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Author(s):
Dumont, Joseph Henry
Crum, Shaylynn LaSonja Amechie
Zhao, Charles
Murphy, Eamonn Conor
Reardon, Sean Duncan
Lee, So Young
Lee, Kwan-Soo
Labouriau, Andrea
Karns, Tristan
Smith, Paul Herrick

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Functional Testing of Alternative Bag-Out Bag for PF-4 Implementation

Joseph H. Dumont (C-CDE), Shaylynn L. A. Crum (C-CDE), Charles Zhao (C-CDE), Eamonn Murphy (C-CDE), Sean Reardon (C-CDE), So Young Lee (C-CDE), Kwan-Soo Lee (C-CDE), Andrea Labouriau (C-CDE), Tristan M. Karns (NPI-9), Paul H. Smith (SSE-2)

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1 Introduction

The Department of Energy (DOE) issued DOE M 441.1-1, Nuclear Material Packaging Manual, to protect workers who handle nuclear material from exposure due to loss of containment of stored materials [1]. Currently, the bag-out bags that are used to move material from a glovebox to a long-term storage container are made of a plasticized polyvinylchloride (PVC) material formed into a bag. In 2015, corrosion was identified during the surveillance of Hagan and SAVY-4000 containers [2]. The corrosion that was identified in storage containers has been attributed to HCl gas generation from radiolytic and thermal degradation of the PVC bag-out bag material [3,4]. PVC is an attractive thermoplastic for such applications due to a number of desirable properties like hydrophobicity, low flammability, and resistance to both acidic and alkaline environments. PVC without additives is a hard and brittle solid, but the insertion of plasticizers like phthalate esters turns it to a soft and compliant material ideal for the manufacturing of plastic bags. Of the 25 different phthalate esters, di(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP) are the most commonly used with PVC. As much as 40% by weight of a PVC product can be non-covalently bonded plasticizer, which depending on environmental conditions can diffuse out of the plastic. By adjusting the amount of plasticizing additives, the manufacturers are able to modify the polymer's mechanical properties as required. Thus, aging and degradation of plasticized PVC (sPVC) are dependent on specific formulations and environmental conditions.

Inspection of sPVC bags removed from long-term nuclear storage containers showed signs of discoloration, unidentified liquid droplets and adhesion to the inner metal container, which also exhibited evidence of corrosion as shown in Figure 1-1. These findings prompted the authors to examine the degradation of these plastic bags and to find replacement candidates. As demonstrated by numerous studies, PVC under exposure to heat or radiation loses HCl when it undergoes dehydrochlorination (DHC); such findings strongly encouraged the development of additives to suppress or delay degradation. DHC of the polymer backbone induces formation of conjugated polyene sequences, discoloration of the polymer, and it can lead to appreciable off-gassing at temperatures as low as 140 ℃. Once polyene sequences are formed, these can react to form a cross-linked PVC structure. The instability of the PVC backbone and the nature of the initiation sites from which the DHC starts has been the subject of debate for many years. Generally, the main proposed degradation mechanism relies on the existence of low thermal stability structural defects produced during manufacturing of the polymer, such as tertiary chloride and allylic chloride groups. A recent review by Starnes addresses this topic in greater detail. [5] Furthermore, the presence of oxygen causes a large increase in the rate of thermal DHC, along with oxidation reactions and chain scission.[6] Also, the presence of hydroperoxides, hydroxyls, and carbonyls generated during thermal oxidative degradation are thought to participate in the DHC process. Similarly to thermal degradation, irradiation of PVC induces formation of polyenyl radicals and DHC of the polymer backbone. In particular, LaVerne and co-workers demonstrated that Cl- yields in the gamma radiolysis of non-plasticized PVC with number average weights of 22000, 47000, and 99000 Daltons were 19.6, 33.8, and 32.5 atoms/100 eV; respectively. [7] These exceptionally large Cl- yields suggest that a chain process involving radicals stabilized on the polymeric chain is responsible for the polymer degradation. Interestingly, those authors demonstrated that Cl- continuously evolves from the polymer for days following exposure to ionizing radiation. Based on all these findings and others, stabilizers were formulated as a way to protect the PVC backbone from damage either promoted by thermal degradation, oxidation or ionizing radiation. For instance, the addition of aromatic compounds helps to decrease the HCl production since the ionizing energy is dissipated by the aromatic ring. The interaction between the polymer and additives under different environmental conditions and their effect on lifetime are thus material-specific and remain a subject of interest.

