

Phosphazene Elastomer Use in Defence and Aerospace

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Biographical Note: Billy W. Goodwin co-founded Materials Science Technology Inc. (MST) along with Dr. Harry Allcock. Mr. Goodwin serves as Chairman of the Board and is a member of the Scientific Advisory Committee, bringing over 30 years experience in business and innovation management. Prior to co-founding MST, Mr. Goodwin held senior-level positions for Fortune 200 chemical companies. He holds a B.Sc. in Chemical Engineering and Chemistry from Louisiana State University (honours) and M.B.A. from Duke University (honours). The author would also like to recognize Harry Allcock and Raymond Stiles for their significant contributions to this paper.

ABSTRACT: *Non-symmetrical fluorinated side-groups substituted on a phosphorus-nitrogen polymer backbone yield elastomeric materials with properties that cannot be achieved with conventional carbon monomer polymers. Properties, including low glass-transition temperatures, high melt-transition temperatures, chemical resistance, fuels and hydrocarbon resistance, low compression set and high modulus, are typical of these elastomers. A fluorinated polyphosphazene (ASTM designation "FZ") product was commercialized for aerospace use within the U.S. Department of Defence. The material was successfully used in elastomer applications requiring O-rings, T-rings, rotor seals and other military and armoured vehicle applications. At the end of the cold war, the sole supplier withdrew FZ from the market citing high costs. Fundamental research continued with gram quantities being produced at the laboratory scale. However, commercial development was impeded due to the unavailability of commercial quantities of phosphazenes and phosphazene starting materials. Materials Science Technology, Inc. (MST) has developed a process and constructed a plant that is currently producing 15,000 kg/yr of FZ gum rubber under the trademark PNF™. This paper discusses the underlying fundamentals of the FZ polymer in relation to aerospace and defence applications.*

Introduction

The chemistry of *phosphorus* is diverse and has led to the creation of a wide variety of advanced materials for use in science and engineering applications. Phosphorus chemistry contains many of the aspects of the related inorganic element silicon, with a wider range of functional capabilities due to the electronic configuration of the phosphorus atom.

The term *phosphazene* refers to a broad array of molecular combinations containing a backbone of alternating phosphorus and nitrogen atoms joined by unsaturated bonds (figure 1.1). The backbone can be linked together to form polymer chains or cyclic rings. Inorganic, organometallic or organic pendent groups (represented by R_n groups) can be attached to the phosphorus atom to achieve a high degree of functionality required for specific applications. Phosphazene polymers differ from conventional polymers in that the backbone is inorganic rather than organic, imparting special properties.

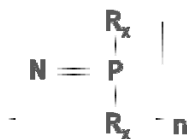


Figure 1.1

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A number of related backbone structures have been synthesized based on application property requirements. Linear and branched chains, cyclics, dendrimers, stars and other architectures, including species with carbon or sulfur as well as phosphorus and nitrogen, are possible. The ability to control backbone architecture (figure 1.2), combined with the addition of a large variety of pendent side-groups makes phosphazenes one of the most diverse classes of polymers in existence today². In addition to mixed-substituent side groups, cure-site monomers are frequently added for later cross linking.

For defense and aerospace industries, elastomer properties can be customized using a tool referred to as *Predictive Analysis*³, an analytical tool used to predict how control variable perturbations influence finished product properties in relation to customer and market applications.

