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Polymer Performance and Aging in a Tritium Environment

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In an ideal tritium system, we would be able to remove all polymer components due the damage incurred by the resulting beta decay and reduce the required maintenance of the systems and its components. However, polymers are an integral material used within the Tritium Facility in sealing, joining, and containment and are used in several different systems within the process. With the loss of certain capabilities, such as the Normetex pump, it is necessary to identify and/or develop polymers that can better withstand exposure to beta radiation in tritium environments. This article reviews the various polymer resins and formulations that are used in a tritium environment, their properties, and their performance.

Keywords: polymer, tritium, beta

I. INTRODUCTION AND BACKGROUND

Polymers can undergo damage from radiation by two methods: chain scission and cross-linking. The primary method of degradation is dependent on the polymer, its chemical structure, and the specific environment. Polymers are more susceptible to radiation damage than metals and ceramics due to the long chain structures that form its properties. The most common resulting physical changes are an increase in hardness or tensile strength and a decrease in elongation and overall toughness or elasticity. An increase in hardness or modulus can be particularly detrimental to sealing applications which rely on material compliance and elasticity to seal and prevent leakage of both gases and liquids. Properties of polymer materials can be affected at different rates or to varying extents in a particular radiation environment. The salient or important properties in different applications may vary. Properties such as elongation are generally more sensitive to radiation damage than other properties such as tensile strength.

One of the earliest issues with polymers in a tritium environment arose with concerns about the degradation of BUNA-N, a synthetic acrylonitrile butadiene rubber [1]. Synthetic rubbers generally experience negligible radiation damage up to an absorbed dose of 10^5 Gy, begin to exhibit some damage up to 10^6 Gy [2], and exhibit very severe damage at higher absorbed doses. Due to the relatively lower tolerance of radiation damage by nitrile rubber, alternative materials such as ethylene-propylene-diene-monomer (EPDM) were investigated and recommended for service. EPDM is in continuous use, although investigations to increase the radiation stability of both EPDM and alternative polymers continue to this day. This article will highlight key polymers found in the operating facilities, summarize their mechanical and chemical properties, as well as discuss recent results from long term exposure experiments.

II. POLYMERS USED IN TRITIUM SERVICE

There are three main categories of polymers used in tritium: elastomers, engineering thermoplastics, and commodity thermoplastics. The three classes are broken down and discussed in detail below, including examples of specific polymers. A list of these polymers, along with their chemical structure, advantages and disadvantages can be found in Table 1.

II.A. Elastomers

Elastomers are polymers with the ability to stretch and bounce back. This is due to the long chain structures with controlled cross linking. They are amorphous polymers and typically are made of a combination hydrogen, oxygen, carbon, and/or silicon atoms.

Butyl Rubber

One of the most widely used polymers in tritium operations is butyl rubber for gloves in glovebox containment. Butyl rubber has some of the best permeation resistance of any elastomeric material. It is commonly used for tire inner tubes and gas bladder applications and even seals in certain radioactive material packages and weapon components. This combined with its low Durometer values (surface hardness), resiliency, and dexterity has led to being the material of choice for glovebox gloves in tritium applications. However, butyl rubber is still permeable to some amounts of oxygen and water, which can create processing issues in glovebox containment.

Ethylene Propylene Diene Monomer (EPDM)

Due to its unique combination of physical properties, EPDM can be found in an unusually broad range of elastomeric products [3]. In tritium applications EPDM finds use in elastomeric sealing applications such as gaskets and O-rings. Its performance has been well characterized in tritium operations at Savannah River Site (SRS)[4, 5]. For example, it has been found that the use of carbon black fillers can increase the radiation resistance of EPDM [4]. This is an important observation that could help the development of future materials with increased radiation resistance that still retain the desirable properties of the base polymer.

