

Engineering Polymers as Structural Materials in Spacecraft Water Systems

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High-performance engineering polymers, such as PEEK, PEI, and PVDF, have found increasing use as structural materials in a broad array of demanding applications, including in the aerospace, medical implant, and chemical processing fields. In many cases, they have replaced passive metals, due to cost or mass savings, improved chemical resistance and inertness, and/or ease of fabrication. As of yet, there has been little concerted investigation considering the replacement of metals in spacecraft water systems to take advantage of these developments. The decision to baseline ionic silver as the biocide of choice for future exploration-class systems motivates considering this change, as rapid Ag^+ depletion to metal surfaces can result in loss of microbial control. The development of inert barrier coatings may enable the continued use of metal alloys in many applications, but introduces additional failure modes and suitable robustness has yet to be adequately demonstrated. In this early work, we began to address the myriad issues of concern associated with materials selection for performance-critical life support hardware. These include mechanical properties, failure mechanisms, design requirements, leaching into potable water, chemical resistance, radiation tolerance, outgassing, flammability, and others. We selected several engineering polymers for initial consideration and conducted Ag^+ compatibility tests on a limited selection of these, including materials with reinforcing fibers or lubricant fillers. We identified useful literature regarding rational materials selection, design, and mechanical behavior of engineering polymers. We found that there is significant potential for use of engineering polymers in spacecraft water systems but note that much work remains to assemble a knowledge and experience base regarding long-term mechanical reliability of pressurized thermoplastic components and to develop relevant design/test qualification practices and standards. Finally, we suggest some directions for future research.

Nomenclature

$^{\circ}\text{C}$	=	degree Celsius
"	=	inch
316L	=	austenitic Fe-Cr-Ni-Mo stainless steel (low-carbon grade)
Ag^+	=	silver(I) ion
AgF	=	silver fluoride
A/V	=	surface area/volume ratio
AES	=	NASA Advanced Exploration Systems
AIAA	=	American Institute of Aeronautics and Astronautics
ANSI	=	American National Standards Institute
cm	=	centimeter
cm^{-1}	=	cm^2/cm^3
COTS	=	commercial off-the-shelf
E	=	elastic (Young's) modulus
EPA	=	United States Environmental Protection Agency
ESC	=	environmental stress cracking
FEP	=	fluorinated ethylene propylene (semi-crystalline) polymer

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<i>g/cm³</i>	=	gram per cubic centimeter
<i>Gy</i>	=	gray (radiation dose, joule adsorbed/kilogram)
<i>ISS</i>	=	International Space Station
<i>kPa</i>	=	kilopascal
<i>MAPTIS</i>	=	NASA Materials and Processes Technical Information System
<i>ml</i>	=	milliliter
<i>NSF</i>	=	NSF International (formerly the National Sanitation Foundation)
<i>PEEK</i>	=	polyether ether ketone (semi-crystalline) polymer
<i>PEI</i>	=	polyetherimide (amorphous) polymer
<i>ppb</i>	=	parts per billion (mass)
<i>ppm</i>	=	parts per million (mass)
<i>PPS</i>	=	polyphenylene sulfide (semi-crystalline) polymer
<i>ppt</i>	=	parts per trillion (mass)
<i>psi</i>	=	pound per square inch
<i>PTFE</i>	=	polytetrafluoroethylene (semi-crystalline) polymer
<i>PVDF</i>	=	polyvinylidene difluoride (semi-crystalline) homopolymer
<i>PVDF-HFP</i>	=	vinylidene difluoride-hexafluoropropylene (semi-crystalline) copolymer
<i>PWB</i>	=	Potable Water Bus
<i>PWD</i>	=	Potable Water Dispenser
ρ	=	density
<i>S_y</i>	=	yield strength
<i>S_u</i>	=	ultimate strength
<i>SMACs</i>	=	NASA Spacecraft Maximum Allowable Concentrations (for Airborne Contaminants)
<i>SWEGs</i>	=	NASA Spacecraft Water Exposure Guidelines
<i>Ti-6Al-4V</i>	=	grade 5, alpha-beta titanium alloy
<i>WPA</i>	=	Water Processor Assembly

I. Introduction

A. Motivation and Background

The collection, purification, storage, and delivery of water are key to human exploration of outer space. Through recycling of humidity condensate, excreta, and other waste streams, up-mass and transit propellant mass can be reduced significantly, at the cost of increased system complexity. Over many decades, great effort has been made to develop and optimize water processing techniques and associated hardware to improve recovery fractions and system reliability. This has culminated in the current American and Russian water systems on the International Space Station (ISS). Future missions to Mars or settlement of the Moon will require yet more advancement in the state of the art. An important part of that work will be the novel application of materials and fabrication techniques to reduce system mass, improve reliability, extend service life, and help enable new physicochemical processes. Critically, the life support system designer must understand and take into account the properties, behaviors, and potential failure mechanisms of a material in a given application. In addition, simulation, experimental characterization, and iterative design are necessary to guide the process, uncover unforeseen fault modes, and improve system performance. Finally, design practices and engineering standards for flight hardware must be regularly updated as new materials and fabrication techniques become available.

One promising approach to improve spacecraft water system performance is the replacement of passive metal alloys with high-performance engineering polymers for structural materials. An important benefit of this approach is improved compatibility vs. passive metal alloys with Ag⁺ biocide, which has been baselined as the biocide of choice for future exploration-class missions. Ag⁺ loss to more inert thermoplastic materials is typically limited by “aging,” or saturation of adsorption sites, while auto-galvanic deposition of silver onto passive metals can proceed at an appreciable rate indefinitely. Inert barrier coatings may enable the continued use of heritage metals, but these introduce additional failure modes and their long-term robustness is yet to be demonstrated. Beyond Ag⁺ compatibility, engineering polymers offer numerous attractive material properties vs. heritage passive metals.

Over the last few decades, there has been a great expansion in the use of engineering polymers in safety and performance-critical applications. Adoption in such fields as aerospace, medical implants, and chemical processing

has been driven by cost savings, improved chemical resistance, mass reduction, and/or ease of production. Engineering polymers offer significantly improved performance over commodity plastics due to their superior mechanical properties and chemical inertness/resistance. However, terrestrial use has largely been limited to high-end applications due to significantly greater cost vs. commodity plastics. Examples of engineering and commodity grade polymers are shown in Table 1. The commodity plastics typically used in terrestrial potable water transport and storage and in chemical processing are generally ill-suited to application in spacecraft for a variety of reasons, which can include high flammability, excessive offgassing or leaching of toxic compounds, and relatively poor mechanical performance.