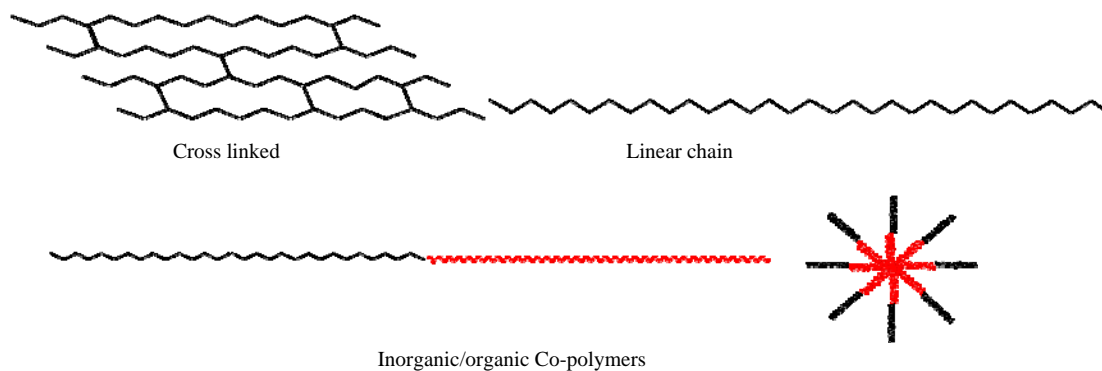


Figure 1.2

Phosphazene History

Harry R. Allcock⁴ first isolated the uncrosslinked version of polyphosphazenes in 1964. He has continued his pioneering work over the past 45 years in his laboratories at The Pennsylvania State University. Professor Allcock was the first to produce an uncross-linked phosphazene polymer by the ring-opening polymerization of $[\text{NPCl}_2]_3$ and convert it to a series of stable organic side group derivatives by the replacement of chlorine atoms by alkoxides, aryloxides and amines to give polymer of the formulae $[\text{NP}(\text{OR})_2]_n$ and $[\text{NP}(\text{NHR})_2]_n$. Dr. Allcock worked with Firestone Tire and Rubber Company laboratories to develop phosphazene polymers for the United States Department of Defense.

Initially used in aerospace applications fluoroalkoxy-substituted phosphazene polymers (FZ) were popularized due to the broad operating-temperature range (-68 to 175 °C), chemical resistance, flexural fatigue resistance and dampening capabilities. Phosphazenes were considered strategic to the U.S. Army and a laboratory was established for FZ development. Outside the military, commercial development has largely been driven by applications within aerospace, biomedical and energy.

In 1984 when Bridgestone purchased Firestone, there were objections to technology transfer, and, the technology was licensed to Ethyl Corporation, a domestic producer. From 1984 to 1994 Ethyl produced FZ under the trademark Eypel-F[®] for the U.S. Military. Aerospace sealing-applications included O-rings, T-seals and helicopter rotor seals. Other defence applications include the plenum seal for M-1 Abrams Tanks, regulator sleeves, hydraulic boots, vibration dampening for turbines and special coatings for radar absorption. In 1994 Ethyl made a decision to withdraw Eypel-F from the market. Their withdrawal was earmarked by a combination of factors including the end of the cold war, high production costs due to process complexity, lack of quality raw materials at a reasonable price and royalty payments under a technology licensing agreement.

² "Chemistry and Applications of Phosphazenes", Allcock, Harry R., **2003**, Wiley-Interscience, John Wiley & Sons, Inc., Hoboken, New Jersey

³ For a full discussion on *Predictive Analysis* see section titled "Engineering Properties".

⁴ Harry R. Allcock is the Evan Pugh Professor of Chemistry at The Pennsylvania State University and a co-founder of Materials Science Technology, Inc. (MST).

Since 1994 there has been no commercial source of FZ. No suitable replacement has been identified although several multinational chemical manufactures have tried unsuccessfully to duplicate the process. Laboratory and small scale quantities have been available through a lab synthesis on a 200 gram scale.

MST was founded in 2007 to manufacture commercial quantities of polyphosphazenes. A process was designed and taken through proof-of-concept to produce the fluoroalkoxy-substituted polyphosphazene (FZ). The process was scaled-up and a production facility was built. In 2009 the newly designed plant and R&D facility were commissioned.

The plant has a name-plate capacity of 15,000 kilograms per year (FZ gum rubber). MST is selling under the trademark PNF™. Quality control testing is conducted in accordance with ASTM standards to comply with the requirements of the aerospace industry⁵. In addition to a full complement of analytical testing equipment, mixing, curing and compounding facilities are located at the facility. The plant is also capable of producing a wide variety of polyphosphazene derivatives important to the specialty elastomer, energy and biomedical industry with engineering configuration changes.

Polyphosphazene Elastomer Properties

Elastomeric properties can generally be attributable to one of two major classifications; properties attributable to the backbone structure and properties of the side-groups. Properties inherent in the alternating phosphorus-nitrogen backbone include torsional mobility, thermooxidative stability, radiation stability, high refractive index and biomedical compatibility during hydrolysis. This paper will only consider properties relevant to elastomers, or torsional mobility and thermooxidative stability.

