Kirk-Othmer Encyclopedia of Chemical Technology.

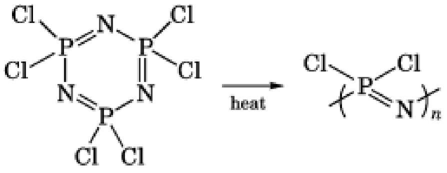
PHOSPHAZENES

Polyphosphazenes have a backbone of alternating nitrogen and phosphorus atoms with two substituents on each phosphorus atom. The backbone is isoelectronic with that of silicones; these polymer backbones share the characteristics of thermal stability and high flexibility. The normal synthesis route provides a large range of possible derivatives. Coatings, fluids, elastomers, and thermoplastics can be produced by varying the polymer molecular weight and the substituents on the phosphorus. These materials have been suggested for use in a wide variety of areas including solid electrolytes for advanced batteries, and biomedical devices, including implants and drug carriers. Other reviews are available covering various aspects of polyphosphazene chemistry and applications (1, 2) (see Inorganic polymers).

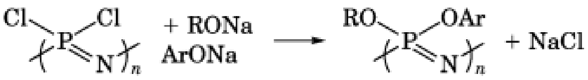
Two elastomers have been commercialized with unique property profiles. One has fluoroalkoxy substituents that provide resistance to many fluids, especially to hydrocarbons. This material also has a broad use temperature range and useful dynamic properties. Aryloxy substituents provide flame retardant materials without halogens.

1. Synthesis

Phosphazene polymers are normally made in a two-step process. First, hexachlorocyclotriphosphazene [940-71-6], trimer **(1)**, is polymerized in bulk to poly(dichlorophosphazene) [26085-02-9], chloropolymer **(2)**. The chloropolymer is then dissolved and reprecipitated to remove unreacted trimer. After redissolving, nucleophilic substitution on **(2)** with alkyl or aryloxides provides the desired product (3).



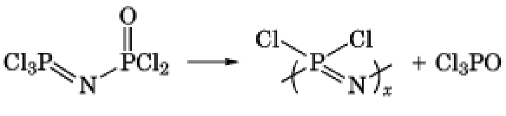
(1) **(2)**



(2)

Production of a high purity linear chloropolymer of appropriate molecular weight is a demanding task. The original approach, a ring opening polymerization of cyclic trimer, can be done without deliberate addition of catalyst, although it is now accepted that ultrapure trimer will not polymerize without some catalyst. This thermal polymerization leads to high molecular weight (typically over one million) and broad molecular weight distributions. Temperatures of 250°C for 24 to 48 hours are frequently employed to obtain conversions of 30 to 50%. Conversions are limited to avoid gelation. Use of a catalyst provides control of molecular weight, and gives significantly higher conversions with soluble (substantially linear) product. With catalysts of appropriate activity, lower polymerization temperatures can be utilized. A large number of catalysts have been studied and catalysts are used commercially in preparing chloropolymer. A patent was issued claiming aprotic Lewis acids as catalysts (4).

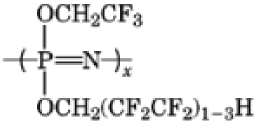
The standard route to chloropolymer requires high purity cyclic trimer, which is expensive. Other potentially less expensive routes have been investigated which may be considered polycondensation reactions. One approach is a multistep procedure involving phosphorus pentachloride and ammonium chloride (5). Another route involves polycondensation of *P*-trichloro-*N*-dichlorophosphoryl monophosphazene **(3)** or the thio analogue, $Cl_3P{=}N{-}P(S)Cl_2$ (6). This approach is being pursued by Atochem. All these syntheses require the processing of extremely corrosive materials at temperatures of 200–300°C.



(3)

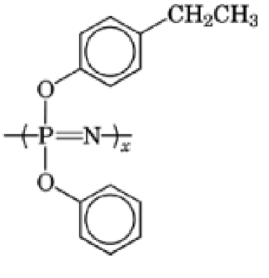
Substitution of chloropolymer is possible using a variety of nucleophiles. The most common are sodium salts of alcohols and phenols. Thermoplastics are obtained using a single substituent, whereas multiple substituents of sufficiently different size lead to elastomers (2). Liquid crystal behavior similar to polysiloxanes has been noted in most homopolymers. The homopolymer formed using trifluoroethanol as a substituent has received a fair amount of academic scrutiny (7).