Table 1. Examples of Engineering and Commodity Grade Polymers

Engineering	Commodity
PA - polyamide	ABS - acrylonitrile butadiene styrene
PAI - polyamide-imide	cPVC - chlorinated polyvinyl chloride
PEEK - polyether ether ketone	PE - polyethylene
PEI - polyetherimide	PET - polyethylene terephthalate
PES - polyethersulfone	PEX - cross-linked polyethylene
PPS - polyphenylene sulfide	PP - polypropylene
PPSU - polyphenylsulfone	PPMA - poly(methyl methacrylate)
PSU - polysulfone	PS - polystyrene
PVDF - polyvinylidene difluoride	uPVC - unplasticized polyvinyl chloride

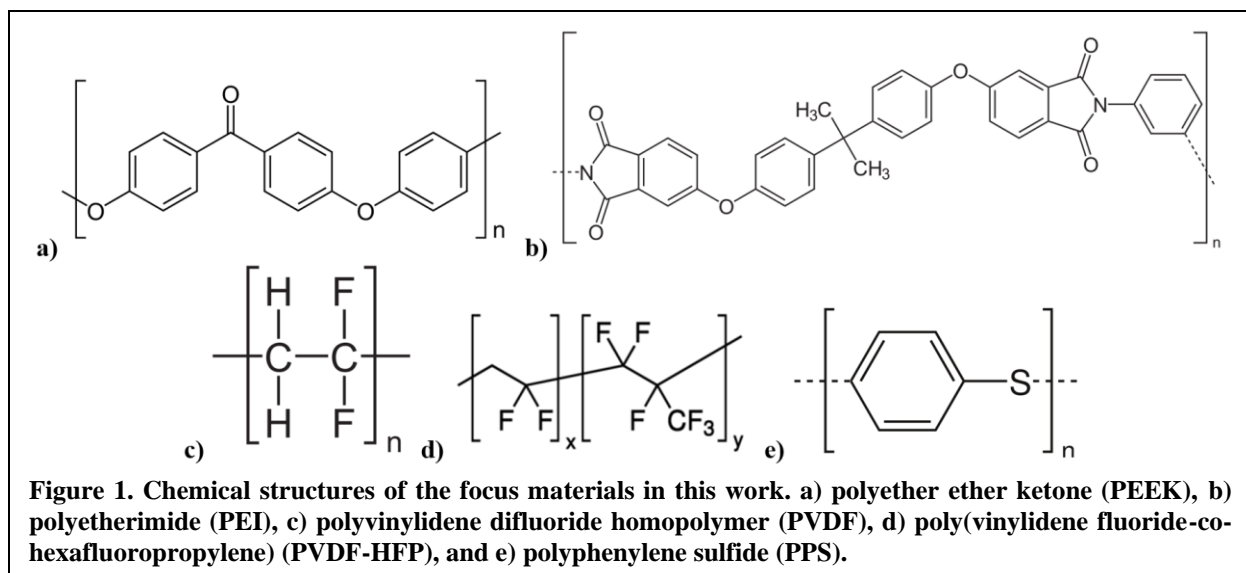
Also of potential use in rigid components are fiber-reinforced thermosetting polymers, such as glass and carbon-fiber reinforced epoxy, which are commonly employed in composite-overwrapped pressure vessels for use in spacecraft. However, these epoxies are generally ill-suited for direct contact with potable water, although certain versions without volatiles may offer better compatibility. In such cases, rotationally-molded thermoplastic liners are typically employed. In the case of tubing and hoses, rubber, silicone, or thermoplastic elastomer materials may offer improved flexibility, but this generally is at the cost of chemical resistance, mechanical durability, and Ag⁺ compatibility. Such materials are beyond the scope of the present work, but may be of future interest.

B. Components and Initial Materials of Interest

After examining the configuration of the ISS Water Processor Assembly (WPA) and Potable Water Bus (PWB), we identified key component categories of interest. These include active components and pressure shells for positive expulsion storage vessels, tubing, fittings, quick disconnects, pumps, valves and valve seats. Selections of COTS components in these categories were identified and reported elsewhere.¹

After surveying the various engineering polymers in commercial production, we identified four to focus on in our initial work. These had interesting combinations of material properties, available processing techniques, and commercial availability of resin and semi-finished/finished goods. The four polymers are: polyether ether ketone (PEEK), polyetherimide (PEI), polyvinylidene difluoride (PVDF) (including copolymers), and polyphenylene sulfide (PPS). The chemical structures of these polymers are shown in Figure 1. These engineering polymers are semi-crystalline at room temperature, except for PEI, which is amorphous. PEEK is the one of the highest performance engineering polymers, and offers excellent mechanical properties and chemical resistance, as well as good availability of semi-finished goods such as stock shapes. It is also available with a range of filler materials such as fiber reinforcements and lubricants. PEI offers similar performance to PEEK, but its much lower melting temperature allows for easier component fabrication, and it is much more suitable for “3D printing” with fused deposition. PVDF offers significantly improved mechanical properties and reduced permeability vs. polytetrafluoroethylene (PTFE), at the cost of somewhat reduced chemical resistance, due to decreased fluorination. It is also available in a wide range of finished goods, such as pipe, fittings, valves, and flexible tubing (PVDF-HFP copolymer). PPS is of interest due to its mechanical strength and chemical resistance, and may be useful for bodies and moving parts in valves and pumps.

Other engineering polymers of interest include polysulfone, polyethersulfone, polyphenylene sulfone, and some of the various polyimides and polyamide-imides. Several fluoropolymers are also of interest, and many offer distinct material properties vs. the classical PTFE, which has found widespread use but has poor mechanical strength and creep resistance. These materials may be the subject of future research.



C. The Present Work

In the present work, we report the results of limited Ag^+ compatibility experiments with PEEK and PEEK with reinforcing fibers and lubricant fillers, PEI, and PVDF homopolymer. We begin to address a range of issues of concern associated with materials selection for life support hardware, and potable water systems more specifically. These include mechanical properties and behavior, failure mechanisms, design requirements, leaching into potable water, chemical resistance, radiation tolerance, outgassing, flammability, and others. We report useful resources regarding rational materials selection, design, and mechanical behavior of engineering polymers. We find that there is significant potential for use of engineering polymers for pressurized components in spacecraft water systems but note that much work remains to assemble a knowledge and experience base to gain confidence in long-term mechanical reliability and to develop relevant design/test qualification practices and standards.