Figure 1-1 Pictures of aged sPVC bags and leached out compounds

The stability of sPVC bags commonly used for storage of nuclear materials was tested by exposing the material to alpha and gamma radiations as well as thermal treatments. Furthermore, commercially available plastic bags made from aromatic polyether urethane and aromatic polyester urethane were also tested under similar harsh conditions as well as a long-term aging study. Changes in chemistry, thermal properties, and mechanical response were assessed by a range of experimental techniques including infrared spectroscopy, mass spectroscopy, thermogravimetric analysis (TGA), and stress-strain response under uniaxial extension, puncture testing and solvent swelling. The combination of these diverse methods provided useful insights on the degradation of these materials when used for the storage of nuclear materials. The objective of this report is to describe and to present the results of the functional testing that has been performed on alternative bag-out bag materials for TA-55 implementation.

2 Methodology

Plastic bag: All plastic bags, i.e. the plasticized polyvinyl chlorine (sPVC), aromatic polyether urethane (APU ether) and aromatic polyester urethane (APU ester) were fabricated by Rich Industries Inc. and purchased from Nuclear Filter Technology. The plastics were used as received.

2.1 Thermal and Radiation Aging

Accelerated Aging conditions employed in this study were the following:

- Samples of sPVC and APU ether were thermally aged at 135°C for 10 days. Samples were aged in air using aluminum canisters sealed with copper discs as shown in Figure 2-1. This sample configuration allows for gas samples to be easily collected and analyzed by mass spectroscopy.
- sPVC, APU ether and APU ester were thermally aged at 75°C for 4 months and 6 months in an oven. This simple setup allows an onsite accelerating aging to quickly characterize the sample and assess the changes they underwent.
- Samples of sPVC and APU ether were gamma irradiated to 200 kGy at 1 Gy/sec. The same sample holder configuration was used to irradiate samples. Exposure to gamma radiation was performed using Co-60 sources available at the Gamma Irradiation Facility at Sandia National Laboratories, New Mexico.
- Samples of sPVC and APU ether were alpha irradiated to 1x1013 alpha/cm2 and to 5x1013 alpha/cm2 using a He+ ion beam operating at 5.24MeV.
- Samples of APU ether and APU ester are being aged under thermal and radiative conditions in a long-term aging study. Irradiation is being provided by Cs-137 sources available at Sandia National Laboratories. The samples are being exposed to gamma irradiation either

at room temperature or at 85°C. Samples are also being aged at 85°C without irradiation. The scheme of the aging study is illustrated in Figure 2.

