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**THE CHEMICAL AND RADIATION RESISTANCE OF
POLYPHENYLENE SULFIDE AS ENCOUNTERED IN THE
NUCLEAR WASTE CLEANING PROCESSES**

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EXECUTIVE SUMMARY

Polyphenylene sulfide (PPS) is extremely resistant to gamma irradiation, caustic solution, and dilute nitric acid. PPS is the material of construction for the coalescers used in the Modular Caustic-Side Solvent Extraction Unit (MCU). After applying the equivalent of 16 years of gamma irradiation and several months of exposures to caustic solution, no dimensional changes nor chemical changes were detected in PPS whether the PPS was in fiber form or in a composite with E-glass fibers.

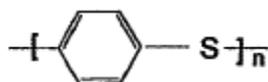
However, PPS acts as a media for heterogeneous nucleation. In particular, PPS appears to favor aluminosilicate formation in saturated solutions of aluminum and silicon in caustic environments.

Parallel testing, in progress, is examining the stability of PPS when exposed to the new solvent formulation under development for MCU. Preliminary data, after two months of exposure, PPS is remarkably stable to the new solvent.

INTRODUCTION

Polyphenylene sulfide (PPS) is a semicrystalline polymer with excellent engineering plastic properties and suitable processing temperatures (1). PPS can also be made containing branches (using a trifunctional monomer) and with crosslinked microstructure (when curing the monomer at high temperature in the presence of oxygen).

PPS is made from the condensation reaction between para dichlorobenzene and sodium sulfide with the assistance of a catalyst (to lower the activation barrier). The synthesis conditions of PPS has evolved since its invention in the 1960's to the optimal conditions developed by the Philips Corporation in the 1970's (2). The resulting polymer consists of chemically stable molecular moieties such as benzene rings and ether like sulfur linkages between the aromatic rings (as shown below).



The resulting PPS polymer is a thermoplastic with a sharp melting temperature around 275 °C that varies (slightly) depending on the polymer processing or aging or storage conditions. The glass transition ranges from 87 (amorphous) to 93 °C (crystalline) giving this polymer a wide temperature range for processing. This wide temperature range allows for easy processing of this polymer into different (molded) shapes and figures. The molecule is relatively stiff such that upon cooling from the melt this polymer has the tendency to readily crystallize. To minimize crystallization at a practical cooling rate, small amount of additives (or trifunctional monomers) are added to screen the interchain interactions. A common additive is diphenyl disulfide.

Combinations of quenching rate, temperature, and aging at temperature allows the polymer to have a controlled degree of crystallinity that in turn “tunes in” the bulk mechanical properties of this polymer. Annealing post quenched PPS reduces residual stresses (from quenching) and nucleates small lamellas throughout the polymer to give the polymer higher tensile, compressive and bending strength as well as toughness (exhibited as an ability to arrest internal crack propagation). Blending PPS with fillers (i.e., glass or carbon fibers) is another way to improve the strength of the polymer (via an increase in the glass transition of the polymer for example). An excellent review of the mechanical properties of PPS that includes impact strength (toughness), fatigue, viscoelasticity (creep), and tensile/compressive strength was given in reference 3.

Heating the polymer at high temperature for short times (less than minutes) in the presence of air introduces crosslinking microstructure into the polymer that can enhance the ultimate tensile and compressive strength.

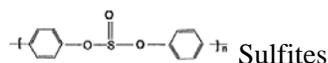
But heating the polymer beyond 350 °C in air introduces significant oxidation reactions (as shown in the table below) that can change the polymer mechanical and chemical stability.

Temperature in

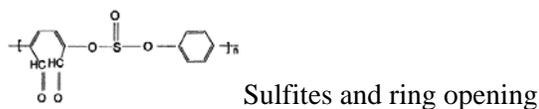
air (°C)

Products

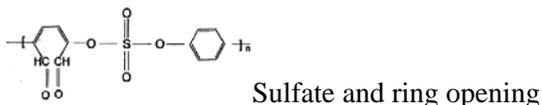
350



380



420



440

R-SO₂-OH and R-SO-OH acids

If heating PPS past 300 °C under a reducing atmosphere, pyrolysis reactions will yield byproducts such as hydrogen, hydrosulfide gases, carbon monoxide, and a carbonaceous residue.

Previous reviews (as Reference 3) have not extensively examined the effect of radiation on PPS and the stability of PPS to solutions including organic liquids. In particular, the data is scarce on the effect of blending of organics liquids with different polarities (hydrophobic and hydrophilic) on the dimensional stability PPS.

PPS undergoes chemical transformation during irradiation with ion bombardment or gamma irradiation. Ion bombardment (with Ar²⁺ at 700 keV under vacuum) on PPS revealed chemical bond disruptions and free radical formation (loss of hydrogen atom) (4). The damage also included additional cross-linking and loss of crystallinity. More beam exposure led to extensive bond conjugation that imparted the PPS with electrical conductivity similar to a semiconductor. The bombardment-induced conductivity disappeared upon exposure to oxygen from air.