II. Ag^+ Compatibility

A. Background on Ag^+ Compatibility

While engineering polymers promise significantly improved Ag^+ biocide compatibility vs. passive metals due to the absence of galvanic reactions, performance must be investigated experimentally to ensure that other loss mechanisms are not significant. In addition, the “aging” phenomena often encountered with inert thermoplastics, in which surface adsorption sites become saturated in time and Ag^+ loss rates decrease, should be quantified in each material. There is significant ongoing work to characterize Ag^+ compatibility with various polymers of interest at Johnson Space Center (JSC), although only preliminary results have been published as of yet.² These suggested that PEEK, PVDF, and PEI, among others, were promising candidate materials. To avoid duplication of effort, we completed limited tests: with PEEK, both neat and with several filler materials, including reinforcing fibers and lubricant additives, which have received minimal attention in JSC tests, and with PVDF homopolymer and PEI. It is likely that the results with the additive materials can be applied generally to composites with other thermoplastic matrix polymers.

B. Ag^+ Compatibility Experiments with PEEK and PEEK with Fillers, PEI, and PVDF.

Samples were fabricated by cutting 3” (7.6 cm) long sections from ¼” (0.635 cm) rod stock of the various materials, with resin grades and fillers listed in Table 2a and 2b. The samples were cleaned methodically to thoroughly remove any labile processing additives or contamination due to handling. They were wiped with isopropyl alcohol (IPA)-soaked laboratory wipes, rinsed with IPA, rinsed with deionized water (DI), soaked in DI for two days, and finally rinsed again with DI. A subset of each material were pre-treated with 100 ppm Ag^+ solution (from AgF) for three days, rinsed with DI, and then allowed to equilibrate with fresh 400 ppb Ag^+ solution in two one-day immersions. The samples were placed in 12 ml flat-bottomed polypropylene tubes, which were filled with Ag^+ solution (ca. 400 ppb ea. Ag^+ , Na^+ and F^-). The effective surface area/volume ratio (A/V) was approximately 1.6 cm^{-1} , and liquid volume

was 6 ml. The experiments were performed in triplicate, with Ag⁺ loss determinations vs. control tubes with a combination ion-selective electrode (ISE) and refilling with fresh solution at 1, 2, 6, 10, 22, and 44 weeks for PEEK and PEEK with fillers, and at 1, 3, 7, 11, and 22 weeks for PEI and PVDF. During measurement, the sample tubes were stirred at 200 rotations/minute using a magnetic cross, with the combination ion-selective electrode inserted into the tube.

The results of these experiments are shown in Tables 2a and 2b. For context, metals used in the flow paths of previous potable water systems typically show near total Ag⁺ loss within a few weeks in tests with similar conditions, although certain surface treatments may reduce loss rates.^{2,3} As expected, neat and PTFE-filled PEEK, PEI, and PVDF had minimal initial and continuing losses, with 100 ppm Ag⁺ pre-treatment having a beneficial or insignificant effect on initial losses. The somewhat increased losses observed at 11 weeks for PEI and PVDF are believed to at least in part be due to instrument drift, observed also during measurement of the control tubes. Glass fiber-filled PEEK had relatively large initial loss after 1 week, possibly due to ion exchange with alkali species at or near the wetted surface of the fibers or adsorption to negatively charged glass surface sites. This slowed appreciably as the exchange and/or adsorption sites became saturated. Carbon fiber-filled PEEK also had moderate initial loss, with loss decreasing in later determinations. We do not yet know if Ag⁺ loss to carbon fiber is due solely to adsorption or if other mechanisms are active. With both the glass fiber and carbon fiber-filled PEEK, 100 ppm Ag⁺ pre-treatment prevented the relatively large initial losses. The inclusion of 10% graphite in the PEEK produced inconclusive results, although pre-treatment with 100 ppm Ag⁺ resulted in significantly reduced losses at the 6 and 10-week determinations. By 22 weeks, the included graphite no longer resulted in significantly increased loss.

Table 2a: Ag⁺ loss testing with PEEK and PEEK with various fillers (A/V ~1.6 cm⁻¹).

Material:	Ag ⁺ loss* [%] with (std. dev.)					
	Total time immersed [weeks]					
	1	2	6	10	22	44
<i>PEEK (KetaSpire KT-820 NT)</i>	1 (1)	0 (1)	0 (<1)	§ -1 (<1)	§ -2 (<1)	0 (1)
<i>PEEK†</i>	§ -1 (3)	1 (<1)	0 (<1)	§ -3 (2)	2 (1)	1 (<1)
<i>PEEK w/30% glass fiber (KetaSpire KT-820 GF30)</i>	18 (2)	3 (2)	4 (<1)	0 (2)	0 (<1)	0 (<1)
<i>PEEK w/30% glass fiber†</i>	§ -4 (3)	2 (1)	0 (<1)	3 (3)	1 (<1)	0 (<1)
<i>PEEK w/30% carbon fiber (Victrex 450 CA30)</i>	11 (5)	2 (2)	4 (<1)	2 (<1)	2 (<1)	3 (<1)
<i>PEEK w/30% carbon fiber†</i>	§ -1 (<1)	0 (<1)	1 (1)	2 (<1)	1 (1)	2 (3)
<i>PEEK w/20% PTFE (Victrex 450 FE20)</i>	2 (<1)	0 (2)	0 (<1)	§ -2 (<1)	0 (<1)	0 (<1)
<i>PEEK w/20% PTFE†</i>	§ -3 (1)	1 (<1)	1 (<1)	2 (<1)	0 (<1)	1 (<1)
<i>PEEK w/10% each carbon fiber, graphite, PTFE (Victrex 450 FC30)</i>	2 (2)	2 (1)	7 (5)	8 (4)	2 (<1)	1 (<1)
<i>PEEK w/10% each carbon fiber, graphite, PTFE†</i>	§ -1 (<1)	1 (<1)	2 (1)	1 (<1)	0 (<1)	§ -1 (<1)

† Pre-treated with 100 ppm Ag⁺.
§ Ag⁺ concentration increase.