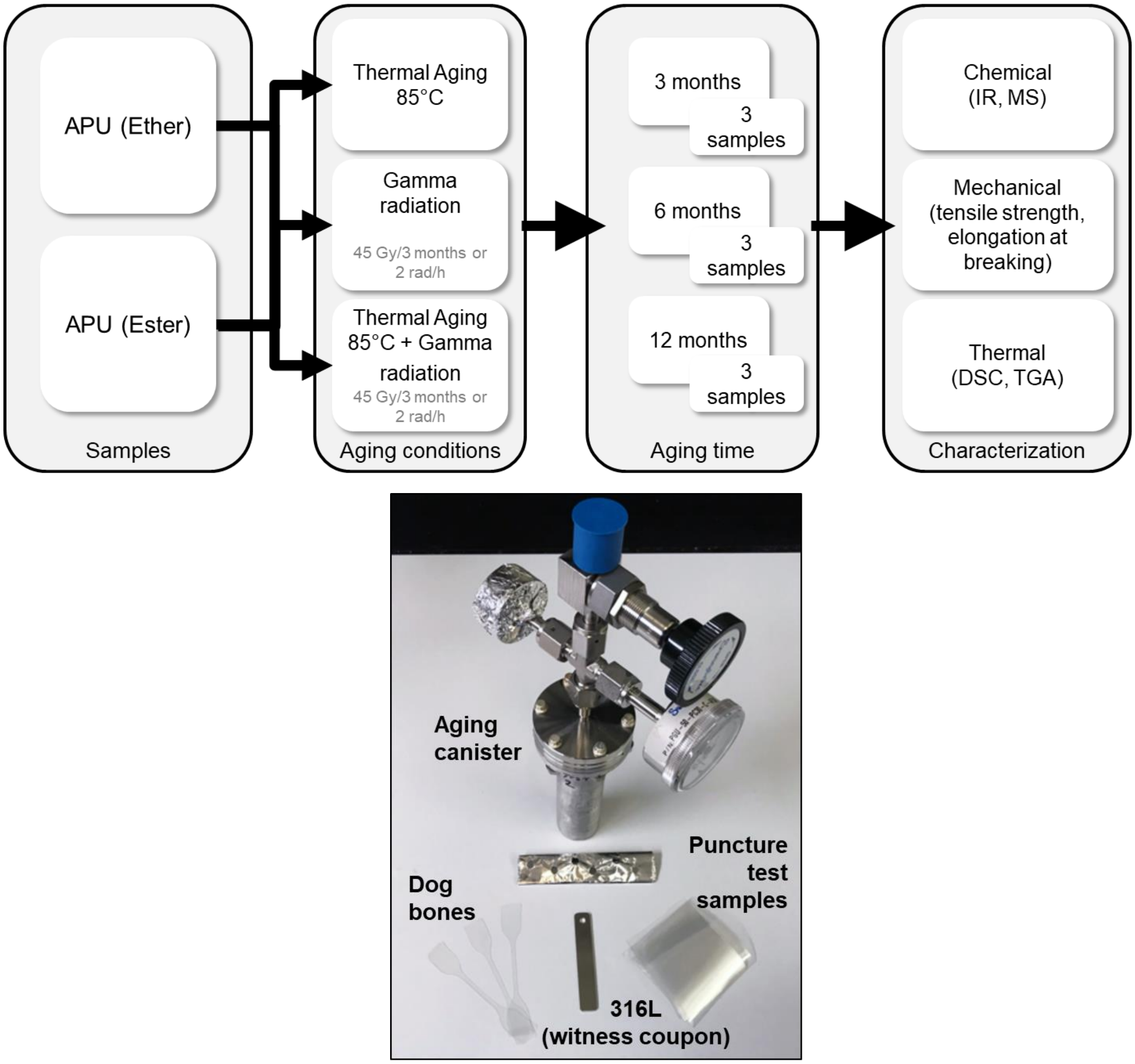

Figure 2-1: Top: Diagram of the accelerated aging study on the aromatic polyurethane (APU) materials, bottom: Picture of the stainless-steel canister in which the samples are aged (thermal and/or radiolysis).

2.2 Tension Tests

Tensile tests were performed using an ADMET eXpert 7601 frame with manual vise GV-1T serrated grips. At least three samples of each bag were cut into dumbbell or dog-bone structures using Die D according to ASTM D412. Samples were tested with the crosshead velocity of 3.84 mm/sec. The elongation and applied force were recorded automatically until the sample reaches the break point.

2.3 Puncture Tests

Puncture tests were performed using ADMET eXpert 7601 frame with screwed ring fixture and steel rod in accordance with ASTM D4883. A circle-cut sample of 50.8 mm diameter was prepared and locked in the fixture. The steel rod applies force against the center of the sample with the crosshead velocity of 5 mm/sec. The resistance force was recorded automatically until the sample reaches the rupture point.

2.4 Thermal Characterization – Thermogravimetric Analysis

Thermogravimetric analysis (TGA) experiments were conducted using a TA Instrument, TGA 5500, Discovery Series. The samples, weighing on average 10 mg, were ramped at 10 °C/min to 850 °C under nitrogen purge.

2.5 Mass Spectroscopy

The headspace of each canister containing the accelerated aged plastics was analyzed by mass spectroscopy using a Finnigan 271 mass spectrometer. Gas samples were collected into small gas bottles using a small vacuum manifold. An aliquot of a sample gas was injected to the mass spectrometer inlet chamber. Detectors were calibrated by known mixtures of gases, wherein detector sensitivities to the ions of specific gases were determined. The NIST mass spectral database was consulted for assignment of hydrocarbons in the headspace analyses.