A similar chemical degradation was seen when PPS was bombarded with hydrogen ions (5). Bombardment with hydrogen led to desulfurization, conjugation formation, and carbonaceous material formation in PPS. These effects (with the exception of carbonaceous materials formation) are similar to laser ablation where a total removal of material occurs. Bombarding PPS with H^+ and other ions (He^+ , C^{2+} , O^{3+} , S^{3+} , Br^{9+} and I^{14+}) led to bond breaking and rearrangement similar to Ar bombardment. The chemical bonds most susceptible to bombardment were C-S and S-S. The aromatic rings in PPS were found to be resistant to ionic bombardment (6).

Under photonic irradiation such as gamma irradiation, PPS has proven to be resistant with no changes to its mechanical properties (tensile strength and elongation at the breaking strength) to 500 kGy or less (7). This is attributed in part to the tendency of the ionized electrons (removed from an atom in PPS) to return to the PPS. However, when the dose is larger than 500 kGy, hydrogen and sulfur losses (indicated by the lost in C-H stretch and bend and C-S stretch in the FTIR spectrum) as well as conjugation was observed (8).

The objective of this work was to investigate the chemical and radiation resistance of PPS in caustic solution and selective organic liquids under gamma irradiation. The data from this work provides the input necessary for using PPS as the polymer media for both filtration and coalescing oil-in-water dispersion.

EXPERIMENTAL PROCEDURE

To evaluate the chemical and radiation resistance of PPS, two forms of PPS were obtained: 1- nonwoven fiber shaped PPS (92 to 93 % porosity), and 2- E glass-filled PPS coupons. We have chosen to evaluate the gamma irradiation resistance of PPS in the E-glass composite form because that configuration packs the most PPS fibers per unit volume (when compared to a non-woven PPS) and the higher the density is the higher is the capture of photons. The E-glass/PPS composite presents a very sensitive configuration to radiation damage that an air-filled non-woven PPS fiber network may not offer.

We obtained several coupons ($2 \times 2 \times 0.25 \text{ cm}^3$ and $5 \times 5 \times 2 \text{ mm}^3$) of Ryton4™ samples (PPS) reinforced with E-fiberglass (20 % by volume). The coupons were used as received and immersed in salt solution (5.6 M [Na], 1.91 M [OH] and 0.31 M [AO₂]) with no mixing.

In some cases, coupons were exposed to gamma radiation at a dose rate of 7.11 E5 rad/h (using a J. L. Sheppard model 109 equipped with a Cobalt source) to give the coupons a total dose of 4.95 E8 rad (or the equivalent of 40,000 years of plant service given that 2.5 mCi/gal is a typical salt solution feed concentration but it is the equivalent of 16 years of service on the stripping process of MCU where solution may contain up to 7.5 Ci/gal) (9). Gamma source temperature and humidity was approximately 35 °C and 60% RH (relative humidity).

Some coupons were exposed to 3 M caustic solutions (3 M NaOH solution is typically used for cleaning purposes at MCU) for different lengths of times. Other coupons received radiation and caustic exposure simultaneously.

After treatment, samples were analyzed by multiple contacts using ATR-FTIR (attenuated total reflectance – Fourier transform infrared spectroscopy).

Some samples were also analyzed by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). TGA is basically a balance placed in an oven where the sample is heated up linearly with time while the sample weight is monitored. In this case, the TGA will be used to determine the amount of polymeric material (PPS) that remains in the composite. The DSC is basically measures the temperature of the samples as the sample is heated up linearly with time. In this case, the DSC will be used to monitor the temperature rise in PPS due to oxidation in air. The lower temperature rise, the less PPS is present relative to the as received E-glass/PPS composite.

PPS fibers were exposed to caustic (1.91 M [OH]) and dilute nitric acid (1 mM) under gamma irradiation for evaluation.

RESULTS AND DISCUSSION

E-Glass/PPS Composite

The effect of gamma irradiation on E-glass/PPS composite is shown in Figure 1. As can be seen from Fig. 1, PPS is very resistance to gamma irradiation until the total radiation (accumulated) exceeded 4.5×10^8 rad. Further exposure clearly shows the breaking of the aromatic rings (oxidation) and the oxidation of the sulfur atom in PPS. The formation of sulfides and sulfates is clearly seen in Fig. 1. This makes the surface more polar and susceptible to wetting.