II.B. Engineering thermoplastics

Engineering thermoplastics are polymers that have been designed to have better mechanical and thermal properties, with the exception of Ultra High Molecular Weight Polyethylene (UHMW-PE), than conventional plastics, often with increased resistance to environmental degradation. A primary benefit of thermoplastics is that they are efficiently manufactured into complicated shapes with a lower density than metals.

<u>Polytetrafluoroethylene (PTFE, TEFLON®)</u>

PTFE has historically been used as a sealing material in many industries. In tritium environments, PTFE has been used for valve seals, valve packing material in higher pressure or high vacuum applications, and where a non-stick surface or low coefficient of friction is required for sealing. However, PTFE use within a tritium environment has been drastically reduced over the years to the point where there are only a few minor instances where it is used in secondary containment applications. The primary reason for this is due to the well-known low radiation tolerance of PTFE and tritium substitution for fluorine on the polymer backbone. This free fluorine can possibly recombine with moisture in the system to generate hydrofluoric acid or other fluorinated compounds, which even at low concentrations are corrosive to the common types of stainless steel used in primary containment. Another polymer used to some extent in earlier years was Kel-F (PCTFE or poly(chlorotrifluoroethylene)), which also suffers from main chain degradation or chain scission. Therefore, halogenated polymers are avoided in primary containment tritium systems wherever possible due to this effect.

Over the years other polymers have replaced PTFE in tritium systems [6],with a primary need for surface compliance, high lubricity, nonstick characteristics and low coefficient of friction. These include UHMW-PE, High Density Polyethylene (HDPE) and polyimide Vespel®. UHMW-PE and HDPE have largely been used as a replacement for PTFE when the physical property and especially high temperature requirements are lower, such as low pressure valve seals, valve seats, and any kind sealing requirement where stiffness needs to be higher than that of an elastomer. In more demanding applications, as well as any higher temperature applications, graphite filled Vespel® has been used as a replacement.

Polyimide (Vespel®)

Vespel® is a polyimide, characterized by the imide group along the polymer backbone, nitrogen bound to two carbonyl groups, and an aromatic structure. Polyimides are some of the most radiation resistant and heat resistant polymers available, in part, due to the aromatic structure of the polymer [7]. For tritium applications, Vespel® is often filled with graphite to impart the low coefficient of friction characteristics similar to PTFE. Commercial valving is often available containing graphite filled Vespel® seats as a replacement to PTFE valve seals, but parts may require special ordering.

Polyetheretherketone (PEEK)

PEEK is an engineering thermoplastic that is traditionally used in physically demanding engineering applications where a high strength to weight ratio is needed and due to high mechanical properties (modulus, tensile strength, use temperature). PEEK is generally processed in a semicrystalline form, but can be processed in an amorphous form to improve ductility. PEEK is currently being used in tritium operations as electrical wire insulation; this is a niche application for PEEK in the nuclear industry due to its good radiation resistance. As with

Vespel/polyimide, PEEK has high radiation tolerance due to its aromatic structure. PEEK also has a broader range of chemical resistance than polymide.

Nylon 6

Due to its good mechanical and electrical properties, nylon 6 has found use in electrical housings and components on various testing and electrical devices within tritium operations. It is currently under evaluation for its aging characteristics within a tritium environment in order to compare it to other polymeric materials were the aging behavior is better understood.

Polybutyleneterephthalate (PBT)

PBT is similar to nylon 6 in that it is used in electrical components within the tritium operations systems. A primary advantage of PBT vs. nylon is that nylon is hygroscopic and can absorb moisture from the environment, leading to some changes in dimension and properties. Usually such changes are not critical and can sometimes be beneficial, but should be evaluated for specific applications. The aging characteristics of PBT are also being evaluated in a materials characterization program for tritium.