Properties of the Phosphorus-Nitrogen Backbone

Elastomers are defined as exhibiting both viscous and elastic characteristics when undergoing deformation. When stress is applied to a viscous material there is a linear response to shear and strain. Elastic materials exhibit instantaneous strain when deformed, but typically return to their original state once the stress is removed. Consider a solid polymer with both viscous and elastic behavior. At a state-of-rest, the polymer is in a natural coiled position (figure 1.3). As stress is applied, the chain will align itself with the applied stress. This energy barrier which must be overcome is a consequence of the *bond torsional mobility*. The bond torsional mobility is considered a good measure of the flexibility inherent in the polymer backbone or skeleton. If this energy barrier is low, changes in stress or temperature alter the shape of the bulk material. Conversely if the energy barrier is high, it will restrict conformational mobility and the polymer will behave as an inelastic solid.

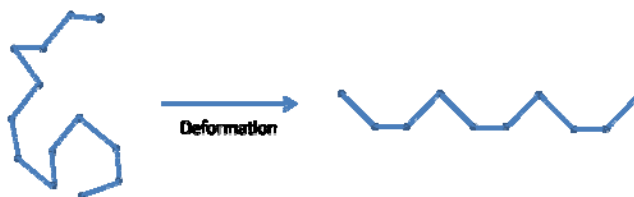


Figure 1.3

Conventional thermoplastic polymers are typically rigid at low temperatures and flexible at high temperatures. This transition state from rigid to flexible occurs at the glass transition (T_g) temperature. The glass transition temperature represents the temperature below which the backbone bonds are essentially frozen-in-place. At temperatures above the glass transition temperature the backbone bonds have sufficient energy to allow torsional motion and the material transitions from a rigid solid to a more flexible elastomer.

Phosphazene torsional barriers are estimated well below 1 kcal/mol/unit with the lowest T_g in the -90 °C to -100 °C range. In comparison, carbon-based organic torsional barriers are estimated at less than 1 to 5 kcal/mol/unit⁶.

⁵ The Society of Automotive Engineers (SAE) Aerospace Division is a self-regulating organization responsible for the approval and use requirements of materials used in the aerospace industry within the United States of America.

⁶ Ibid, p. 400

Other factors influencing torsional mobility include the presence of side-groups, bond angles, bond lengths and other intermolecular forces.

The wider the bond angles the more distance between the side groups and the greater the flexibility. Side-groups impose their own inflexibility and the greater the distance from each other the less likely the influence on torsional motion. The phosphorus bond angle in the linear phosphazene is estimated to be near 119° , while the angle at nitrogen is estimated to be between 130° to 160° ⁷. By comparison, the carbon bond angle for the linear alkane is 109.5° ⁸.

A similar analogy can be used to understand the influence of bond length. The longer the length between atoms, the further apart the side groups and the less influence exerted on torsional barrier height. According to Allcock, the average skeletal bond lengths in polyphosphazenes are estimated in the range of 1.55 to 1.60 Å, compared to a linear carbon-carbon bond of 1.54 Å for the linear alkanes⁹.

Polyphosphazene thermal stability is due to the inherent high-bond energy of the phosphorus-nitrogen bond. Carbon-based polymers cleave homolytically, generating free radicals when exposed to high temperatures, visible, ultra-violet, gamma-ray, x-ray or electron-beam radiation. Conversely, polyphosphazenes do not readily undergo cleavage when subjected to thermooxidative attack due to the high bond energy (70 kcal/mol ¹⁰) inherently resistance to homolytic cleavage. It is also important to note that polyphosphazenes are largely resilient to oxidation since the phosphorus atom exist in the most stable oxidation state (pentavalent) within the backbone.

Properties of Fluoroalkoxy Side Groups

Although the polyphosphazene skeleton plays an important role in defining polymer properties, of equal importance is the influence of the side group constituents and their effect on polymer properties. One also must take into consideration *cure-site monomers* or *cross linking agents*. Therefore, actual polymer properties are from the backbone, side group(s), cross linker selection, chain length, chain architecture and intermolecular forces.