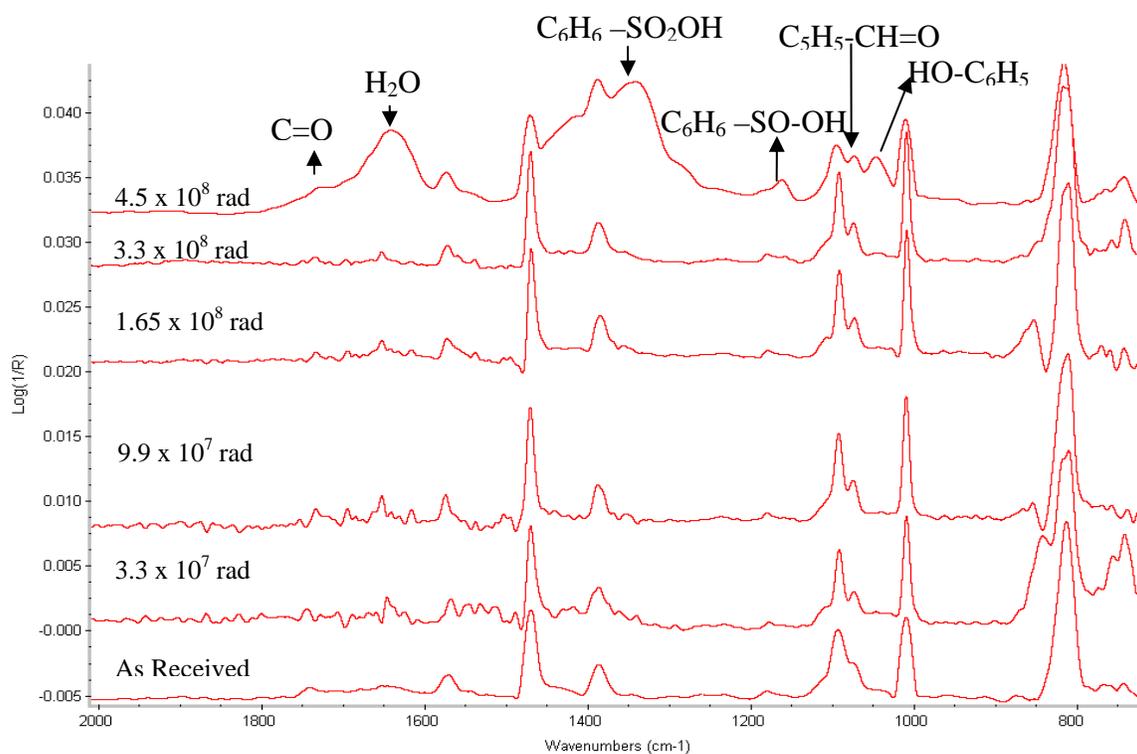
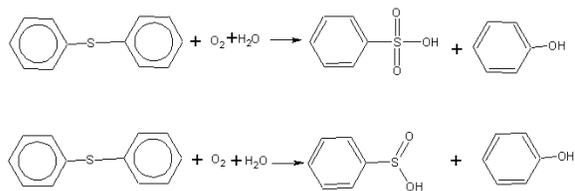


Figure 1. FTIR of the surface of PPS as a function of radiation (given in rad).

The formation of sulfide and sulfate groups on PPS can be summarized in the reaction below.



Exposing the E-glass/PPS composite beyond 4.5 E8 rad clearly affected the surface texture of the composite. The surface appeared more smoothed with wider pits as a result of the large irradiation (see Figure 2).

The irradiation also affected the thermal behavior of E-glass/PPS as shown in Figure 3.



Figure 2. An optical picture of glass-reinforced PPS before (bottom) and after gamma irradiation (top).

