluation of poly(fluoroalkoxyphosphazene) elastomer vulcanizates were as follows: (1) ASTM D-3196T, Tentative Method of Tension Testing Solid Urethane and Other Rubbers; (2) ASTM D-573, Accelerated Aging of Vulcanized Rubber by the Oven Method (ASTM D-3196T tensile specimens were used for stress-strain determinations); (3) ASTM D-471, Change in Properties of Elastomeric Vulcanizates Resulting from Immersion in Liquids (ASTM D-3196T tensile specimens were used for stress-strain determinations); (4) ASTM D-3137, Hydrolytic Stability of Elastomeric Vulcanizates (a test temperature of 100°C was used instead of the 85°C specified) (ASTM D-3196T tensile specimens were used for stress-strain determinations); (5) ASTM D-1053, Measuring Low-Temperature Stiffening of Rubber and Rubber-like Materials by Means of a Torsional Wire Apparatus; (6) ASTM D-395, Compression Set of Vulcanized Rubber.

## RESULTS AND DISCUSSION

Many essentially chloride-free elastomeric or plastic poly(fluoroalkoxyphosphazenes) have been prepared following the reaction sequence shown<sup>3</sup> by eqs. (1) and (2):



Only polyphosphazene derivatives which contain  $\text{CF}_3\text{CH}_2\text{O}$ — and  $\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O}$ - substituents will be discussed in this paper because polymers which contain these groups are being commercialized at the present time. The physical and chemical characteristics of a copolymer are determined by the side chains and their relative proportions in the final polymer.

Representative properties for an uncured  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O})_2\text{PN}]_n$  copolymer or a



terpolymer, where  $x \cong y$ ,  $x$  and  $y \gg z$ , and the sum of  $x$ ,  $y$ , and  $z$  is equal to 6, are shown in Table I. For convenience, the terpolymer is simply referred to as a  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O})_2\text{PN}]_n$  terpolymer. The fluoroelastomer is a soft gum with good green strength and little or no cold flow. The  $T_g$  is quite low ( $-67^\circ\text{C}$ ). Weight-average molecular weight is usually in the millions, and polydispersity ranges<sup>4</sup> from 3 to about 20. Specific gravity of the polymer is 1.72.

Horizons Incorporated has conducted a fairly extensive compounding effort with  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O})_2\text{PN}]_n$  copolymers and terpolymers (small amount of cure site) to evaluate these elastomers as replacements for

TABLE I  
Typical Properties for  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  Elastomers

Physical state	elastomer
Glass transition temperature	-67°C (DTA)
Initial decomposition point in air, by TGA, 2.5°C/min	325°C
$[\eta]$ at 30°C (in acetone)	2.0–5.0 dl/g
Soluble in	ethanol, acetonitrile, Freon TA
Insoluble in	hexane, benzene, Freon E-2
Chemical and oxygen resistance	excellent

TABLE II  
Typical Range of Physical Properties for  
 $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  Elastomer Vulcanizates

100% Modulus	1.4–10.5 MPa
Tensile strength	7.0–17.5 MPa
Elongation	100–350%
Hardness, Shore A	40–90
Compression set, 70 hr/150°C	20–50%
Tear strength	5.3–53 kN/m

existing materials used in extreme service lip seal, O-ring, and gasket applications.<sup>5-9</sup> An assortment of fillers and curatives were studied, and the properties in Table II are typical of the wide range possible.

Typical  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  elastomer formulations consist of three major components: fillers (reinforcing or extender types); a high-activity magnesium oxide (Elastomag 170) for efficient cure and enhanced thermal stability; and a peroxide curative. Auxiliary ingredients such as silanes, coagents, stabilizers, and process aids have all found use in compounds for specialized applications.