Table 2b: Ag⁺ loss testing with PEI and PVDF (A/V ~1.6 cm⁻¹).

Material:	Ag ⁺ loss* [%] with (std. dev.)				
	Total time immersed [weeks]				
	1	3	7	11	22
<i>PEI (Mitsubishi Duratron UI1000)</i>	5 (2)	2 (<1)	3 (<1)	7 (<1)	5 (2)
<i>PEI†</i>	§ -1 (1)	1 (<1)	3 (<1)	5 (3)	6 (1)
<i>PVDF Homopolymer (McMaster-Carr, grade unknown)</i>	2 (<1)	2 (1)	2 (<1)	8 (2)	4 (<1)
<i>PVDF Homopolymer†</i>	0 (<1)	2 (<1)	3 (1)	5 (<1)	3 (<1)

† Pre-treated with 100 ppm Ag⁺.
§ Ag⁺ concentration increase.

The results of these experiments suggest that some combination of inherent inertness and “aging” with 400 ppb Ag^+ or short-term pre-treatment with 100 ppm were successful in limiting Ag^+ loss rates to minimal levels with all of the materials tested. This should allow for retention of appreciable Ag^+ concentration (and biocidal control) for long periods of static exposure (even at relatively high A/V), as would be found during system dormancy. However, further optimization of “aging” or high-concentration pre-treatment is likely possible. The results also suggest that the inclusion of glass fiber, carbon fiber, or PTFE fillers in engineering polymers should pose minimal Ag^+ compatibility issues, while the suitability of graphite at moderate to high mass fractions remains uncertain, and should be investigated further.

III. Mechanical Properties, Degradation, and Failure Mechanisms of Engineering Polymers

A. Materials Selection and Mechanics of Materials

While a thorough review of materials selection and the mechanics of materials is beyond the scope of the present work, we identified several resources that should be helpful for our future work, and for researchers in the field without significant backgrounds in materials science or mechanical engineering. These include primers on: materials science,⁴ polymer chemistry,⁵ the mechanical behavior of polymeric materials,^{6,7} the stress and strain states in components of various geometries and loading conditions,⁸ and the field of rational materials selection, pioneered by Ashby.⁹

B. Component Design and Processing with Thermoplastic Materials

The design of components constructed from thermoplastic engineering polymers must take into account their mechanical properties and available fabrication techniques. A limited selection from the many available handbooks from manufacturers and the academic press are given in Refs. 10-13. Areas of interest include proper design of joints, welds, and geometric configurations to efficiently strengthen components while minimizing mass.

C. Differences in Material Performance and Component Design in Thermoplastics vs. Metals

Due to differences in chemical composition and microstructure, thermoplastic engineering polymers have significantly different materials properties than the passive metal alloys traditionally employed in spacecraft water systems. Responses to various chemical environments can be very different as well. Thermoplastics typically have much lower yield stress, S_y , and ultimate failure stress levels, S_u , than metal alloys, as well as significantly lower elastic moduli, E .¹ Compared with metals, thermoplastic materials can generally withstand much greater strain before yielding or failing, although these occur at much lower stress levels. For a given loading scenario, some combination of increased material thickness and/or increased elastic deformation (strain) must be accepted. In pure tensile loading, the mass required to support a load is determined by the specific strength (S_y/ρ) of a material, where ρ is density.⁹ *The specific strength* for many high-performance engineering polymers approaches that for typical metal alloys such as 316L and Ti-6Al-4V. In more complicated loading configurations, such as flexure of a beam or plate, the figure of merit becomes S_y^x/ρ , where $x < 1$, and engineering polymers can become more competitive vs. metals. However, as discussed below, due to fatigue and creep, stresses in non-reinforced thermoplastic components must be significantly below S_y to allow for significant service life. This limitation is frequently not an issue, as stress levels can be minimal in many classes of components. As discussed below, the inclusion of reinforcing fibers in a thermoplastic matrix can significantly increase yield stress and elastic modulus, often enabling replacement of metals in highly-stressed components such as pressure vessels and structural members with significant mass savings.

In many cases, lower elastic modulus is desirable to allow for flexible components; some examples include flexible tubing, valve seats, bladders, and diaphragms. Reduced modulus can also improve sealing action by increasing contact area between two parts.

Another important example is tubing for fluid conveyance, as the minimum wall thickness of metallic tubing for use in low-pressure (≤ 30 psi, 200 kPa) spacecraft water systems is not controlled by the hoop stress of the tubing. Instead, the wall thickness must be significantly larger than if that were so, in order to prevent tube collapse/kinking/buckling during bending or other handling. Polymer tubing, with proper selection of material properties and wall thickness, can be flexible or rigid for ease of handling and installation, while still offering sufficient service pressure (and safety factor) and kink resistance, even at similar or reduced linear density.

Unlike in metals, thermoplastic engineering polymers are viscoelastic, and time-dependent plastic deformation or strain (creep) can be significant under moderate stress at room temperature. When stress levels are at a significant fraction of a materials yield strength, engineering polymers may exhibit creep deformation over time, as well as

material thinning. Additionally, a transition from ductile to brittle failure modes may occur, ultimately resulting in stress fracture. Over time, the limiting failure mechanism may change as the material undergoes plastic strain, crack growth, and microstructural evolution. In addition, fatigue (the initiation and propagation of cracks due to cyclic loading) may proceed much faster in many thermoplastic materials than in typical metal alloys. Creep and fatigue data for the engineering polymers considered in this work have been compiled elsewhere.¹ As the necessary service life of a component in a spacecraft water system may be several years, or even decades, design stress levels in pressurized engineering polymer components will by necessity be limited to some relatively small fraction of yield strength. In cases where fatigue and creep resistance and mass minimization are critical, the inclusion of reinforcing fibers can result in greatly improved performance.¹ Issues associated with long-term materials reliability will be focus topics for future research.