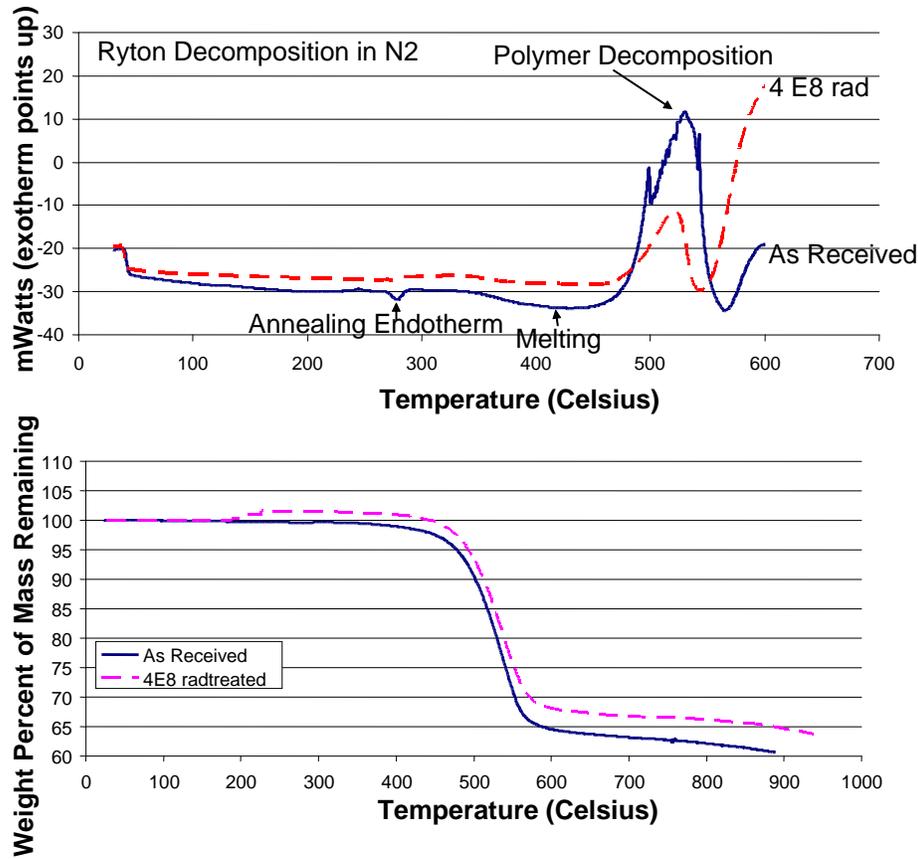


Figure 3. Both the DSC (top) and TGA (bottom) indicate that the gamma irradiation reduced the amount of organic (PPS) material at the surface.

As can be seen in Figure 3, the DSC clearly showed less oxidation (reaction with air) occurred in the E-glass/PPS sample that was irradiated since the irradiation process has oxidized the surface leaving less original material for additional oxidation. The TGA data clearly shows that more material volatilized off (under nitrogen) the “as received” composite than the irradiated E-glass/PPS (36 wt % loss versus 33 wt % loss). Again, this is an indication of more loose material resulting from the irradiation. Note that these changes only occurred after the composite was

exposed to the equivalent of 40,000 years on the extraction process and 16 years on the stripping process of service at MCU.

Exposing the E-glass/PPS composite to caustic salt solution containing aluminum led to the formation of aluminosilicate on the surface of the composite. Figure 4 showed the formation of aluminosilicate after one month of exposure. The presence of aluminum in solution probably reacted with the silica in E-glass to form the aluminosilicate. The probable mechanism may have included the dissolution and transport of silicon from inside the composite to the surface when it reacted with aluminum to deposit a film of aluminosilicate. Figure 5 shows a picture of E-glass/PPS before and after exposure to caustic clearly showing the presence of film on the irradiated sample. Note the picture was taken after 5 months of exposure where the film is thick enough to be optically visible.

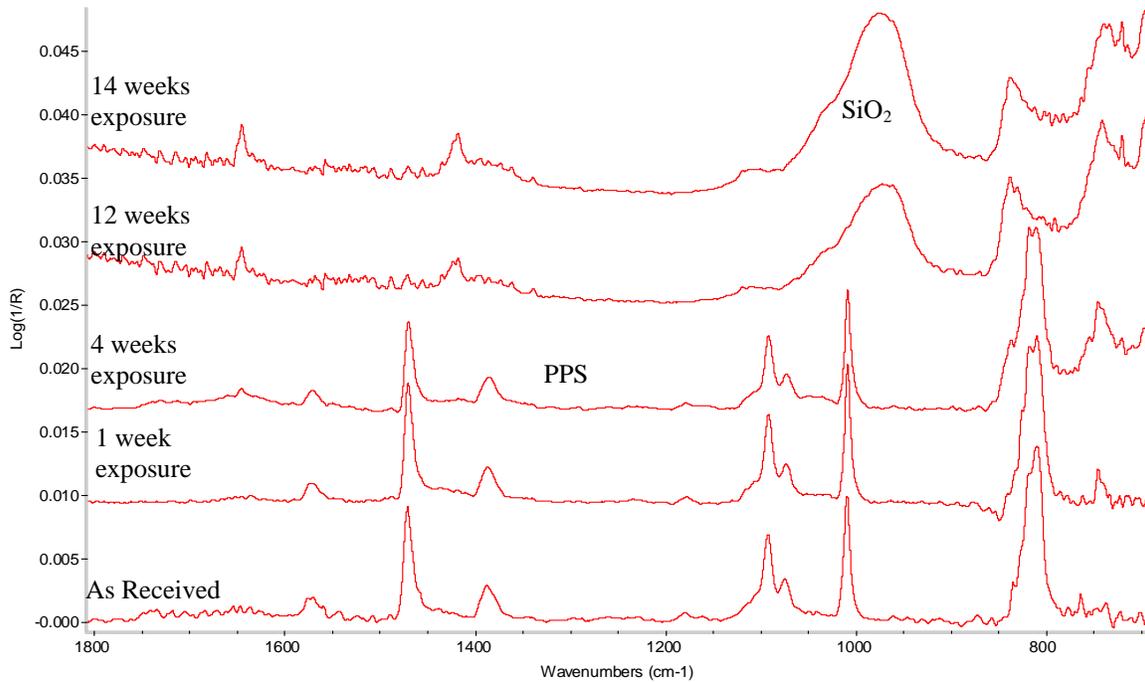


Figure 4. FTIR of the surface of PPS after exposure to a 5.6 M NaOH solution. Further evidence of the change in the surface of the E-glass/Ryton composite is shown in Figure 6

where the texture of elongated E-glass fibers disappeared after exposure to a salt solution containing aluminum. Using a microthermal analyzer (which is an atomic force microscope equipped with a thermal probe), both the topography and thermal conductivity of the surface of the composite changed as a result of the exposure. In this case, the resulting aluminum silicate has a bumpy texture (raised elevations that resemble mountains).