2.6 FT-IR

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Nicolet iS50 FT-IR from ThermoFisher on pristine and aged (thermal and radiological) polyvinyl chloride (PVC), Aromatic polyether urethane (APU ether) and aromatic polyester (APU ester) materials. The spectra were obtained in attenuated total reflection (ATR) mode, using an average of 32 scans from 500 to 4000 cm^{-1}. A background spectrum was collected before each sample.

2.7 Solvent Swelling

Samples of each bag were weighed “as received” and then soaked in toluene for 24 hours. After soaking, the excess toluene was removed and the samples were weighed once again to determine the solvent intake. The samples were subsequently dried at 35ºC in a vacuum oven for 24 hours and then weighed determine any loss of material.

2.8 Contact Angle Measurements

Contact angle measurements were performed using a Drop Shape Analyzer (DSA30) from Krüss. An automated, computer-controlled drop dispensing and deposition system was used to perform the measurements. A drop of 2 µl deionized (DI) water was deposited on the test surface and the static contact angle was then determined by the computer software. A minimum of 5 trials were performed on each surface of the test sample and the values reported are an average of the measurements.

2.9 In-Glovebox Sample

APU ether and sPVC samples were cut from a bag-out bag procured through Nuclear Filter Technology, Inc. (NFT, Inc.). Each sample was cut into approximately 6 inch squares. Three types of bag materials were used in this portion of the study: APU ether, APU ester and sPVC. One set of samples were placed into a low dose glovebox in PF-4 and a set of samples were placed in a drop box in the Pu-238 area of PF-4. The low dose set of samples included one APU ether sample and one sPVC sample. The high dose set included two APU ether samples, two APU ester samples and two sPVC samples. To help in identifying the samples from one another the low dose samples were written on with a Sharpie® pen and the high dose samples had holes punched into the different bag materials. To eliminate possible sources for further degradation in the high dose samples the holes were used. After a period of time the samples were inspected for degradation, e.g. discoloration, embrittlement and loss of flexibility. All of the criteria are to be considered qualitative and no quantitative data was collected.

2.10 Cold Bag-Out Trial

Bags of both the alternative bag materials and the current sPVC bags were used to evaluate the impacts the new materials have on bag-out operation. This study took advantage of the cold gloveboxes at TA-55 in building 39 to perform bag-outs using all three materials, APU ether, APU ester and sPVC. All of the cold bag-out trials were performed using an approximately identical negative pressure to mimic the suction on the bags while performing the tasks. First, a bag was attached to the bag-out bag port and a dummy item was bagged out which included applying a stub by twisting the bag and taping the twist to seal the bag. Once the item was cut fry a new bag of the same material type was placed on the bag-out bag port to mimic a bag change. These operations were completed for each of the three bag materials. The operators, Vincent Garcia, Harvey Decker and Diane Spengler were then given a chance to comment on how the material felt in comparison to a typical bag-out.

3 Results

3.1 Tension Tests

Tensile testing was performed on the sPVC, aromatic polyether urethane and aromatic polyester urethane bags. The samples were subjected to a controlled tension until failure. These tests are essential to determine the ultimate tensile strength, breaking strength and maximum elongation. The mechanical properties obtained from tension tests allows for verification that i) the materials meet the requirements established for bag-out bags and ii) predict how the material will perform in use under normal and extreme conditions.

Initial tests were conducted on pristine bag samples to set a baseline for tension tests after thermal aging and radiolysis of the materials. The performance of the pristine bags shown in Figure 3-1 below exhibit a maximum elongation of 276 %, 570 % and 403 % and a maximum stress of 24 MPa, 57 MPa and 83 MPa corresponding to the pristine sPVC, APU ether and APU ester bags, respectively. The three bag samples show very different mechanical properties; with the sPVC showing inferior elongation and stress at break. Both aromatic polyurethanes show overall better performance with the APU ester showing the highest stress at break with 83 MPa and the APU ether demonstrating superior compliance with a maximum elongation of 570 %.