Common side groups for elastomer formation include are listed in Table 1.1.

Elastomer Side Groups
--OCH ₂ CF ₃
--OCH ₂ OC ₂ H ₅
--OC ₃ H ₇
--OC ₄ H ₉
-- OCH ₂ CH ₂ OCH ₃
-- OCH ₂ CH ₂ OCH ₂ CH ₃
-- OC ₆ H ₅ and --OCH ₂ (CF ₂) _x CF ₂ Y ¹¹ (where x is an even integer and Y is a hydrogen or fluorine atom)

Table 1.1

While carbon-hydrogen side groups are common in polymers, fluorinated side groups are frequently selected for their chemical and oxidation resistance. Properties of fluorinated side groups generally include chemical resistance, hydrophobicity, fire resistance and an increase in the glass transition temperature of the polymer.

When substituting with single-substituent fluorinated side groups the polymer is typically stiff due to crystallinity¹². The crystalline structure inhibits mobility of the backbone when compared to a random or amorphous structure. Similarly, mixed-substituent short-length (or similar) fluorinated side groups lead to crystallinity and care must be taken to understand the crystallinity requirements in relation to the degree of amorphousness required for elastomer design as this ratio can have a significant impact on mechanical properties.

⁷ Ibid, p. 404

⁸ "Organic Chemistry"; Solomons, T.W. Graham; 4th Edition **1996**; John Wiley & Sons; New York, N.Y.

⁹ "Chemistry and Applications of Phosphazenes", Allcock, Harry R., p. 405

¹⁰ Ibid, p. 407

¹¹ Ibid, p.410

¹² Ibid, p. 411

The presence of two or more side groups (mixed-substituent groups) lowers molecular symmetry and in general leads to an amorphous structure. Fluorinated side groups consisting of molar ratios of $\text{NaOCH}_2\text{CF}_3$ and $\text{NaOCH}_2(\text{CF}_2)_x\text{CF}_2\text{Y}$ were some of the first elastomers discovered by Rose^{13,14}. They are still considered as an important class of elastomers for commercial applications. These mixed-substituent elastomers have been marketed under the trademark(s) PN-F[®] and Eypel-F[®] for aerospace and defence applications.

Although glass transition temperatures are primarily a function of the torsional mobility inherent in the backbone, T_g is also influenced by the presence of fluorine atoms present in the side groups. Also of importance is the length of the side group¹⁵. The absence or presence of a terminal fluorine atom also plays a significant role in solution thermodynamics and inherent stability of the polymer.

The thermal characteristics of FZ polymers are some of the broadest in the aerospace industry, with glass transition temperatures in the region of -70°C for the gum rubber. Once cross-linked, FZ is stable for extended periods up to 175°C and for short times up to 315°C . As previously discussed, the high-temperature stability depends on several factors including compound additives such as cross linking curative and fillers.

Engineered Properties

Typical compound values using standard PNF[™] FZ gum rubber are listed in Table 1.2.

Physical Property	Units	Value Range
Compression Set (70 hr @ 150°C)	%	15 – 55
Elongation	%	75 – 250
Tensile	MPa, (psi)	6.9 - 13.8 (1000 - 2000)
Density	g/ml	1.70 - 1.85
Hardness	Shore A	35 – 90
TR-10	$^\circ\text{C}$	-56
Glass Transition (T_g)	$^\circ\text{C}$	-68
Temperature Range	$^\circ\text{C}$	-65 to 175
100% Modulus	%	2.8 – 13.8 (400 – 2000)

Table 1.2

PNF[™] elastomer compounds have good adhesion properties (fabrics, metals and substrates), excellent vibration dampening, dynamic fatigue resistance, broad range of chemical resistance, flame resistant, physiologically inert, liquid oxygen compatible and excellent weatherability.

To help customers understand the impact of control-variable perturbation to exploit finished product properties, MST has developed a *Predictive Analysis tool*. Using this tool, MST works with compounders and component parts manufacturers to customize finished properties in relation to upstream control attributes (table 1.3)¹⁶.