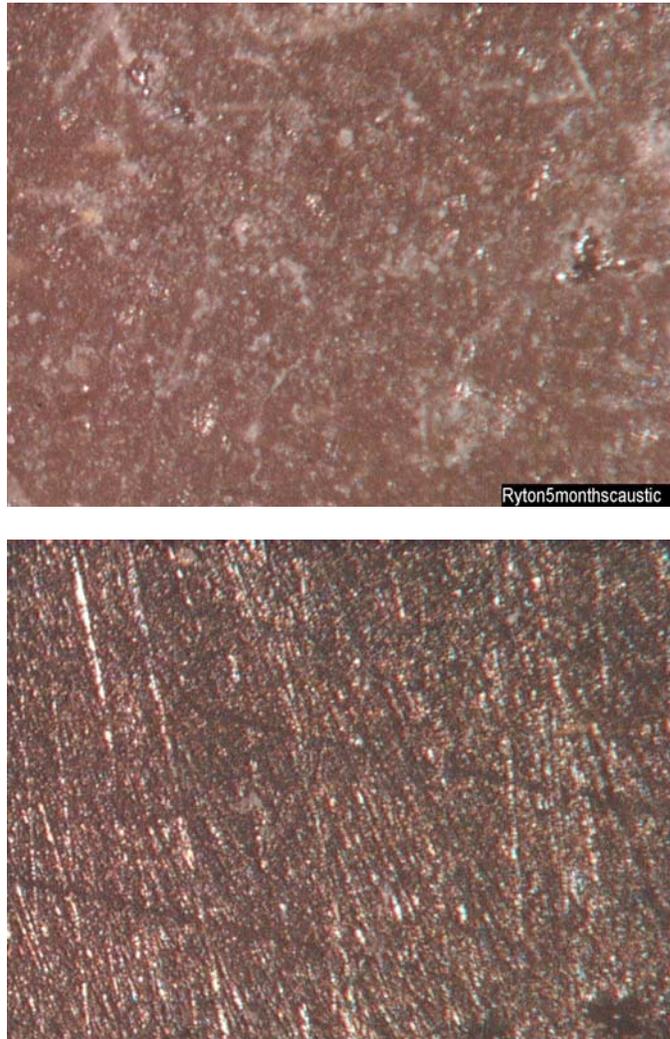


Figure 5. An optical picture of the surface of PPS after exposure to a 1.91 M [OH] solution (top) compared to the same surface before the exposure (bottom).

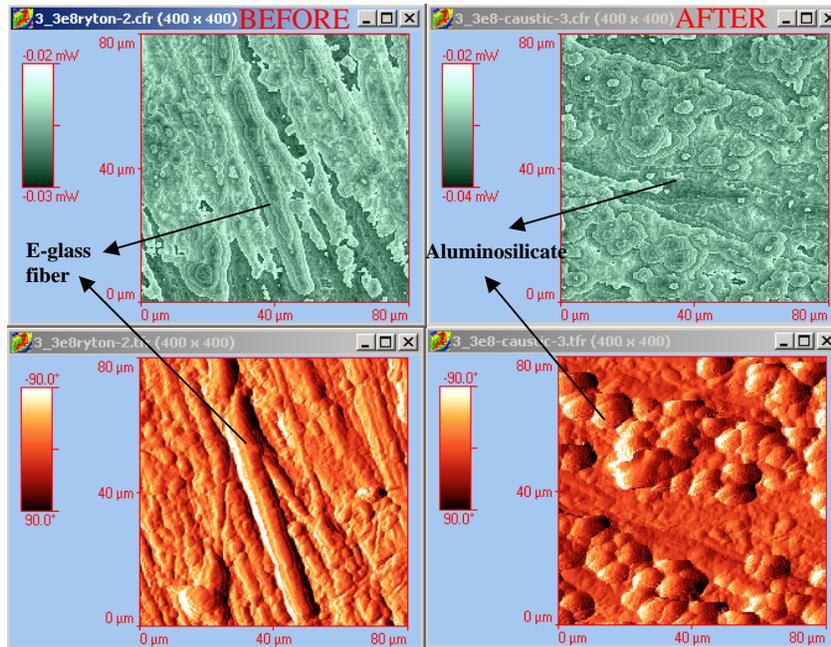


Figure 6. A microthermal analysis of the E-glass/Ryton composite before (left) and after (right) exposure to salt solution containing aluminum. Thermal conductivity (top) and topography (bottom) are shown.