The best vulcanizate properties are obtained with fillers which have a neutral or basic pH. Filler loadings range from 10 to 100 parts per hundred rubber. Silane-treated silica fillers, either fumed (Tullanox 500) or precipitated (Quso WR82), and silane-treated clays (Nulock 321L, Burgess KE) are the fillers of choice for good mechanical properties and thermal stability. Carbon black fillers produce excellent vulcanizate properties, but they are limited in long-term service in the 135°–150°C range.

Peroxide curatives such as dicumyl peroxide, 2,5-dimethyl-2,5-di-*tert*-butylperoxyhexane and  $\alpha,\alpha$ -bis(*tert*-butylperoxy)diisopropylbenzene have been utilized successfully for effective cure and enhanced thermal stability. Peroxide concentrations of 0.2–2 parts per hundred by weight of rubber have been used for  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  terpolymers. Copolymers generally require higher peroxide levels. Sulfur cures have been accomplished with some terpolymers, but they are not recommended when thermal stability is a prerequisite.<sup>10</sup> Compounded stocks can be processed on conventional rubber process equipment.

Low-temperature flexibility of  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  vulcanizates compares favorably with other commercial fluoroelastomers, as shown by the Gehman subzero flexibility data depicted in Figure 1. The

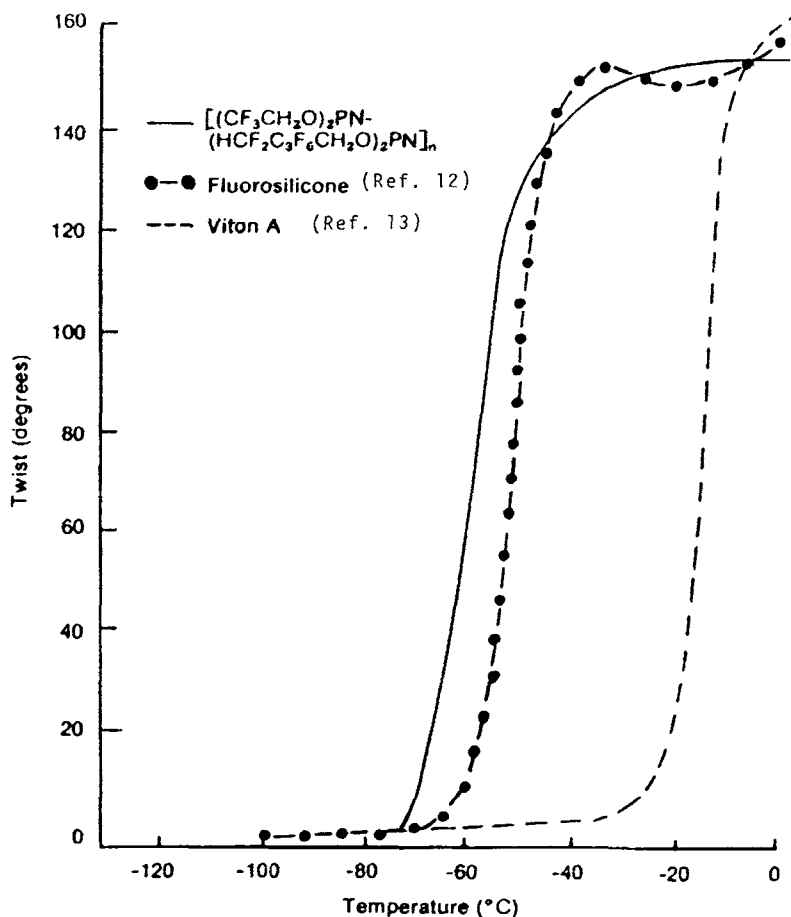


Fig. 1. Comparison of low-temperature Gehman properties of extreme service fluoroelastomers.

$[(CF_3CH_2O)_3PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  vulcanizates have low-temperature flexibility superior to that of fluorocarbon rubbers and comparable to, or better than, that of fluorosilicone rubbers.