Ultra High Molecular Weight Polyethylene (UHMW-PE)

UHMW-PE has frequently been used in tritium to replace PTFE. This is due to a unique combination of properties: non-stick/low coefficient of friction, high toughness, and abrasion resistance and absence of deleterious species such as halides. Due to the high molecular weight in excess of 3,000,000 g/mol, UHMW-PE exhibits among the highest toughness of any non-reinforced polymer, this is one reason it is categorized as an engineering thermoplastic. This high molecular weight also makes UHMW-PE more difficult to process than typical thermoplastics, generally requiring ram or powder extrusion. The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. This combination of properties makes UHMW-PE a good choice for valve seats, and even orthopedic joint implants. A primary limitation of UHMW-PE in industrial or engineering applications is its lower maximum use temperature of around 90°C in comparison to other polymers such as PTFE and Vespel®.

II.C. Commodity Thermoplastics

Commodity thermoplastics are typically made in large batches, helping to drive down the costs of the materials. The low cost is often offset by poor mechanical properties and chemical resistance; however they are very important polymers due to their ability to be used in a wide range of applications. These include polystyrene and many varieties of polyethylene.

High Density Polyethylene (HDPE)

HDPE is similar to UHMW-PE in many properties (tensile and modulus), the largest-difference is in toughness. Izod impact strength of UHMWPE is at least five times greater than HDPE, which is due to the difference in molecular weight. Due to the lower molecular weight of HDPE, generally between 20,000 and 100,000 g/mol, the molecular chains are more efficient at packing into crystalline regions during cooling from the melt. This results in slightly higher crystallinity and density than UHMW-PE. HDPE is defined by a density of greater or equal to 0.941 g/cc, whereas the density of molded and extruded UHMWPE is generally around 0.93 g/cc. HDPE is truly a commodity thermoplastic in that it has widespread use, the most familiar being plastic milk jugs. It is easily identified by the recycling symbol 2.

III. SAVANNAH RIVER SITE POLYMER TESTING

The Savannah River National Laboratory (SRNL) is unique within the National Laboratory system in that SRNL has historically been a plant support Laboratory, including supporting Tritium facilities. Due to this roll, SRNL has developed tritium capabilities to perform long-term tritium exposure testing of various types of materials including polymers that do not exist at other National Laboratories. This is an important considering the beta radiation decay behavior of tritium gas, which is far less characterized than gamma or neutron irradiation. Using a unique combination of physical property testing and chemical structure testing, SRNL has the capability to evaluate the aging behavior of polymers caused by tritium radiation decay over time. Polymers that have been investigated using the tritium exposure systems include PTFE, Nafion®[8], Vespel®, UHMWPE [9], and EPDM.

III.A. Dynamic Mechanical Analysis (DMA)

DMA is widely used in the polymer industry to evaluate the mechanical/thermal response and viscoelastic behavior of polymers. For tritium-exposed materials, DMA is performed on samples before and after tritium exposure. The data found in Table 2 demonstrate the type of testing that can be accomplished using DMA in conjunction with the unique tritium exposure capability at SRNL. Scans can be taken from cryogenic temperatures at -150 C to as high as 600 C to determine the mechanical properties of selected materials such as Storage Modulus, a measure of sample stiffness.

Previous research shows that the changes in sample stiffness in Vespel® are not as great as that in the UHMW-PE [9]. However, in these experimental results provided in Table 2, we found a dramatic increase in Storage Modulus of Vespel® upon irradiation. This can be explained by an increase in cross-linking density of the material. Experience has shown that parts made with Vespel® will not likely need to be changed out as often as those made with

UHMW-PE. Measurement of off gassing in the exposure cells also confirms the greater radiation resistance of Vespel®. In making decisions on which materials to use for tritium operations use, the engineer should take into account other differences in properties, cost, material availability, and part life.