Proof that a film of aluminosilicate formed on the sample shown in Fig. 5 is shown in Fig. 7 where the 100 and 300 microns of material was peeled off from the composite sample in Fig. 5. As can be seen from Fig. 7, the FTIR spectrum show the signal from the aluminosilicate disappeared when 300 microns of material was peel off from the sample. Thus, proving that a finite film of aluminosilicate formed on the sample exposed to caustic solution containing aluminum.

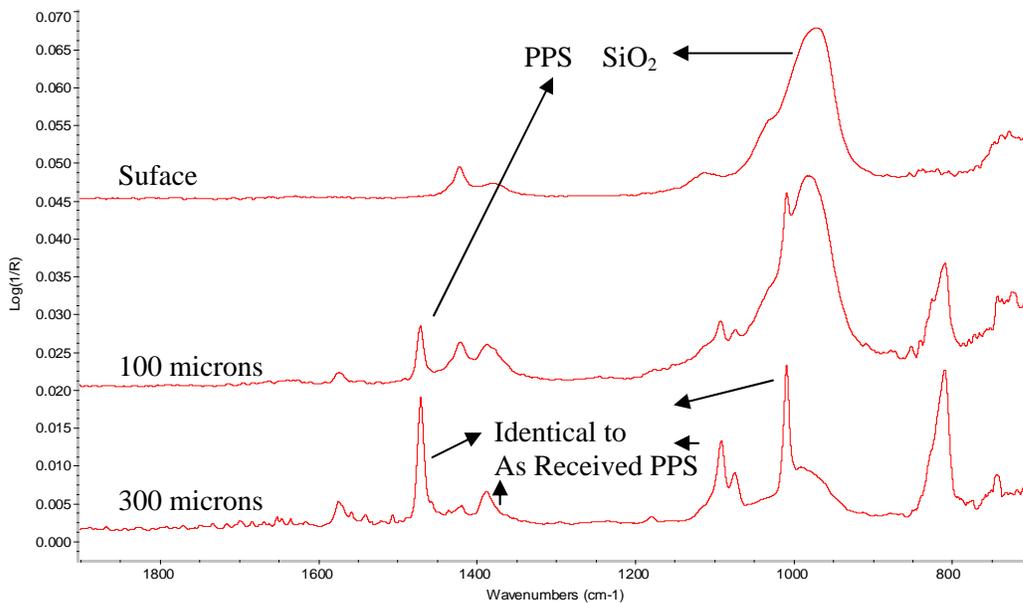


Figure 7. FTIR of the surface of PPS after shaving off 100 and 300 microns of material from the surface of PPS that was exposed to 1.91 M [OH] solution containing 0.31 M AlO_2^- .

We then investigated the combined effect of exposing a composite sample to both gamma irradiation and exposure to caustic solution containing aluminum. Exposing the sample to two forms of stress may accelerate degradation of the composite. As shown in Figure 8, a complete aluminosilicate deposition on the E-glass/PPS composite surface occurred approximately within 29 days before the gamma irradiation damage on the PPS can be detected (approximately 4.95 E8 rad). This aluminosilicate deposition was faster than that observed in Figure 4. Given that everything was the same (conditions and material used) except for the presence of gamma irradiation, it is possible that gamma irradiation facilitated the rapid nucleation of aluminosilicates on the surface of the E-glass/PPS composite by either changing the solution composition near the surface or by changing the surface itself enough to facilitate rapid heterogeneous nucleation.

On the other hand, the aluminosilicate deposition simply masked the signal from the PPS as shown in the symmetry (mirror image) between the two curves in Figure 9. Since no discernible damage to the PPS was seen (of the type saw in Figure 1) before 29 days of exposure (or before 4.95 E8 rad were irradiated), there is no synergistic effect between gamma irradiation and caustic exposure on the chemical stability of PPS in the E-glass/PPS composite. As can be seen in Figure 9, the surface of the E-glass/PPS composite is completely covered with aluminosilicate after irradiating the sample to 4.95 E8 rad.