The  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  vulcanizates possess good thermal stability. Isothermal aging data for lip seal materials, shown in Table III, indicate lifetimes of about 500 hr at 177°C and 200 hr at 200°C. Tensile strength decreases gradually with exposure time, but thermal history has only minor detrimental effects on moduli, hardness, or elongation. Compression set remains quite low after exposure to these temperatures. Comparable vulcanizates can be expected to be serviceable in excess of 1000 hr at 150°C. Preliminary results<sup>11</sup> with a stabilizer, zinc 8-hydroxyquinolate, are extremely promising and suggest that this stabilizer may further improve thermal stability of the vulcanizates when used with appropriate fillers.

Fluid resistance of  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  polymers in general is good to excellent. Immersion studies for seal formulations in several lubricants and a hydraulic fluid are presented in Tables IV and V. The test vulcanizate displayed excellent retention of stress-strain properties, low volume swell, and hardness change after more the 1000 hr of immersion at 125°C in MIL

TABLE III  
Thermal Stability in Air of  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  Vulcanizates

	0 hr	72 hr	144 hr	240 hr	504 hr
	At 177°C				
50% Modulus, MPa	3.5	3.6	3.7	3.5	3.5
100% Modulus, MPa	9.9	—	—	—	—
Tensile strength, MPa	10.2	9.6	9.3	8.6	8.7
Elongation, %	105	95	85	90	95
Hardness, Shore A	70	—	—	—	73
Compression set, %					
70 hr/150°C in air	23				
70 hr/177°C in air	46				
	0 hr		24 hr		68 hr
	At 200°C				
Tensile strength, MPa	10.2		7.7		4.9
Elongation, %	70		70		50
Hardness, Shore A	83		81		83
Compression set, %					
22 hr/150°C in air	26				
22 hr/200°C in air	49				

TABLE IV  
Lubricant Compatibility of a  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  Vulcanizate

	125°C			150°C	
	0 hr	504 hr	1008 hr	72 hr	168 hr
	MIL-7808G <sup>a</sup>				
50% Modulus, MPa	3.1	2.6	2.2	2.8	2.8
100% Modulus, MPa	9.7	8.9	7.4	8.9	8.4
Tensile strength, MPa	11.3	9.3	8.3	9.8	8.4
Elongation, %	110	105	115	115	100
Hardness, Shore A	77	70	71	72	69
Volume change, %	—	+9.9	+11.3	+9.2	+14.0
Compression set, %					
70 hr/150°C in air	21				
	MIL L-23699 <sup>a</sup>				
50% Modulus, MPa	3.1	3.1	2.8	3.0	3.0
100% Modulus, MPa	9.7	9.3	8.1	9.4	9.1
Tensile strength, MPa	11.3	10.0	9.5	10.0	9.7
Elongation, %	110	110	120	110	110
Hardness, Shore A	77	73	73	74	74
Volume change, %	—	+5.2	+6.0	+3.0	+4.4
Compression set, %					
70 hr/150°C in air	21				

<sup>a</sup> Commercial synthetic ester lubricants.

L-7808G and MIL L-23699 lubricants. The same vulcanizate also held up well at 150°C for the time period tested.

As shown in Table V, operational lifetime for a vulcanizate in MIL H-83282 flame-retardant hydraulic fluid should be about 500 hr at 177°C. Further improvements in the solvent resistance and thermal stability of the base elastomers or improved compounding may significantly extend lifetimes and increase service temperatures.

TABLE V  
Hydraulic Fluid Compatibility of a  
[(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> Vulcanizate

	0 hr	168 hr	336 hr	504 hr
MIL H-83282 <sup>a</sup> at 177°C				
50% Modulus, MPa	3.5	3.2	2.6	2.9
100% Modulus, MPa	9.9	—	—	—
Tensile strength, MPa	10.2	8.4	7.2	6.3
Elongation, %	105	90	90	95
Hardness, Shore A	70	—	—	—
Compression set, %				
70 hr/150°C in air	23			
70 hr/177°C in air	46			

<sup>a</sup> Commercial synthetic hydrocarbon fluid.