Elastomers formed using alkoxide salts of trifluoroethanol and higher fluoroalcohols have been found to have an interesting range of thermal and fluid resistance. These materials were developed under U.S. Army sponsorship, and initially commercialized by Firestone using the name PNF, later sold by Ethyl Corp. as EYPEL-F elastomer. ASTM has reserved the designation FZ for elastomers of this class which have the nominal structure given as **(4)**.



$$\left(\overset{\mathrm{OCH_2CF_3}}{\underset{\mathrm{OCH_2(CF_2CF_2)_{1-3}H}}{\mathrm{P}}} = \mathrm{N} \right)_x$$

(4)

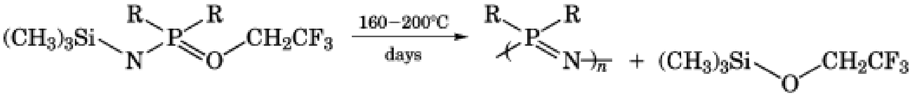


(5)

Roughly 65% of the substituents are trifluoroethoxy, and 35% are telomer alcohols prepared from tetrafluoroethylene and methanol. About 0.5 mol % of an allylic substituent is used as a cross-link site. The substituent pattern is believed to be strictly statistical.

Another elastomer to find use is the substitution product of phenol and *p*-ethylphenol along with an allylic monomer to provide cross-link sites **(5)**. This is trademarked EYPEL-A elastomer [66805-77-4] by Ethyl Corp., and designated PZ by ASTM. The substitution ratio is roughly 52 mol % phenol, 43% *p*-ethylphenol, and 5% allylic substituent.

Routes to prepare substituted polymer directly were pioneered with the polymerization of *N*-trimethylsilylphosphoranamines to form low to moderate molecular weight polyphosphazenes **(6)** where R is alkyl or aryl (8).



(6)

These polymers differ from those prepared in the traditional two-step routes in that there is a direct carbon–phosphorus bond instead of a potentially weaker O, N, or S linkage to phosphorus. A related approach has been discovered using a catalyzed polymerization of tris(trifluoroethoxy)-*N*-(trimethylsilyl)phosphoranimine (9). This allows greater synthetic variation while still giving the control of a one-step polymer synthesis. Neither of these approaches are practiced commercially. The monomers required are costly, and frequently the polymer molecular weights are low.

2. Toxicology

Hexachlorocyclotriphosphazene (cyclic trimer) is a respiratory irritant. Nausea has also been noted on exposure (10). Intravenous and intraperitoneal toxicity measurements were made on mice. The highest nonlethal dose (LD_0) was measured as 20 mg/kg (11). Linear chloropolymer is also believed to be toxic (10). Upon organic substitution, the high molecular weight linear polymers have been shown to be inert. Rat implants of eight different polyphosphazene homopolymers indicated low levels of tissue toxicity (12). FZ has been found to be reasonably compatible with blood (13), and has lower lipid absorption than fluorosilicone.

3. Fluoroalkoxyphosphazene Elastomers

3.1. FZ Characterization

FZ elastomer is a translucent pale brown gum with a glass-transition temperature, T_g of -68 to -72°C. The gum can be cross-linked using peroxides such as dicumyl peroxide and α,α'-bis(t-butylperoxy)diisopropylbenzene. It is provided in compounded form for specific applications, or in masterbatch form to allow custom compounding. Surface treated silica and semireinforcing carbon black are preferred fillers (qv). Acidic fillers such as precipitated or fumed silicas and small particle carbon blacks inhibit the peroxide cure and lead to poorer thermal stability and compression set. Clays, silicates, and nonreinforcing blacks can be used as extending fillers. Compounding is performed using an internal mixer, and completed using a roll mill. Gum physical properties are as follows (14):

T_g, °C	−68
Mooney viscosity, $ML1+4$, 100°C	20
specific gravity	1.75
refractive index	1.41

The gum is soluble in lower ketones and esters, amide solvents, methanol, and tetrahydrofuran.

Compounds can be processed using most conventional rubber processing equipment. Roll milling of low durometer stocks is easiest using a warm roll. Mooney viscosities of these compounds range from 30 to 140 at 100°C. This typically leads to easy flow in molding, although significant orientation is often noted. Selected compounds are suitable for calendering and extrusion of profiles. These contain at least some carbon black as filler.