A critical parameter for elastomers at low temperature is the glass transition temperature (Tg). For low-temperature flexibility, it is important for the service temperature to be significantly above the Tg value to the extent possible. Below the glass transition, a polymer is glassy and above, it is more rubbery. For thermoplastics, the polymer will melt or flow at some point above Tg; for thermosetting elastomers there is no melt due to crosslinking of the chains. Thermosetting elastomers remain rubbery until they degrade. The low-temperature performance of elastomers could be significantly affected by changes in the Tg value. No observable Tg was found for Vespel®, which is in agreement with [10]. Often times the polymer backbone in engineering thermoplastics are so stiff, due to the presence of rigid benzene rings, that workable melting of the polymer does not occur until well above Tg or the degradation crosslinking temperature. PTFE and UHMW-PE were both too brittle to measure after three years exposure and PEEK was outside of the measured range.

III.B. Fourier Transform Infrared Spectroscopy (FTIR)

Another technique commonly used for the chemical characterization of polymers is Fourier Transform Infrared (FTIR) Spectroscopy. SRNL has the capability to perform FTIR using an Attenuated Total Reflectance (ATR) technique to determine chemical changes occurring on the polymer surface during tritium exposure. This is demonstrated in Figures 1 and 2 showing the sample surface spectra for UHMWPE ,PTFE, Vespel®, and PEEK through a three year tritium exposure experiment. In all four cases, the surface structure becomes more amorphous.