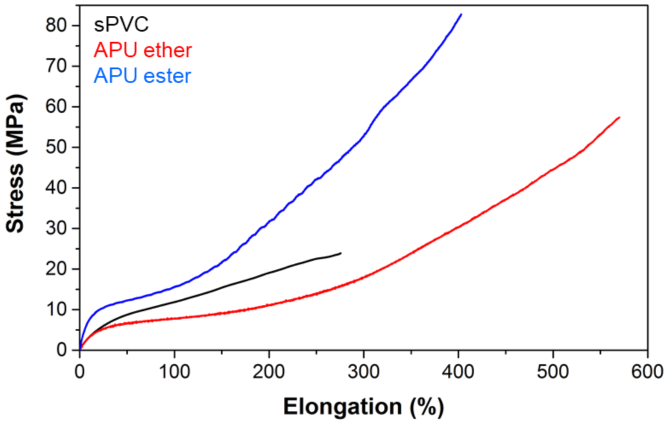

Figure 3-1: Stress-strain curves of pristine sPVC, APU ether and APU ester bags

Tension test after thermal aging and radiolysis of sPVC were performed and compared to the pristine performance. The aging conditions include:

- Thermal aging for 10 days at 135°C, 4 and 6 months at 75°C;
- Thermal and radiolysis aging in a SAVY container for 10 months;

The recorded stress-strain curves are displayed in Figure 3-2 below. The pristine sPVC bags show a maximum elongation of 276 % and a maximum stress of 24 MPa. Thermally aged samples show a maximum elongation of 258 %, 250 % and 255 % and a maximum stress of 26 MPa, 25 MPa and 24 MPa corresponding to the 10 days at 135°C, 4 months at 75°C and 6 months at 75°C, respectively.

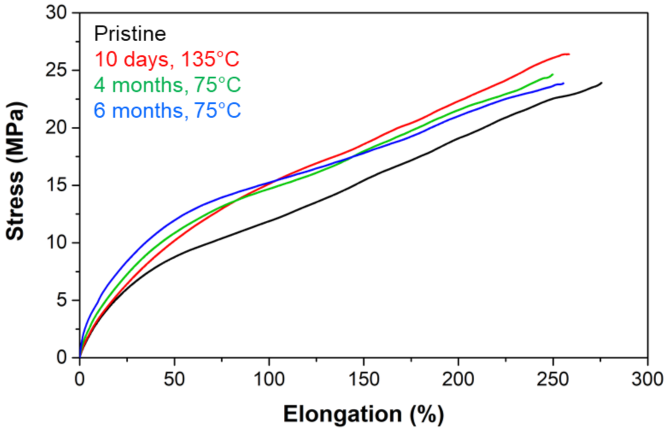

Figure 3-2: Stress-strain curves of pristine and accelerated aged sPVC bags

The SAVY-aged and thermally aged APU ether bag was tested under tension, the recorded stress-strain curves are displayed in Figure *3-3* below. While the pristine APU ether bags show a maximum elongation of 570 % and a maximum stress of 57 MPa, the bag sample aged for 10 months in a SAVY container shows a maximum elongation of 578 %, and a maximum stress of

68 MPa. The bag aged for 10 days at 135°C shows a slightly lower maximum stress to the pristine sample 45 MPa *vs*. 57 MPa but offers more compliance with a maximum elongation at break of 687% *vs*. 570%. The APU bag aged for 4 months at 75°C demonstrates a maximum stress and elongation at break of 60 MPa and 556% while the bag aged for 6 months at the same temperature shows a maximum stress and elongation at break of 42 MPa and 564%. While the performance of these thermally aged bags still outperform sPVC bags on all levels, their performance has changed under elevated temperatures, likely due to a slight oxidation of the material accompanied by a reorganization of the polymer chains. Finally, tension tests were performed on thermally aged and irradiated APU ether bags aged at Sandia National laboratory. The recorded stress-strain curves are displayed in Figure 5 below. The pristine APU ether bags show a maximum elongation of 570 % and a maximum stress of 57 MPa. Aged samples show a maximum elongation of 624 %, 547 % and 586 % and a maximum stress of 63 MPa, 60 MPa and 63 MPa corresponding to 3 months at 85°C, 3 months at room temperature under gamma radiation and 3 months at 85°C under gamma radiation, respectively. The performance of these bags after 3 months of accelerated aging under temperature and/or radiolysis demonstrate their superior mechanical stability with little to no change in both maximum stress and maximum elongation at break.