Most applications have been parts molded using compression molding, although transfer molding has been used and injection molding has been demonstrated. Parts made have varied from O-rings weighing under a gram to complex seals weighing over 20 kg. Good adhesive bonds to metal can be achieved during the cure cycle using silane-type primers. Molding cycles of 20–30 min at 160°C are typical using dicumyl peroxide. Shorter cycles are obtainable at higher temperatures, but curing above 200°C is not recommended. Linear mold shrinkage of roughly 3% is typical for 70 durometer compounds molded at 170°C. Post-cure in a 175°C oven for four hours provides optimal modulus and compression set values. The range of typical compound property values is given in Table 1.

The decreases in tensile strength and elongation values as the temperature is elevated are modest when compared to specialty elastomers having higher glass transitions (Fig. 1). This aids in actual use as well as in molding and other processing. A continuous use temperature of 175°C is based on retention of 50% of both tensile strength and elongation after a thousand hours of aging at this temperature (Fig. 2).

The excellent low temperature properties of FZ have been indicated in Table 1. Modulus curves were obtained using dynamic mechanical spectroscopy to compare several elastomer types at a constant 75 durometer hardness. These curves indicate the low temperature flexibility of FZ is similar to fluorosilicone and in great contrast to that of a fluorocarbon elastomer (vinylidene fluoride copolymer) (Fig. 3) (15).

Dynamic mechanical analysis uses a small sinusoidal mechanical deformation to measure the modulus of the material. Modulus values obtained in the tensile mode are designated with the symbol E, whereas G is used for shear moduli. In viscoelastic materials, the deformation is not in phase with the force applied. The modulus can be resolved into a storage modulus, E' (elastic response) and a loss modulus, E'' (viscous response). The ratio of loss to storage moduli, E''/E', also known as the loss tangent or tan δ, peaks at transitions in the mechanical behavior of the material. These are related to polymer morphology changes, but are also a function

Table 1. Properties of FZ Compounds

Property	Value
density, g/mL	1.75–1.85
durometer hardness, Shore A	35–90
tensile strength, MPa[a]	6.9–13.8
100% modulus, MPa[a]	2.8–14.8
ultimate elongation, %	75–250
compression set, 70 h at 150°C, %	15–55
tear resistance, die B, kN/m[b]	to 26
retraction temperature, TR-10, °C	−56
brittle point, °C	−68
weatherability and ozone resistance	excellent
flame resistance, LOX[c]	39–46

[a] To convert MPa to psi, multiply by 145.
[b] To convert kN/m to ppi, divide by 0.175.
[c] Limiting oxygen index.

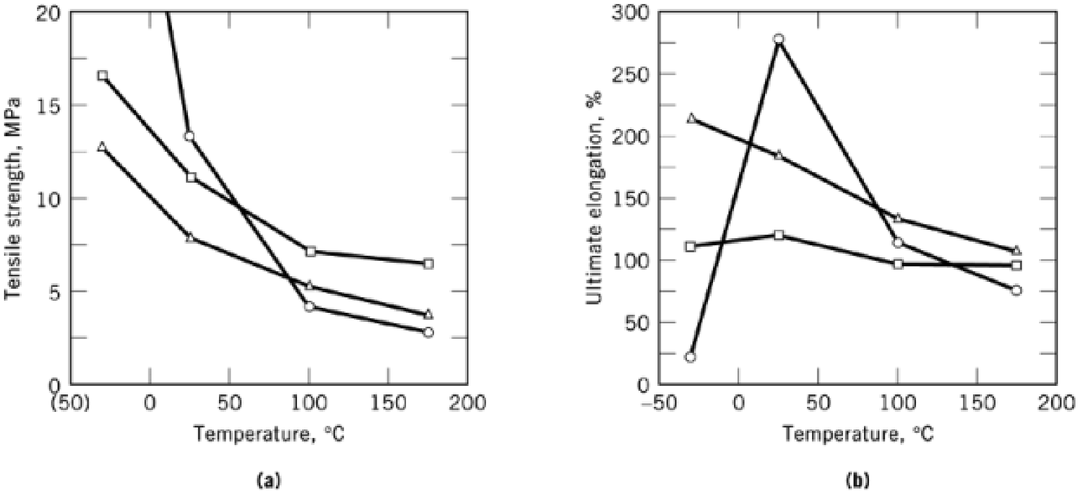


Fig. 1. Comparison of fluoroalkoxy FZ, □; fluorosilicone FVMQ, △; and fluorocarbon FKM, ○, elastomers (**a**) Tensile strength; (**b**) elongation. To convert MPa to psi, multiply by 145.

of the applied oscillation frequency. Highly resilient materials have low tan δ values, while damping materials have high values in the range of temperature and frequency of interest.