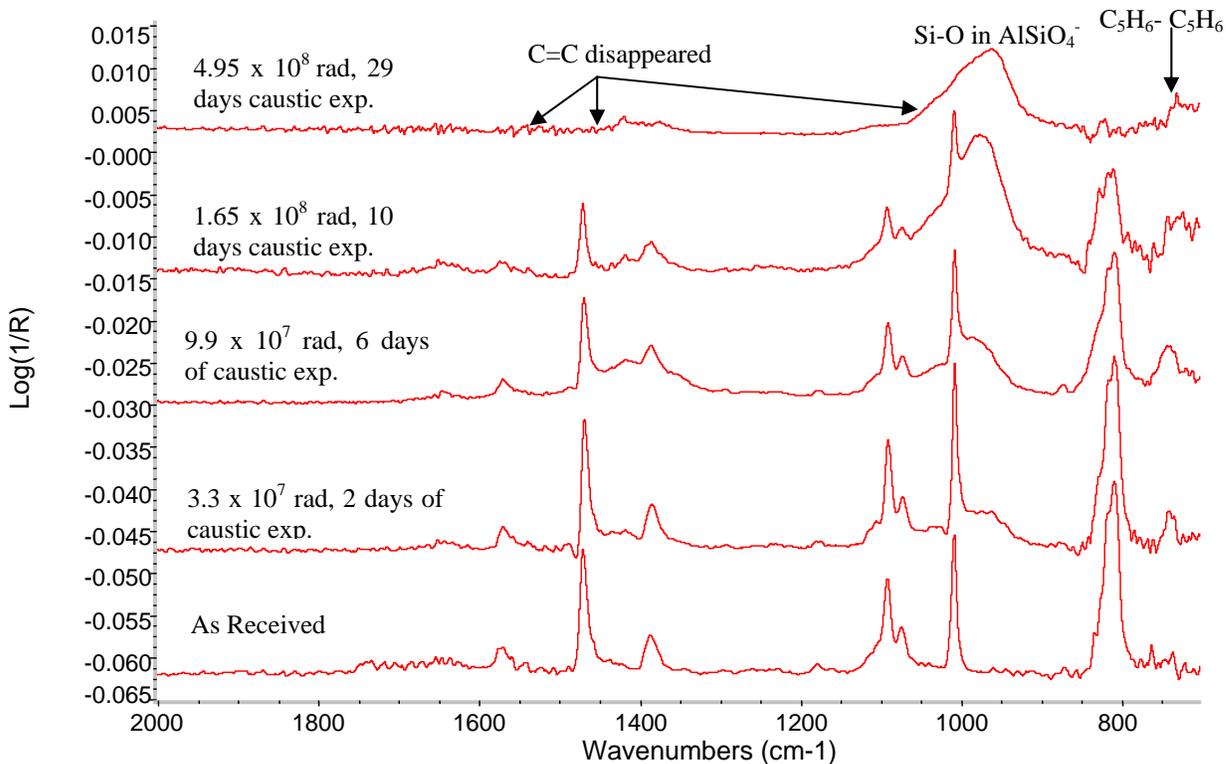


Figure 8. FTIR of the surface of PPS after exposure to caustic solution and under gamma irradiation (combined effect).

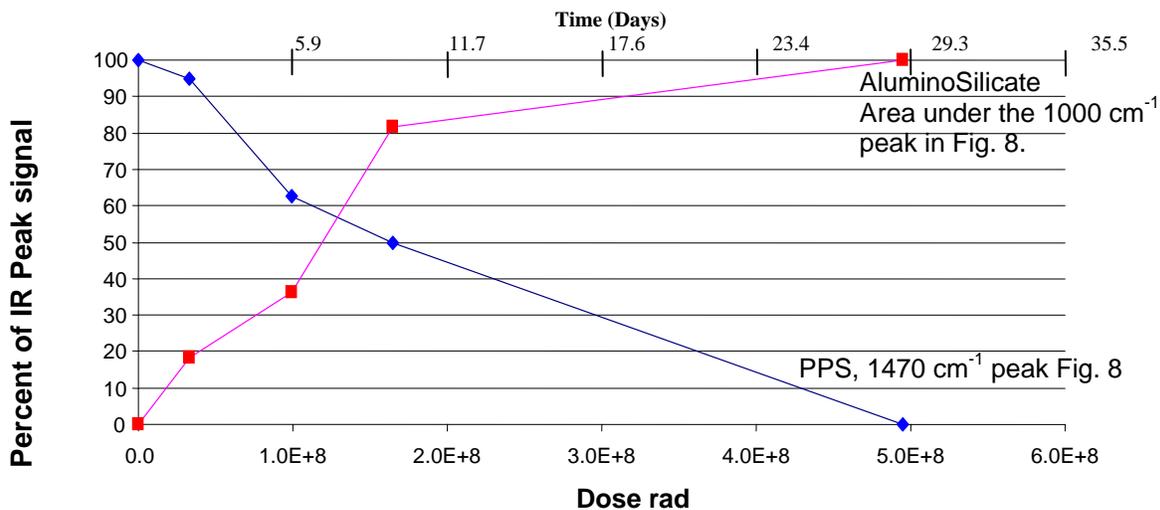


Figure 9. A summary of the peak area of the FTIR data in Figure 8 showing the lifetime of PPS (its surface) in a caustic solution containing aluminum and under gamma irradiation is around 29 days ($= 4.95 \text{ E } 8 \text{ rad} / 7.11 \text{ E } 5 \text{ rad per hour}$).

Nonwoven Fiber Shaped PPS

Since 2008, the Savannah River Site has utilized nonwoven PPS fibers (in a cartridge form) as a coalescing media for oil in water dispersion. During that time, PPS fibers have been exposed to both gamma irradiation (in some cases up to 7.5 Ci per gallons) and exposure to caustic salt solution containing aluminum as well as to dilute nitric acid (1 mM).