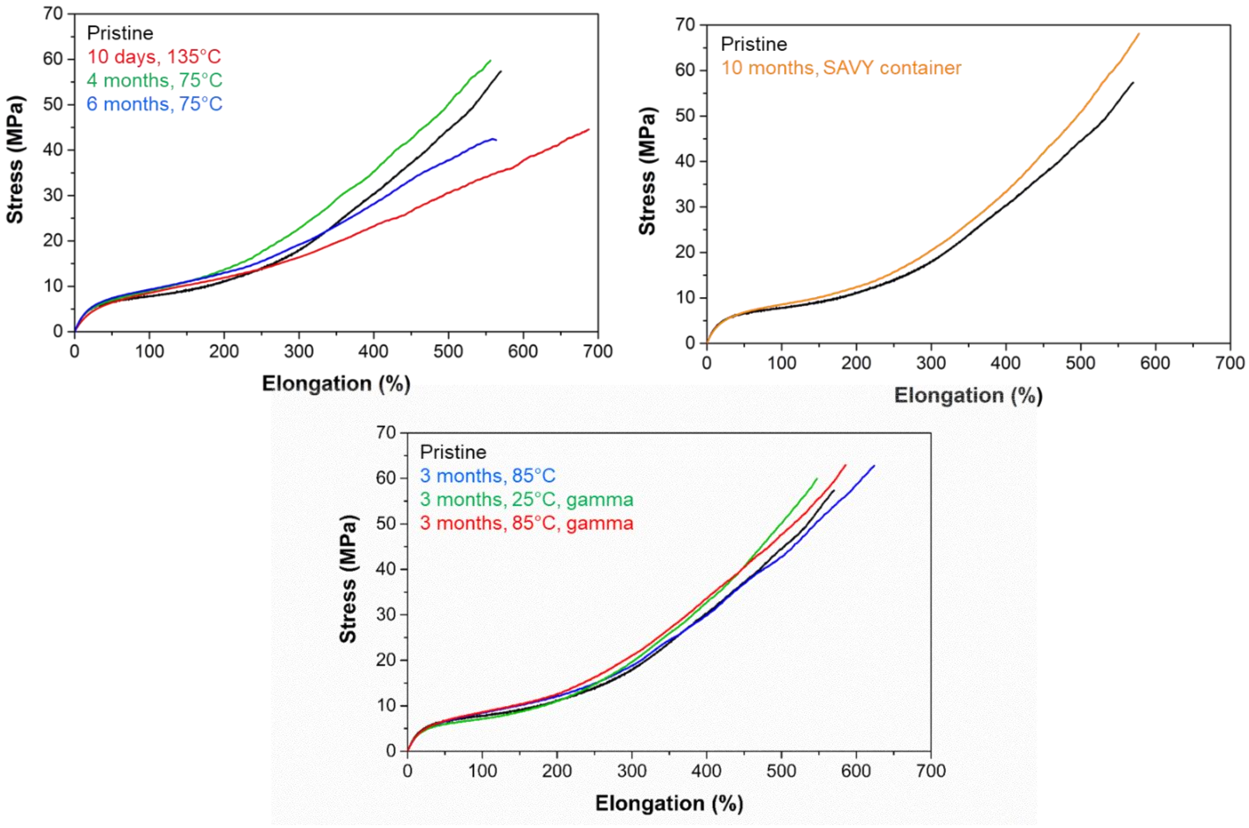

Figure 3-3: Stress-strain curves of pristine and accelerated-aged APU ether bags

Finally, APU ester bags that were aged at Sandia National laboratory under temperature and/or radiolysis were also tested. The recorded stress-strain curves are displayed in Figure *3-4* below. The pristine APU ester bags show a maximum elongation of 403 % and a maximum stress of 83 MPa. Aged samples show a maximum elongation of 519 %, 442 % and 512 % and a maximum stress of 72 MPa, 73 MPa and 76 MPa corresponding to 3 months at 85°C, 3 months at room temperature under gamma radiation and 3 months at 85°C under gamma radiation, respectively. The performance of these bags after 3 months of accelerated aging under temperature and/or radiolysis, despite slight changes, exhibit superior resistance to thermal/radiolysis aging with little decrease in maximum stress and increased maximum elongation at break.