¹³ Rose, H.S., *Journal of Polymer Science, Series B*, **1968**, 6, 837-839

¹⁴ Rose original work was confined to mixed-substituent side groups with terminal fluorine atoms only and relatively low molecular weight species.

¹⁵ Although the term *length* is used in this paper, one must consider molecular structure (i.e., degree of branching) in addition to molecular weight of side groups in design of polymer properties.

¹⁶ MST selection matrices are based on the Quality Function Deployment Matrix (QFD) originally developed in Japan for improving communication between customer, design, engineering, marketing and manufacturing. For a full discussion, see “Strategic Management of Technology and Innovation”, Schilling, Milissa A., **2005**, McGraw-Hill Irwin, 1221 Avenue of the Americas, New York, N.Y. 10020

Market/Customer Requirements	Engineering Attributes	Importance	Glass transition	Side group ratio	Molecular structure	Batch size	Compounding	Cross linking agent
	Sealing capability	25	5	25	5	5	20	10
Temperature range	20	25	5	5	5	5	5	
Flexural fatigue	15	5	20	15	5	10	10	
Adhesion	10	5	10	5	5	5	10	
Life testing	25	5	10	10	5	5	5	
Fluid compatibility	25	5	15	10	5	5	5	
100% Modulus	10	5	15	5	5	5	10	
Elongation	10	5	20	5	5	5	10	
Durometer	15	5	15	15	5	10	10	
<i>Relative importance of engr. Attribute</i>			65	135	75	45	70	75
Design targets			4	1	2		3	2

Table 1.3

This tool is used to develop a correlation between a set of control variables (Engineering Attributes) which can be manipulated to influence finished product properties¹⁷. The process leads commercial and technical personnel through an organized framework with the aim of understanding how MST can influence upstream properties inherent to the polymer manufacturing process.

First, the customer identifies market requirements specific to the application. For example, Table 1.3 lists some of the sealing requirements of the aerospace industry. Next, the customer prioritizes the requirements in terms of value-add that the customer brings. With market requirements prioritized, MST lists engineering attributes that can be controlled upstream in the process. Attribute weighting and correlation is based on *major* or *minor* influence on finished product properties. MST assists customers in developing an understanding of the affects of variable attributes in relation to the specific market requirements. Next the team fills in the body of the matrix, multiplies the customer requirement by the engineering attribute and sums the columns to get the relative importance of each attribute. From here a number of steps can be taken to clarify project objectives and design requirements.

PNF™ Manufacture

The linear chloropolymer is manufactured from hexachlorocyclophosphazene. This “cyclic trimer” starting material is linearized through a ring-opening polymerization (figure 1.4).



Figure 1.4

The resultant poly(dichlorophosphazene) is highly reactive due to the phosphorus-chlorine bonds. After contaminant removal the polymer is further treated and stored for a subsequent reaction with a reagent. During the

¹⁷ This tool is used in accordance with MST standard non-disclosure agreement.

polymerization process the degree of polymerization (n), degree of branching and other morphological characteristics critical to the back-bone design are engineered to specified properties.

Side groups are then prepared via a sodium exchange to form the alkoxide. Commercially a wide variety of side-groups have been examined including alcohols, amines and phenols. For the purposes of this paper, discussion will be limited to side-groups consisting of trifluoroethanol and a mixed-chain fluorinated alcohol. Stored chloropolymer is reacted via a nucleophilic addition with mixed alkoxides to yield the FZ gum rubber (figure 1.5). The ratio of alcohol side-groups is varied to achieve specificity. Cure-sites are incorporated by interspersing an unsaturated cross-linker which can be cured using peroxide-based or other recognized cure techniques.

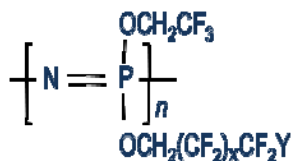


Figure 1.5

The finished FZ gum rubber is of high purity containing less than 0.07 wt% chlorides and less than 0.5 wt% solvents. The weight percentage of cross-linking agent is quantified according to finished good specifications. Using the qualified gum rubber, carbon, silica, alumina-silicate filled master batches are mixed and sold to specialty compounders for further optimization. Base-compounds are commercially available with durometers ranging between 35 and 90. Base-compounds are also available with or without cross-linkers, depending on application requirements.