There has been significant work in understanding the long-term creep behavior and associated stress-rupture of thermoplastic materials, and standards have been made to certify pipes for service life of 50 years by limiting hoop stress.¹⁴⁻¹⁶ Service life can often be predicted by extrapolating failure data taken at elevated temperature and stress levels or with dynamic (cyclic) loading, however, this must be done judiciously. The combined effects of creep and fatigue in spacecraft water system components, which may see continuous pressurization and extensive cyclic loading, can result in complex phenomena, including qualitative changes in failure modes such as ductile-brittle transitions and accelerated failure. For further information on these topics, see Refs. 7 and 16-24. Understanding such behaviors will be key subjects of future work in this area. The risks of failure due to stress-rupture (creep) or fatigue can be reduced by limiting stress levels, and given the low pressure levels in spacecraft water systems (≤ 30 psi, 200 kPa), such issues are of greater concern in thin-walled storage vessels of large diameter than in thick-walled tubing and fittings of small diameter. Thick- and thin-walled tubing/vessels have to do with the ratio of component's radius versus wall thickness with the boundary being at a factor of 5-10.

D. Damage Tolerance, Fracture Toughness, and Impact Strength

It is necessary to understand the fracture mechanical behavior of thermoplastic engineering polymers, particularly when defects are larger than those assumed in typical fatigue response experiments. Intrinsic defects such as voids produced during molding or extrusion, or extrinsic defects produced during machining, assembly, or handling, can be sources of crack propagation and ultimate brittle failure. In long-term service, fracture toughness may be reduced due to microstructural evolution, and this can be more severe in viscoelastic polymers. Impact toughness may be of concern if potable water systems may be subject to inadvertent impact during handling or collision with loose hardware in microgravity. Proper design of enclosure hardware or protective covers may mitigate the risk of damage due to mechanical impact.

E. Chemical Degradation, Hydrolysis, and Environmental Stress Cracking

Thermoplastic engineering polymers are not subject to corrosion in the traditional sense (electrochemical oxidation) associated with metals. However, depending on their composition and chemical environment, thermoplastics can be subject to various forms of degradation such as hydrolysis and other oxidative attack. No significant deleterious effects from water immersion at low pressure are expected with these materials. However, care should be taken to confirm that water absorption and resultant swelling are minimal during selection.

Crazing, or surface crack formation, is of concern in amorphous polymers. In certain environments, amorphous polymers subjected to continuous or cyclic tensile stress can exhibit brittle failure due to environmental stress cracking (ESC), analogous to stress corrosion cracking in metals. Certain liquid chemicals (specific to the polymer) accelerate the growth of cracks, resulting in failure at lower stress levels than would otherwise be required.²⁵ However, semi-crystalline thermoplastics, such as PEEK, PVDF, PPS, and certain amorphous polymers, such as PEI, have not been found to be subject to ESC with near-neutral water, and are reported to have generally excellent chemical resistance.¹ However, specific material compatibility with dilute halogen biocides in potable water, concentrated biocide solutions, or urine treatment solutions should be confirmed prior to engineering polymers being applied to a specific application.

F. Composites: Fiber Reinforcement and Lubricant Fillers

In some cases, the mechanical properties of "neat" (pure) thermoplastic engineering polymers may not be satisfactory. Composite materials can offer useful combinations of properties not available in any single material. Carbon and glass fibers are commonly used to significantly improve strength and rigidity (as well as fatigue and creep resistance) and these can be of various lengths and geometric configurations, with corresponding processing methods. Short fiber composites can be processed with typical thermoplastic molding techniques (injection, rotational, blow,

extrusion), while continuous and woven fibers may be shaped and then impregnated with the polymer matrix material, or pre-impregnated tapes or filaments may be wound or deposited to produce various geometries, including larger volume vessels than could be made economically by molding. One recent example of interest is the experimental work with cryogenic pressure vessels constructed by overwrapping a rotationally-molded PEEK liner with laser-welded carbon fiber-reinforced PEEK tape.²⁶ Fiber-reinforcement can also be used to reinforce flexible materials, such as in wire or fabric reinforced elastomeric hoses, bladders, and diaphragms. Filler materials are commonly used to improve tribological properties, such as reducing wear or friction on sliding surfaces. Typical examples include PTFE and graphite particles.

While reinforcing fibers and other fibers may offer significantly improved mechanical properties under certain conditions, they also significantly complicate the material system by introducing fiber-matrix interfaces. The interface between reinforcing fibers or lubricant fillers and the polymer matrix material will have limited strength and may be subject to delamination. This problem is aggravated when the fiber and matrix materials have significant mismatch in elastic modulus. These interfacial failures may play an important role in fatigue behavior by serving as crack nucleation sites. Subsequently, bridging fibers may help arrest crack growth. In our application, the composite may be saturated with absorbed water, and this may result in accelerated interfacial weakening and failure. In general, it seems that water-induced interfacial failure is of greater concern with glass fiber composites than with carbon fiber, possibly due to etching of the fiber in certain (alkali) water chemistries. Various fiber coating chemistries have been developed to improve interfacial strength/adhesion, and these may be present in some composite materials. Most experimental fatigue data for fiber-reinforced composites is taken in air with non-condensing humidity, and as such is potentially not applicable for designing spacecraft water system components. Potential water-induced Interfacial failure presents different concerns with lubricant-filled materials, as wear/sloughing can be accelerated. The use of non-reinforced thermoplastic liners in wetted components could eliminate these concerns.

G. Compatibility with Radiation in Deep Space

The radiation environment beyond the protective magnetosphere and Van Allen belts of the Earth, discussed comprehensively in Ref. 27, is much more severe than on Earth or in low-Earth orbit. As such, risks to astronaut health, microelectronics, and potentially, structural materials, are much greater. However, the absorbed doses for exploration class missions, which are of concern for human health, and associated NASA crew life-time dose limits,²⁸ are much smaller (typically $\ll 10^{-3} \times$) than that expected to cause appreciable bulk damage to most thermoplastic polymers.^{29,30} A notable exception is PTFE, which can exhibit significant mechanical degradation at ~ 1 kGy in air, and further investigation is necessary to determine if this material is suitable for use under relevant loading conditions in exploration-class missions. However, polymer materials still have poor radiation tolerance compared with metals, and suitable performance in safety-critical life support hardware should be confirmed with high-confidence.