Optical and FTIR analysis of those aged cartridges have revealed that PPS is extremely resilient to gamma irradiation and that heterogeneous nucleation, such as aluminosilicate deposition, more likely affects PPS performance. As shown in Figure 10 and 11, the deposition of aluminosilicate is clear and occurs well before PPS degradation induced by irradiation. In the same process, PPS is exposed to mixtures of alkanes and fluorinated alcohols, none of which reacts but some irreversible sorption may occur on PPS.

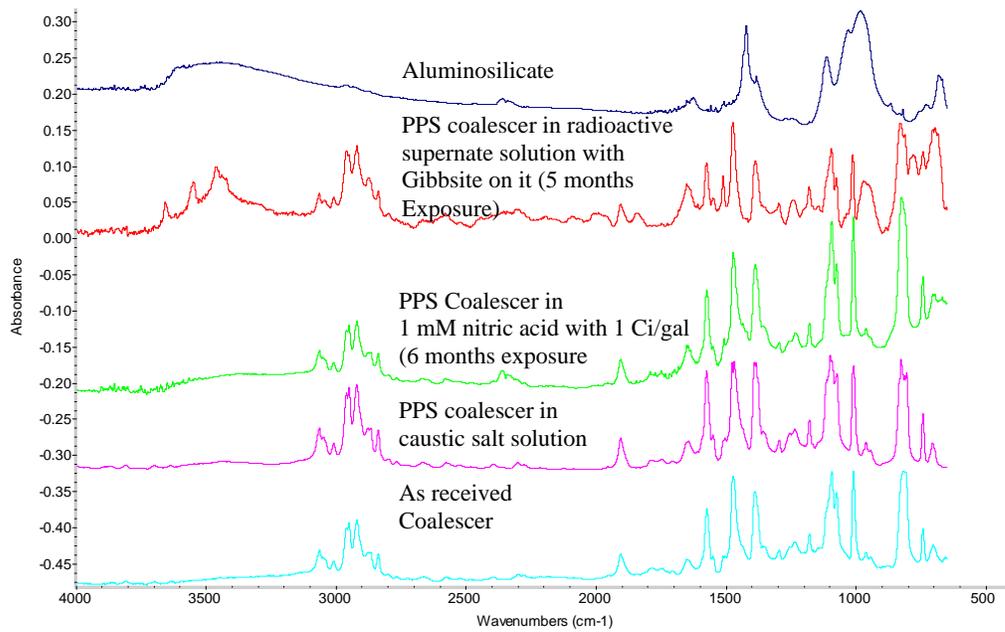


Figure 10. The FTIR of nonwoven PPS that was exposed to 1 mM nitric carrying approximately 1 Ci/gallon for approximately 5 months.

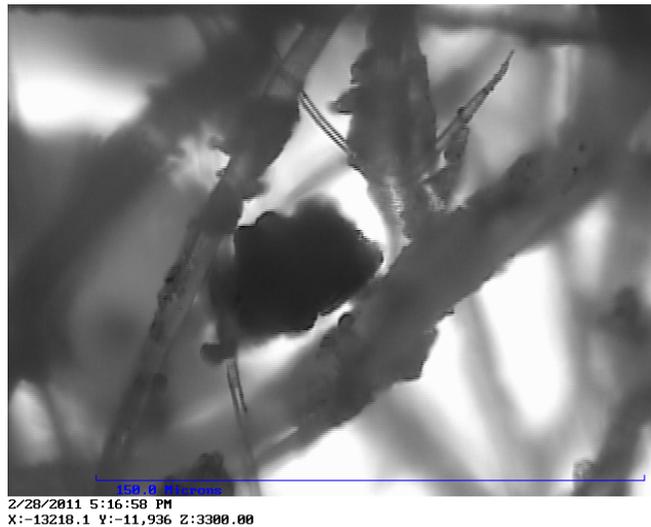


Figure 11. Aluminosilicate formation and trapping of other particles in the nonwoven PPS cartridge that was

exposed to salt solution for approximately 6 months (20

X: Scale bar should read 37.5 microns).

CONCLUSIONS

PPS is extremely resistant to gamma irradiation, caustic solution, and dilute nitric acid. PPS is the material of construction for the coalescers used in the Modular Caustic-Side Solvent Extraction Unit (MCU). After applying the equivalent of 16 years of gamma irradiation (assuming a stripping solution concentration of 7.5 Ci/gal) and several months of exposures to caustic solution, no dimensional changes nor chemical changes were detected in PPS whether the PPS was in fiber form or in a composite with E-glass fibers.

However, PPS acts as a media for heterogeneous nucleation. In particular, PPS appears to favor aluminosilicate formation in saturated solutions of aluminum and silicon in caustic environments.

Parallel testing, in progress, is examining the stability of PPS when exposed to the new solvent formulation under development for MCU. Preliminary data from two months of exposure indicates that PPS is remarkably stable in the presence of the new next generation solvent.

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