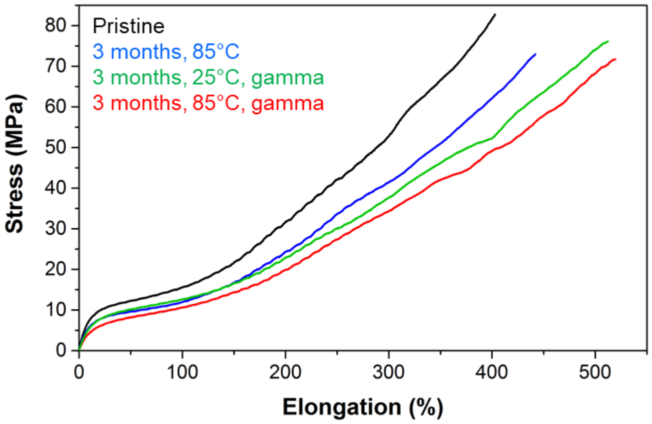

Figure 3-4: Stress-strain curves of pristine, thermally aged and irradiated APU ester bags

3.2 Puncture Tests

Similarly to the tension tests, sPVC, aromatic polyether urethane and aromatic polyester urethane bags were subjected to puncture testing. This test determines the ability of a material to inhibit the intrusion of a foreign object. The properties obtained from puncture tests will allow for verification that i) the materials meet the requirements established for the puncture resistance of bag-out bags and ii) predict how the material will perform in use.

Initial tests were conducted on pristine bag samples to set a baseline for puncture tests after thermal aging and radiolysis of the materials. The performance of the pristine bags shown in Figure *3-5* below exhibit a maximum displacement of 22 mm, 47 mm and 32 mm and a maximum load of 101 N, 172 N and 248 N corresponding to the pristine sPVC, APU ether and APU ester bags, respectively. The three bag samples show very different mechanical properties; with the sPVC showing inferior displacement and load at break. Both aromatic polyurethanes show overall better performance with the APU ether showing the highest displacement at break with 47 mm and the APU ester demonstrating superior load at break with 248 N.

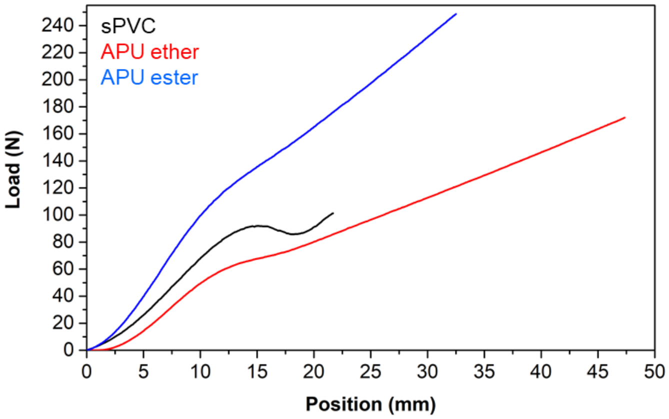

Figure 3-5: Puncture tests of pristine sPVC, APU ether and APU ester bags

Similarly to the tension tests, puncture tests were conducted after thermal aging and radiolysis of the materials and compared to the pristine performance. The aging conditions are identical to the ones described earlier. The thermally aged sPVC bags were tested for puncture resistance, the recorded load-displacement curves are displayed in Figure *3-6* below. The pristine sPVC bags show a maximum displacement of 22 mm and a maximum load of 101 N. Thermally aged samples all show a maximum displacement of 24 mm and a maximum load of 139 N, 126 N and 131 N corresponding to the 10 days at 135°C, 4 months at 75°C and 6 months at 75°C, respectively. This higher load at break for thermally aged samples can be explained by the loss of plasticizer inside the material. In fact, as stated earlier, the presence of plasticizer renders PVC flexible and thus fit to be used as a bag. When the plasticizer is leached out under thermal aging, radiolysis or solvent swelling, the PVC becomes stiffer and therefore harder to puncture.