Properly formulated FZ compounds have demonstrated excellent fatigue resistance. One measure of this is the Monsanto fatigue-to-failure test (ASTM D4482) which emphasizes crack propagation. Superior fatigue life was observed at elongation ratios under 2, ie, elongations under 100% (Fig. 4), in a comparison of 50 durometer specialty elastomers. This property is utilized in diaphragms, both in applications involving contact with hydrocarbons and in those without fluid contact.

Shock isolation is also possible using the damping characteristics of FZ elastomer. Dynamic mechanical analysis indicates multiple transitions and a broad damping peak. This damping can be enhanced using formulations containing both silica and carbon black fillers.

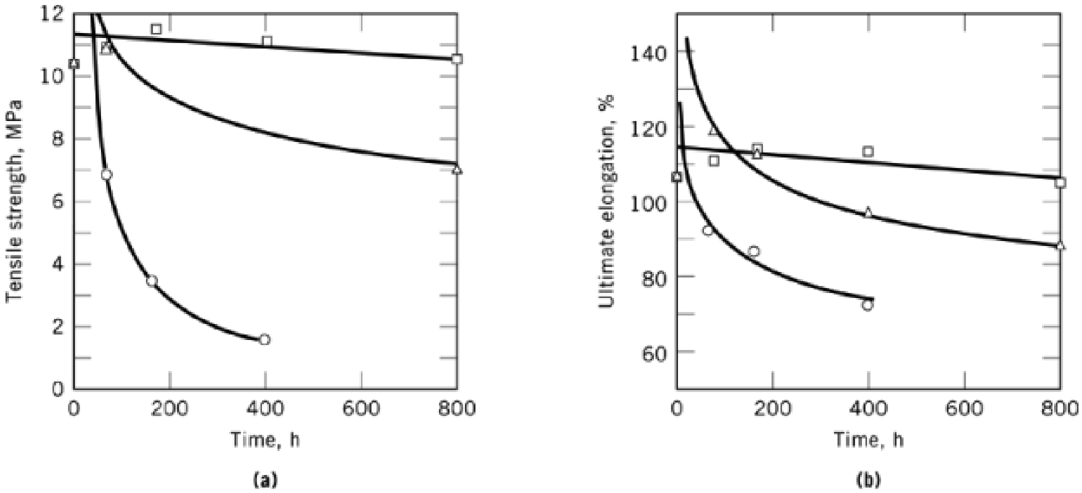


Fig. 2. Tensile strength and elongation retention after aging of FZ. Aging temperature □, 150°C; △, 175°C; ○, 200°C. To convert MPa to psi, multiply by 145.

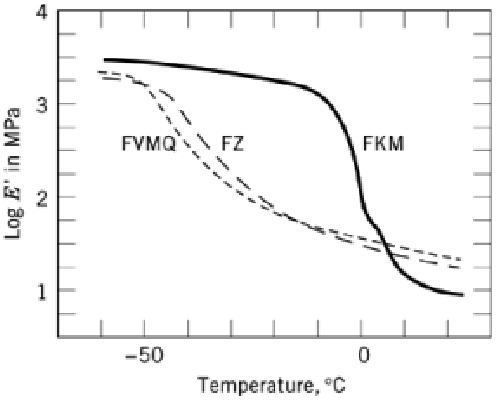


Fig. 3. Modulus comparison at low temperature of FZ, FVMQ, and FKM elastomers.

FZ elastomers have excellent resistance to hydrocarbons and inorganic acids as expected for a fluorinated elastomer. They are strongly affected by polar solvents, but are more resistant to amines than most other fluorinated elastomers as shown in Table 2.

3.2. Economic Factors

Annual usage is under 10 metric tons, and is largely consumed in the United States. Minor quantities are used in both Europe and Japan. Prices vary by application but exceed $200/kg. Ethyl Corp. has announced its intent to divest or exit this business. At present they are the sole supplier.

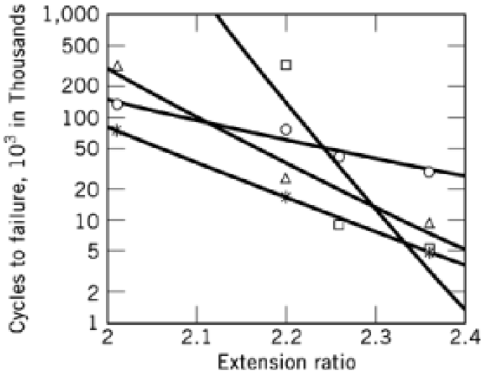


Fig. 4. Tensile fatigue, the Monsanto fatigue-to-failure FTF test, for several elastomers: □, FZ; △, ethylene–acrylic; ○, nitrile (NBR); and *, FVMQ.