TABLE VI  
Resistance of a [(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> Vulcanizate to Jet Fuel

	0 hr	24 hr	120 hr	312 hr	Retention, %
JP-4 at 115°C					
Tensile strength, MPa	11.4	10.5	9.4	7.9	69.3
Elongation, %	80	75	75	75	93.8
Hardness, Shore A	80	77	75	72	90.0
Fluorosilicone tensile retention <sup>13</sup> 72 hr/115°C, 45%					

Hydrocarbon fluids have a limited effect on [(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> vulcanizates, as would be expected of an elastomer with high fluorine content. Volume swell in the ASTM fuels is minimal, with the most pronounced swell observed in Fuel C, which has a high aromatic content and is the most polar of the fuels. Resistance of



vulcanizates to military jet fuel also is impressive, as shown in Table VI. Compare the vulcanizate's tensile retention after 312 hr at 115°C in JP-4 with a fluorosilicone after 72 hr immersion. Similar results have been obtained in JP-5, JP-7, and A-1 jet fuels.

Seals, gaskets, and coatings often are exposed to high humidity conditions. Therefore, they must be hydrolytically stable to remain functional. After nearly 900 hr at 100°C and 100% relative humidity, the vulcanizate shown in Table VII retained almost 85% of its original tensile properties.

The [(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> elastomers also are stable to aqueous alkali at temperature, as shown in Table VIII. Dilute acids have only minor effect on vulcanizate properties; however, strong mineral acids and glacial acetic acid cause loss in physical properties. Further work in the area is planned because compounding variables may have a role in acid resistance.

Poly(fluoroalkoxyphosphazene) elastomers have demonstrated the capability to function in severe dynamic applications. For example, lip seals (1<sup>7</sup>/<sub>8</sub> in. I.D.) performed for over 1000 hr at 5500 rpm in MIL L-7808G lubricant at 115°C.<sup>5,9</sup>

TABLE VII  
Hydrolytic Stability of a Typical  
[(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> Vulcanizate at  
100°C and 100% Relative Humidity

	0 hr	168 hr	384 hr	888 hr
100% Modulus, MPa	10.1	8.6	8.8	6.1
Tensile strength, MPa	12.1	12.2	11.6	10.1
Elongation, %	115	135	135	145
Hardness, Shore A	55	69	70	70

TABLE VIII  
Alkali Resistance of a [(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> Vulcanizate<sup>a</sup>

	0 hr	24 hr	120 hr
Tensile strength, MPa	12.1	8.7	8.3
Elongation, %	120	110	110
Hardness, Shore A	60	60	61

<sup>a</sup> 30 wt-% aqueous KOH at 93°C.

O-Ring seals based on [(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> terpolymer withstood 1000 hr of dynamic qualification testing in a rod seal test apparatus over a temperature range of -54°-163°C and pressure up to 21 MPa. Upon completion of the test, the seals remained soft and flexible. Newer seal compounds based on [(CF<sub>3</sub>CH<sub>2</sub>O)<sub>2</sub>PN-(HCF<sub>2</sub>C<sub>3</sub>F<sub>6</sub>CH<sub>2</sub>O)<sub>2</sub>PN]<sub>n</sub> terpolymer are expected to perform for 1000 hr in air or fluids at -60°-177°C with intermittent service at 200°C possible. Additional dynamic tests with these new compounds are contemplated.

In summary, poly(fluoroalkoxyphosphazene) elastomers are a unique class of polymers capable of extreme service use. Their novel preparative route only requires a single polymerization step after which a variety of different polymer types can be prepared. Copolymers and terpolymers are readily prepared, and polymer properties can be tailored by proper choice of substituents. Vulcanizates possess a combination of low-temperature flexibility, thermal stability, good mechanical properties, petrol-oil and lubricant compatibility, and resistance to chemical attack and hydrolysis. These elastomers can be used for seals, O-rings, gaskets, diaphragms, hose, and protective coatings—in general, any application that requires a versatile, extreme-service elastomer.

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