The spacecraft pressure hull and associated shielding block primary ultraviolet radiation (UV) and atomic oxygen (found in low-earth orbit), although secondary UV radiation may be of concern with extremely sensitive materials. The radiation types of greatest concern originate from primary galactic cosmic radiation and solar energetic particle radiation. These include electromagnetic radiation (gamma and x-rays) and heavy particle radiation (swift heavy ions), which can penetrate radiation shielding with sometimes minimal energy loss. Primary light particle radiation (proton, alpha, electron, neutron) are of lesser concern since they will be stopped rapidly by the spacecraft hull or shielding, and secondary radiation of these types produced locally by primary radiation (e.g., gamma rays) is likely to be of minor concern. The expected absorbed radiation dose to thermoplastic polymers inside a spacecraft habitat are expected to be significantly below 10 or 100 Gy for 1,000 day Mars transit and landing or 10,000 day Moon settlement missions, respectively.^{31,32}

Depending on radiation type/energy and material chemistry/structure, radiation can result in various chemical and mechanical changes in polymeric materials. For the polymers of interest in this work, significant mechanical degradation was not found below $\sim 10^5$ - 10^6 Gy with high dose rate gamma radiation,²⁹ and electromagnetic radiation (gamma and x-rays) at relevant doses are not expected to result in appreciable reduction of tensile strength or elastic modulus. Further investigation would be beneficial to determine if significant deleterious effects on fatigue or creep resistance have been observed at doses below 10^3 Gy, although this is not expected. Radiation tolerance experiments are often done in inert atmospheres, under vacuum, or with high dose rates, such that conditions are essentially non-oxidizing. In conditions relevant to life support hardware, materials will be saturated with some combination of air and water, and dose rates will be low. In such conditions, the deleterious effects of radiation, for example, on mechanical properties may be seen at 1-2 orders of magnitude lower adsorbed dose than in non-oxidizing conditions.³⁰ The relative effect of gamma vs. swift heavy ion radiation on potential mechanical degradation at small doses should be considered, and the appropriateness of gamma radiation experiments as proxies must be determined. In particular,

the specific bulk degradation mechanisms corresponding to swift heavy ion irradiation should be understood. However, these are topics for future research.

The effects of ion irradiation on polymers is discussed in depth in Ref. 33. Swift heavy ions leave disordered (amorphized), chemically altered tracks, with diameters in the order of 10 nm.³⁴ In some materials, these can be rapidly etched by concentrated acids, bases, or oxidants. The initial selective etching can produce a cylindrical or conical nanopore that is then non-selectively etched, potentially allowing for micropores of up to ~mm length and diameters of up to tens of microns. We were unable to find any information suggesting that long-term immersion in near-neutral water can result in similar etching of ion tracks in materials of interest; however, this is of potential concern. More aggressive aqueous chemistries, such as concentrated oxidant/acid solutions used for urine treatment and oxidizing biocide concentrates are of greater potential concern. The disordered (mechanically weakened) regions, or voids left by etching, could potentially serve as initiation sites for crack growth and fatigue failure, or result in material porosity and increased water or air transport. Further investigation is necessary to evaluate probable ion track density, the possibility of etching in relevant aqueous chemistries, and whether ion tracks and etch pores are significant threats to component life and mechanical reliability. In a previous work, modeling was used to predict the fluence and corresponding energy deposition of heavy particles in human tissue,³⁵ and a similar approach could be used with polymeric materials. Alternatively, terrestrial particle accelerators, such as the system found at the NASA Space Radiation Laboratory³⁶ could be used to irradiate polymer samples prior to water immersion and mechanical characterization. The worse-case effect of defects due to ion tracks on bulk mechanical properties such as tensile strength and modulus can be estimated with the rule of mixtures by calculating the fluence of ions and the assuming an associated cylindrical void diameter. Given the small ion fluence levels involved, such effects should be minimal unless very significant etching occurs. By a similar method, the potential increase in material permeability could be modeled. The effects of such defects on fatigue resistance and crack formation/growth could be addressed with a micromechanics-based approach, and again, these are expected to be minimal unless significant etching occurs and pore diameter becomes large.

H. Materials Performance under Long-Term Service with Multiple Challenge Mechanisms

The most useful information for predicting long-term performance of materials comes from characterization of components in service under relevant loading and environmental conditions. When such data are not available, it is necessary to use models (mechanistic, empirical, or combined) to extrapolate behavior from accelerated short-term experiments. While these are not discussed in detail here, we note that there is a well-developed field of research concerned with understanding and certifying performance of thermoplastic water pipes with service life of several decades. Such efforts often consider how combined fatigue and creep result in crack growth and ultimate failure. Accelerated testing using dynamic loading and/or elevated temperature/stress levels, as mentioned above, has been used with some success to provide inputs for extrapolated models. Similar techniques, assisted by experimental work, will be needed to characterize thermoplastic materials and certify pressurized components, particularly when stress levels are a significant fraction of yield strength. The literature concerning long-term mechanical behavior introduced in a previous section should provide a useful starting point for this topic.^{7,16-24}

IV. Materials Suitability and NASA Standards for Human-Rated Spacecraft Hardware

A. Materials and Process Requirements, Design Factors, and Fracture Control

In order to limit the risk of mechanical failure in pressurized components, several agency standards have been implemented. These include controls on materials selection, sourcing, and certification,³⁷ as well as design and construction standards to prevent failure from short (yielding or ultimate failure) and long-term failure mechanisms (including creep, fatigue, and accompanying crack growth and rupture/fracture), which were discussed in the previous sections. In addition to controlling the risk of mechanical failure, the standards require that materials/components employed do not pose excessive risk to spacecraft safety or crew health.

The mechanical design and test requirements/factors for spaceflight hardware are given in NASA STD-5001B³⁸ and JSC-65828,³⁹ which also call out the more comprehensive ANSI/AIAA S-080A-2018⁴⁰ and ANSI/AIAA S-081B-2018 standards,⁴¹ for metallic pressurized vessels/components and composite overwrapped pressure vessels, respectively. As human-rated spaceflight hardware, mechanical components in NASA spacecraft water systems are also subject to more stringent fracture control requirements beyond those given in STD-5001B. These are given in NASA STD-5019A⁴² and JSC-25863⁴³ with varying levels of rigor, depending on the use case of a given component and potential hazards associated with failure. Fracture control is also addressed in the ANSI/AIAA standards.^{40,41} We were unable to determine the extent of the applicability of these controlling standards to pressurized thermoplastic

components, and at present it is unclear what the appropriate design and test requirements should be. It is expected that thermoplastic polymers will require similar or larger factors of safety for short-term yield and ultimate failure as well as fatigue and creep life compared with metal components. We expect that effective fracture control in long-term service will require operational material stress levels to be significantly reduced vs. yield stress (perhaps to <10-20% of yield strength) to minimize the risk of stress rupture and control crack growth. An analogous standard to ANSI/AIAA S-080A-2018 that addresses the failure mechanisms specific to and design/testing techniques appropriate to engineering polymers should be identified or written.