Table 2. Fluid Resistance of FZ

Fluid	Rating[a]
Aqueous solutions	
inorganic acids	G–E
organic acids	P–F
bases including amines	F–G
ethylene glycol	G
Fuels	
unleaded gasoline	G–E
gasohol	F–G
diesel, jet fuel	E
Hydraulic fluids	
hydrocarbon	E
phosphate ester (Skydrol)	P
ester	G
silicone	E
Organic solvents	
hydrocarbons	E
chlorinated hydrocarbons	G
chlorofluorocarbons	P
carbonyl compounds (acids, ketones, esters), ethers, methanol	P
other alcohols	G

[a] E, Excellent; G, good; F, fair; P, poor.

3.3. Specifications

FZ compounds meet class EK in the SAE automotive rubber classification J200. Line callouts have been developed for 50, 70, and 80 durometer materials. Specific compounds meet requirements for O-rings for military aerospace applications identified in MIL-P-87175, AMS-7261/1-3, and AMS-7284.

3.4. Applications

Initial applications have been largely in military and aerospace areas. These include hydraulic seals for military aircraft and fuel seals and diaphragms for both military and civilian aircraft. Shock mounts for FZ are used on aircraft engines. Large fabric-reinforced boot seals are used in the air intake system on the M-1 tank. The material's useful temperature range, fuel and fatigue resistance, and fire resistance were determining factors in this application.

There are also a number of nonaerospace civilian applications for this material. Small diaphragms have found limited use in automotive and related applications. These are used because of the material's excellent fatigue life and hydrocarbon resistance. A compound containing methacrylates functions as a soft liner for dentures (16), providing extended life, shock isolation, and resistance to microbial attack.

4. Aryloxyphosphazene Elastomers

4.1. Properties and Applications

Aryloxyphosphazene elastomers using phenoxy and *p*-ethylphenoxy substituents have found interest in a number of applications involving fire safety. This elastomer has a limiting oxygen index of 28 and contains essentially no halogens. It may be cured using either peroxide or sulfur. Peroxide cures do not require the allylic cure monomer. Gum physical properties are as follows (17):

T_g, °C	–18
Mooney viscosity, ML $1+4$, 100°C	40–70
specific gravity	1.25

The gum is soluble in tetrahydrofuran, toluene, and cyclohexane.

Initial uses of aryloxyphosphazenes have focused on areas where fire safety is a paramount concern. Cross-linked aryloxyphosphazene networks form an intumescent char on heating. The gum accepts fairly high filler loadings. Nonreinforcing fillers like alumina trihydrate can be used to make compounds with limiting oxygen indexes above 40. Smoke density of these compounds is also low as measured in the NIST procedure (maximum in flaming mode can be <100). Early research on toxicity of combustion products to small animals rated PZ compounds as roughly 1.5 times as toxic as Douglas fir. Other common synthetics rated from 6 to 25 times as toxic as fir (18).

These advantages in fire safety have been pursued in several product areas. Flexible closed cell foams have been produced with typical densities of 72 kg/m^3 (4.5 lb/ft^3). Thermal conductivity is only 0.37 W/(mK) and water vapor permeability is low. This product is used in hull and pipe insulation on naval ships and submarines, and has elicited interest for use on aircraft. These foams meet the requirements of specification MIL-I-24703. Dense sheeting made using high gravity fillers is also used in acoustic damping applications by the U.S. Navy. In both these applications, the glass and higher transitions contribute to appreciable damping at ambient temperature and acoustic frequencies.

Wire and cable insulation based on vulcanizates of PZhas also been studied. Again, low fire risk was the target property, and this was achieved. The need to vulcanize the coating, somewhat modest tensile properties, tensile strength of 5.2 to 12.2 MPa (760 to 1770 psi), and high dielectric constant (4–5 at 10,000 Hz) limited interest in this application (19).

4.2. Economic Considerations

Gum production by Ethyl Corp. is under 20 metric tons per year. Products are sold primarily for use in U.S. and N.A.T.O. naval applications. The materials are sold as finished goods, and thus elastomer pricing is not appropriate. Ethyl Corp. has announced that it will either divest or exit this business. Atochem has developed their technology and has constructed a pilot plant to produce aryloxyphosphazenes.

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