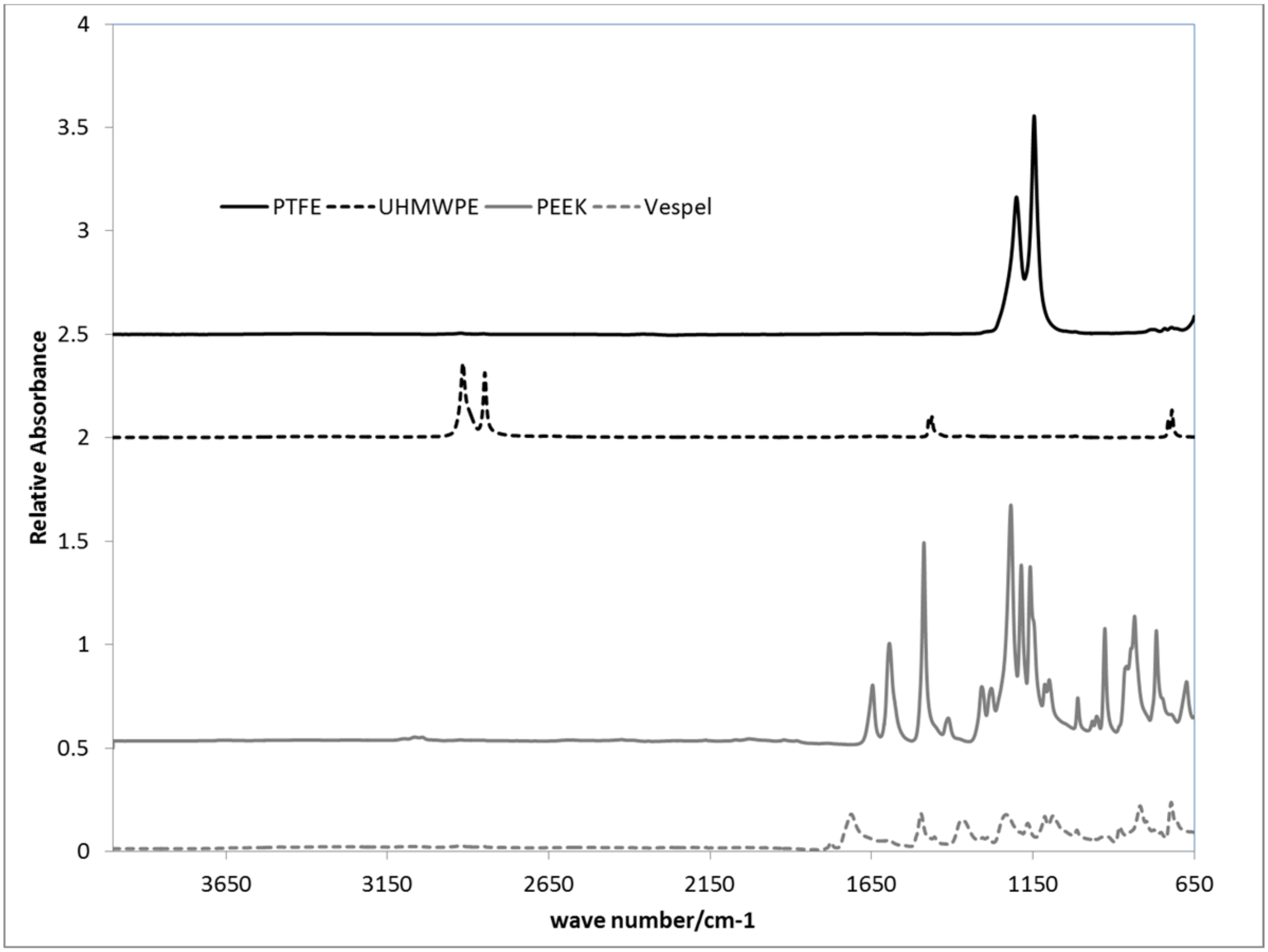

Figure 1. FT-IR analysis of unexposed Vespel®, UHMWPE, PTFE, and PEEK.