However, we did find an example of a pressurized thermoplastic component in flight hardware, a polypropylene filter housing in the ISS Potable Water Dispenser ORU⁴⁴ (believed to be a Pall DFA model) that sees 30 psi (200 kPa) service pressure and is replaced annually (service limited by filter lifespan). This may be useful case to investigate in the future.

B. Flammability

Unlike most metals, engineering polymers can be potential fuel sources for fire and are more easily damaged by flame or elevated temperature. As such, their use in manned spacecraft must be judiciously controlled to mitigate associated risks to crew safety and spacecraft performance, particularly in atmospheres with elevated oxygen concentration. In general, non-metallic materials (or assembled articles) used in NASA spacecraft hardware must be non-flammable or self-extinguishing, or else hardware configuration must be designed to prevent fire propagation. Such requirements for flight hardware are controlled by NASA STD-6001B.⁴⁵ The standard's Upward Flame Propagation Test (Test 1) is used to characterize a material's flammability by measuring burn time and length before self-extinguishing, among other behaviors. Testing must be done at the worst-case anticipated use environment (most importantly with respect to oxygen concentration, air pressure, and material thickness), with test results for various materials available on the MAPTIS Materials Selection database.⁴⁶ Selected flammability ratings from MAPTIS for PEEK, PEI, PVDF, and PPS of various grades and thicknesses were compiled;¹ these materials generally satisfy the requirements of the standard at thicknesses of 0.060" and greater in standard atmospheric conditions.

In general, increasing material thickness reduces flame propagation as the greater areal density results in greater heat capacity and aids in self-extinguishing. A maximum fractional oxygen concentration for a given cabin pressure, which typically decreases with increasing total pressure, can be determined for a given material and thickness. Changes in gravitational environment can also affect flammability, complicating materials selection for Lunar, Martian, and microgravity missions, as testing is generally done in terrestrial conditions.⁴⁷ Retesting is required for MAPTIS validity every 10 years. Unfortunately, changes in the standard and the passage of time have made much of the older data unacceptable for certification purposes. However, these results remain useful for preliminary assessment of a material's suitability. The UL 50W (20 mm) Vertical Burning Test⁴⁸ is similar, although not equivalent, to the NASA STD-6001B Test 1, and should be useful for preliminary assessment. Results from a very extensive range of materials is available from the UL Prospector database.⁴⁹

Engineering polymers that are inherently nonflammable (e.g., certain fluoropolymers) or self-charring, or contain flame-retardant additives can often satisfy the self-extinguishing requirement at all relevant material thicknesses. However, in certain cases it may be desirable to use non-compliant materials to satisfy other performance requirements. While selection of non-flammable or self-extinguishing materials is certainly preferable, NASA recognizes that total elimination of flammable materials, although desirable, is not always possible due to performance considerations and engineering effort. Instead, a strategy of preventing fire propagation has been adopted which includes such methods as limiting the dimensions of flammable components, insertion of firebreaks, and coverage with non-flammable materials. This approach to analysis and control of flammability is described in detail in JSC Standard 29353B.⁵⁰ In many cases fire risk can be reduced and safety standards met by covering or containment with non-flammable materials. This approach would enable the use of otherwise non-compliant engineering polymers in components of limited thickness such as tubing, vessels, and bladders/diaphragms.

C. Offgassing and Leaching

Offgassing of volatiles from hardware inside spacecraft is governed by NASA STD-6001B,⁴⁵ and again, engineering polymers are of greater potential concern than typical passive metal alloys. Included in the standard is the Determination of Offgassed Products (Test 7), which is used to characterize materials and assembled articles by heating them in a sealed chamber at 50 °C for 72 hours, with the resulting atmosphere analyzed to determine the identities and concentrations of the offgassed compounds. The maximum masses for the materials employed inside a spacecraft of a given internal volume are thus limited such that total atmospheric contaminants do not exceed an unsafe level, as given in the Spacecraft Maximum Allowable Concentrations for Airborne Contaminants (SMAC) standard.⁵¹

It should be noted that the SMAC standard addresses only a limited number of volatile compounds, and materials may offgas other harmful compounds that must be limited to protect crew health. Results from NASA outgassing tests are available on the MAPTIS Materials Selection Database under the Toxicity heading.⁴⁶

Measured offgassed chemical species/concentrations and mass allowances for ISS and Orion class spacecraft are available in their associated material test reports. In most cases, significant quantities (i.e., >100 lb for an Orion-class spacecraft volume) of PEEK, PEI, PVDF, and PPS were reported acceptable.¹ Results with different grades and manufacturers of the same class of material are often conflicting, and further experimental work with engineering polymers of interest would be helpful. As is evident, selection of an appropriately “clean” polymer resin or stock is desirable. Preconditioning, i.e., with vacuum and/or moderately elevated temperature (as long as resulting microstructural or chemical changes to the polymer are insignificant), is likely to be useful in reducing outgassing of volatiles in actual service. This can be taken into account with the above testing, potentially allowing for increased mass allowance for a given material while satisfying the standard. In certain cases, there can be exemptions from testing, particularly for assembled articles with limited non-metallic mass.

Sources of offgassed volatile species in polymers can include processing solvents and additives, degradation products, and residual reactants and byproducts from synthesis. In general, the engineering polymers investigated here emit significantly less volatile mass than commodity plastics such as PVC. However, some of these species may be of concern even at low concentrations, such as perfluorinated compounds associated with fluoropolymer synthesis and processing, which are discussed further below with respect to leaching in water. An additional example is the diphenyl sulfone solvent employed in the high-temperature synthesis of PEEK, which may remain at low levels in finished resin.⁵² Diphenyl sulfone is solid below 123 °C, but may potentially sublime appreciably at or above room temperature.