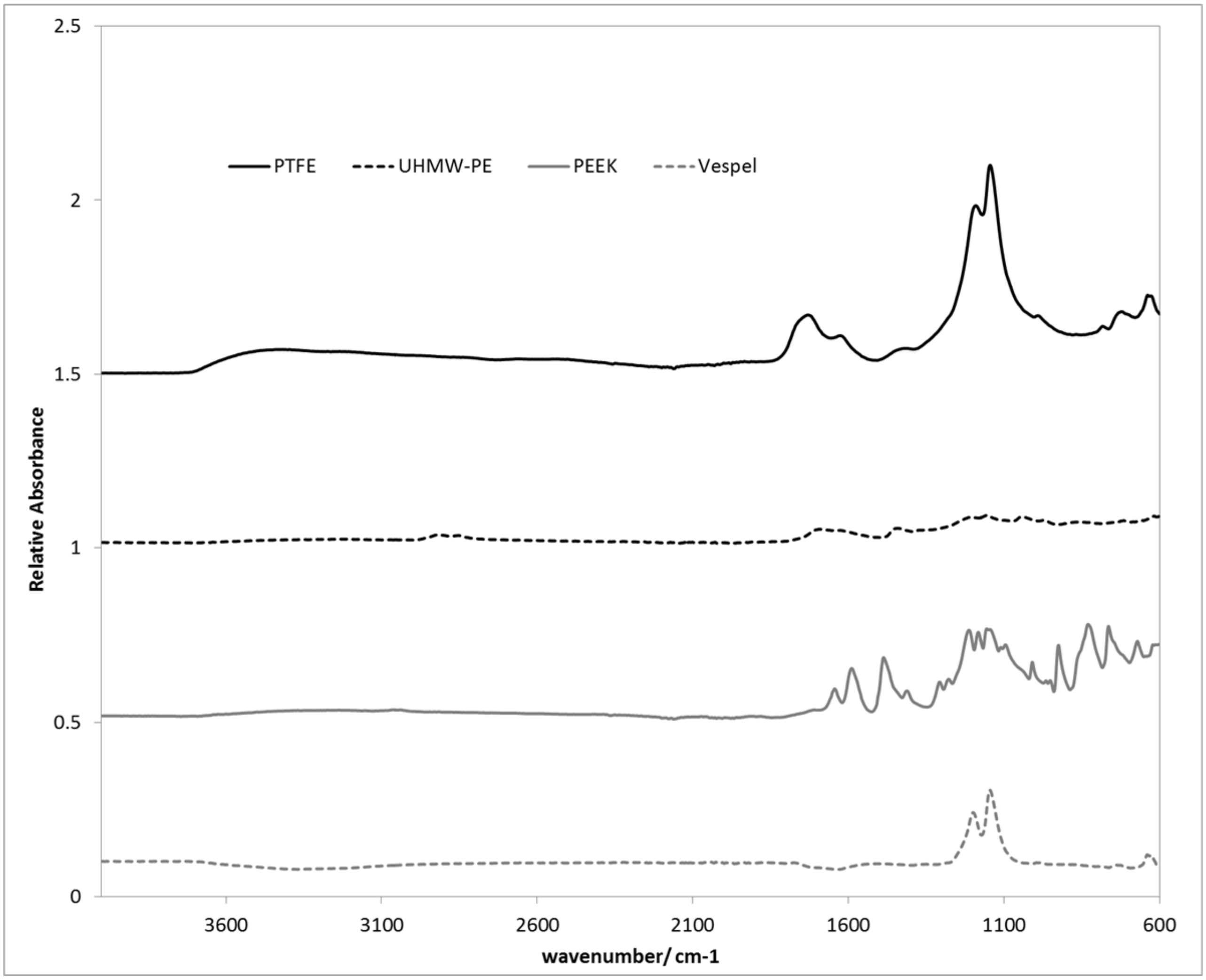

Figure 2. FT-IR analysis of Vespel®, UHMWPE, PTFE, and PEEK exposed to 1 atmosphere of 99.95% tritium for three years.

III. Summary and Conclusion

Polymers have many uses within the tritium facility. When identifying the proper polymer for each job, it is important to take into consideration radiation resistance as well has physical and chemical properties of the material. Understanding the chemistry of the polymer can help determine life time and best practices for their use as well has potential methods to mitigate radiation damage to the material. Long term studies are important to help evaluate life extension and the resulting cost savings from increasing maintenance intervals and replace part costs.

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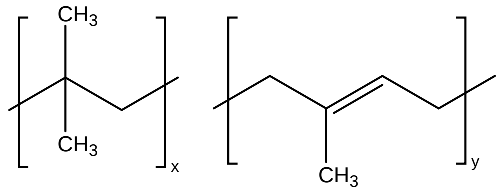
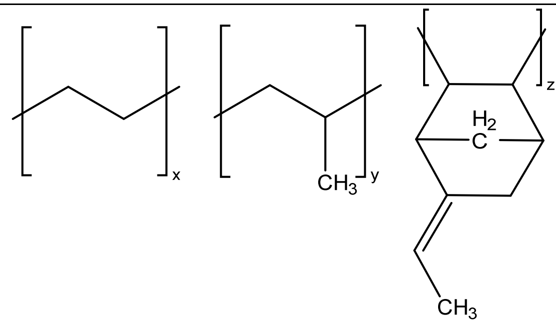
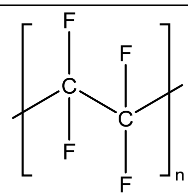
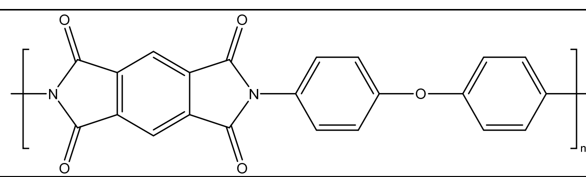
Table 1. The chemical structure, used, advantages and disadvantages of common polymers found in tritium service.

Base Polymer	Chemical Structure	Uses	Advantages	Disadvantages
		CATEGORY I: Elastomers (Rubber)		
Polyisobutylene (Butyl Rubber)		Containment gloves	Low permeability, allows for good dexterity, non-halogenated	Allows some permeation of water, oxygen, and tritium
Ethylene Propylene Diene Monomer (EPDM)		Gaskets, O-rings	Creep resistant, permeation resistant, aging resistant, non-halogenated	Becomes brittle in tritium environments over time.
		CATEGORY II: Engineered Thermoplastics		
Polytetrafluorethylene (PTFE)		Valve seats, non-stick surfaces	Low coefficient of friction, non-stick, excellent chemical resistant, good thermal resistance	Subject to creep, becomes brittle in a tritium environment, can generate HF and other fluorinated compounds in containment, use is restricted
Polyimide (Vespel™)		Valve seats	Heat resistant, chemical resistant, creep resistant, high radiation resistance, low off-gassing	Expensive, slightly hygroscopic, difficulty in processing

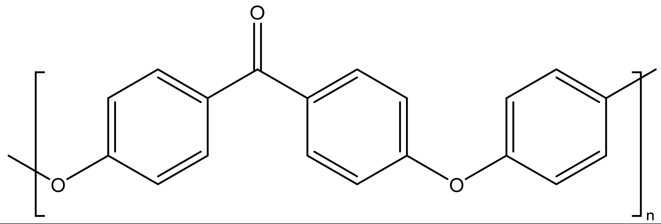
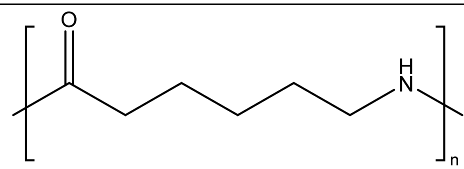
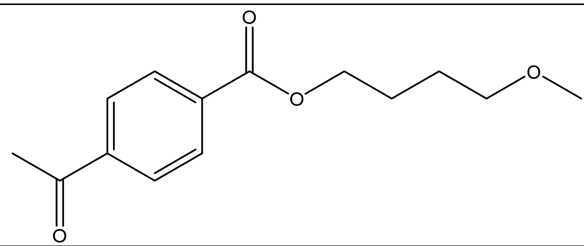
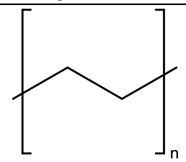
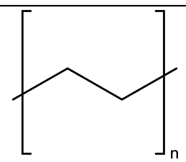
Polyether ether ketone (PEEK)		Bearings, cable insulation, high vacuum applications	Very good chemical/solvent resistance, thermal resistance, mechanical properties	Susceptible to attack by halogens and strong acids (particularly nitric)
Nylon-6		Electrical housings, fittings, bearings, gears	High tensile strength, toughness, good elasticity	Hygroscopic
Polybutylene terephthalate (PBT)		Electrical housings and components	Wear resistant, heat resistant, mechanical properties, resistant to solvents, dimensional stability	Sensitive to water above 60°C
Polyethylene - Ultra High Molecular Weight (UHMWPE) MW > 3,000,000		Valve seats, valve seals	High strength to weight ratio, low coefficient of friction, abrasion resistant, uniquely high toughness	Becomes brittle in tritium environments (more resistant than PTFE), lower temperature resistance than engineered thermoplastics
CATEGORY III: Commodity Thermoplastic				
Polyethylene - High Density (HDPE) MW= 20,000 - 100,000		Gloveport plugs and seals	High strength to weight ratio, low coefficient of friction	Same as UHMWPE and lower toughness than UHMWPE

Table 2. Tg and Storage Modulus for PEEK, Vespel, UHMW-PE, and PTFE that is unexposed and exposed to 1 atm of 99.995% tritium for three years.

Polymer	Tg		Storage Modulus at 25°C		Physical Appearance	
	Unexposed	**Exposed**	**Unexposed**	**Exposed**	**Unexposed**	**Exposed**
PTFE	34.6°C	Sample to brittle to measure	1456 MPa	Sample to brittle to measure	Opaque white	Light tan
UHMWE-PE	56.1°C	Sample too brittle to measure	844 MPa	Sample too brittle to measure	Milky white	Black
PEEK	148.3°C [11]	Not within measurement range	3830 MPa [11]	3216 MPa	Light tan	Tan with darker brown edges
Vespel	Not observable	Not observable	2760 MPa	4039 MPa	Medium brown	unchanged