In the potable section of the water management system, the minimization of harmful leachates is necessary to protect astronaut health, prevent undesirable odor or taste, and remove the need for water purification prior to dispensing. In addition, leachates can serve as microbial nutrients, potentially facilitating the growth of biofilms or pathogens. The sources for leachate contaminants are similar to that of offgassed compounds, however in this case dissolution in water can liberate otherwise non-volatile species. On NASA spacecraft, the maximum allowable concentrations of various contaminants is controlled by the Spacecraft Water Exposure Guidelines (SWEGs).⁵³ Again, we must note that such an understanding and quantification of all harmful leachate contaminant species produced by the materials used in a potable water system is necessary, as the list of compounds in the SWEGs is not exhaustive. Other sections of the spacecraft water system, where leaching does not pose a direct risk to astronaut health, is not controlled by the SWEGs. However, if significant, leachates may potentially bypass or deleteriously affect wastewater processing systems (e.g. urine treatment chemicals, distillation systems, adsorbents, ion-exchange resins, or catalytic reactors). When more aggressive chemistries or elevated temperature are used (e.g. in urine treatment vessels), leaching behavior should be considered, as degradation kinetics or contaminant solubilities may be increased. Sloughing of micro-plastics must also be considered and minimized by proper selection of engineering polymers. Preconditioning by cleaning with benign solvents or surfactants, or flushing with water, may be useful to remove the more labile chemical species and particles, reducing contaminant loading.

Prima facie evidence for a material’s suitability with a spacecraft potable water systems (with respect to leaching) can be found in certification for use in drinking water system by a relevant standards body, such as to NSF/ANSI 61 standard.⁵⁴ NSF/ANSI 61 requires that leachate contaminant levels of certain species satisfy US EPA limits, when extant, or be below a quantified threshold of evaluation when such limits have not been set. Various grades of PEEK, PEI, PVDF, and PPS resin have been approved to the NSF/ANSI 61 standard. Some materials certifications for potable water contact can be found in public databases, such as those hosted by the NSF⁵⁵ and British WRAS.⁵⁶ Engineering polymer resin and stock shape manufacturer literature can be helpful in identifying certified materials (e.g., Ref. 57). Alternatively, FDA approval for food contact or human implantation, or cytotoxicity studies in the literature, can be suggestive. Testing for NSF/ANSI 61 and similar certification is specific to a particular conditions, such as water temperature, exposure time, and (in some cases) A/V ratio. As with outgassing volatiles, potable water compatibility standards do not necessarily address all leaching compounds of interest, and all harmful compounds must be identified and limited to minimize risk to crew health.

Even with such certifications, there remains controversy about the human health risks of leachate contaminants from various engineering polymers, particularly with some compounds that may be harmful with chronic exposure below the threshold of evaluation (i.e. at sub-ppb levels) and/or have not received adequate attention from regulatory bodies. Fluoropolymers and other thermoplastic engineering polymers typically have more robust chemical bonding than commodity plastics, resulting in much lower production of leachate contaminants, and are typically free of plasticizers. In addition, chemical degradation/release in moderate conditions is also less of a concern. However, the

amount of residual compounds from synthesis and processing (solvents, reactants, byproducts, and processing aids) can be significant, and these may be released by evaporation, sublimation, or dissolution into water. One main area of concern and debate is the per- and polyfluoroalkyl substances, which have been used as additives in fluoropolymer synthesis and processing (such as PTFE and PVDF),^{58,59} and the US EPA has established advisory limits on certain of these compounds below 70 ppt (0.07 ppb),⁶⁰ significantly below the current ANSI/NSF 61 limits.⁵⁴ Fluoropolymer manufacturers have worked to modify processing methods when necessary to remove or reduce the use of such compounds. Similarly, synthesis ingredients, processing additives, byproducts, and degradation products of certain non-fluoropolymer engineering polymers, such as bisphenol A (used in PEEK and polycarbonate synthesis), have been subject to various levels of health and regulatory concern over the past two decades.

V. Future Work

The bulk of the continuing work in the near future will address long-term mechanical behavior of thermoplastic engineering polymers and associated design and test requirements for flight-certified life support hardware. In addition, further investigations regarding leachate toxicology and the effects of particle radiation on mechanical properties are necessary. Design, construction, and testing of realistic test articles and analog water systems for mechanical reliability would help build confidence in the performance of engineering polymers. Investigation of any pressurized thermoplastic components in use on manned and unmanned spacecraft and any relevant lessons learned would be beneficial. In addition to rigid engineering polymers, future work should consider flexible thermoplastic materials and elastomers more closely, particularly those with low permeability and low Ag⁺ uptake, for use in bladders, diaphragms, and bellows in positive expulsion tanks. Investigation of various tubing and fitting/connection systems, pressure vessels, the permeability of polymer components to air and water vapor, and potential biofilm formation on materials of interest (including the effect of biocide type/concentration) would be valuable. As development proceeds, increased collaboration between researchers, flight hardware designers, and NASA standards developing bodies will be necessary.

VI. Conclusions

During this investigation, we have found no immediate disqualifying factors for the use of engineering polymers as structural materials in spacecraft water systems, and this approach remains an attractive way to enable the use of Ag⁺ biocide. Further development of standards and engineering practices for design and test qualification of pressurized thermoplastic components is necessary because of NASA's limited previous use. However, the chemical and microstructural characteristics of such materials, and associated viscoelastic behavior, result in greater required effort to understand and mitigate complex mechanical failure modes vs. heritage metal alloys, and reliable long-term service may require limiting stress levels to small fractions of material yield strength. This becomes less of a concern in thick-wall tubing in relatively low-pressure service, where hoop-stress levels may be orders of magnitude smaller than in large diameter thin-wall pressure vessels. The use of composite thermoplastic materials with reinforcing fibers may allow for thin-walled vessels with significantly reduced mass/wall thickness vs. neat polymers for similar service lives.

Initial Ag⁺ compatibility experiments with PEEK and various reinforcing fiber and lubricant material fillers, PEI, and PVDF showed promising results.

Concerns regarding flammability can be addressed by proper materials selection, system design, and in some cases shielding with non-flammable material. Outgassing of polymeric materials must be controlled, but MAPTIS data indicates that appropriate materials selection and processing could satisfy this requirement. Terrestrial potable water materials compatibility ratings suggest that many grades of the materials of interest are suitable for use with potable water, but risk assessment regarding certain trace-level leachate contaminants may be necessary.

Bulk radiation damage does not appear to be of significant concern in exploration class missions as material dose limits far exceed those of the crew. However, we have yet to assess if ion track formation and potential etching could result in significant mechanical degradation or unacceptable porosity.

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