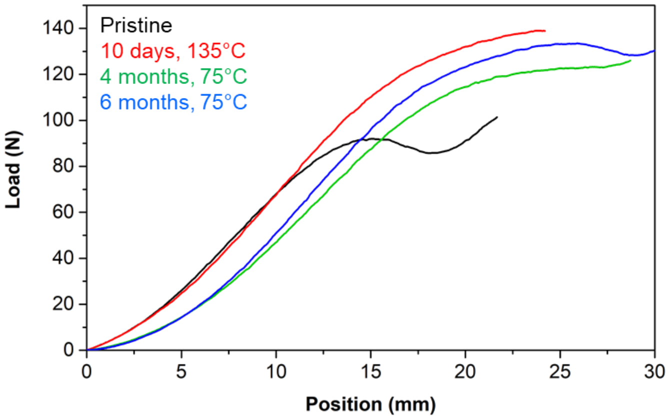

Figure 3-6: Puncture tests of pristine and thermally aged sPVC bags

Further, the puncture resistance of the thermally aged APU ether bags was tested, the recorded curves are displayed in Figure 9 (left). The pristine bag shows a maximum displacement of 47 mm and a maximum load of 172 N. Thermally aged samples show a maximum displacement of 34 mm, 41 mm and 43 mm; and a maximum load of 115 N, 160 N and 151 N corresponding to the 10 days at 135°C, 4 months at 75°C and 6 months at 75°C, respectively. While the performance of these thermally aged bags still outperform sPVC bags on all levels, their performance has changed under elevated temperatures, and more specifically for the samples aged for 10 days at 135°C that likely underwent more severe changes such as oxidation.

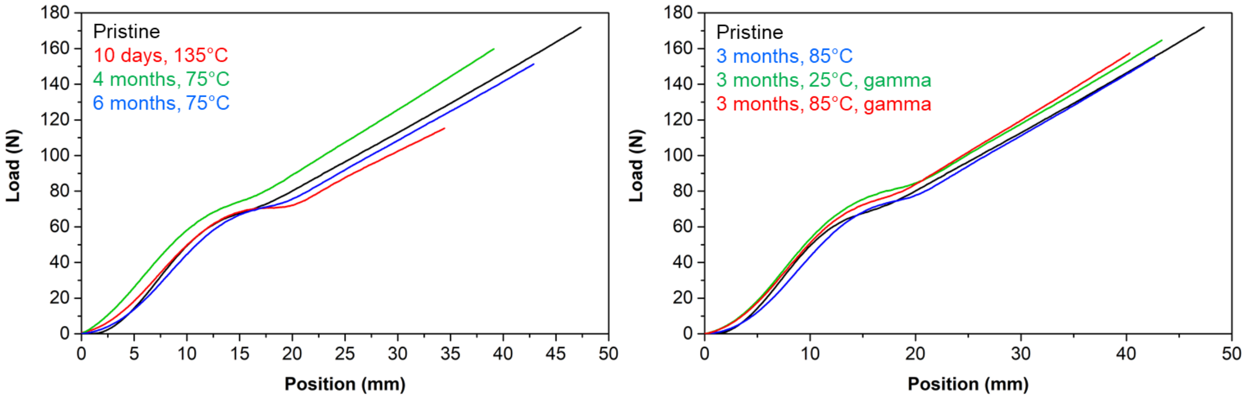

Figure 3-7: Puncture tests of pristine and thermally-aged APU ether bags

Additionally, puncture tests were performed on thermally aged and irradiated APU ether bags aged at Sandia National laboratory. The recorded load-displacement curves are displayed in Figure 3-7 (right). The pristine APU ether bags show a maximum displacement of 47 mm and a maximum load of 172 N. Aged samples show a maximum displacement of 43 mm, 43 mm and 40 mm and a maximum load of 151 N, 162 N and 157 N corresponding to 3 months at 85°C, 3 months at room temperature under gamma radiation and 3 months at 85°C under gamma radiation, respectively. The performance of these bags after 3 months of accelerated aging under temperature and/or radiolysis demonstrate their superior resistance with little to no change in both load and maximum displacement at break.

Finally, the puncture resistance of APU ester bags was also tested after aging of the materials. First, APU ester bags were aged for 4 months at 75°C (Figure 10 (left)). The aged sample show a higher displacement compared to the pristine sample 32 mm *vs*. 38 mm and a lower load at break, 248 N *vs*. 212 N. This slight change of performance can be explained by the light oxidation that the material undergoes as well as the reorganization of the polymer chains.

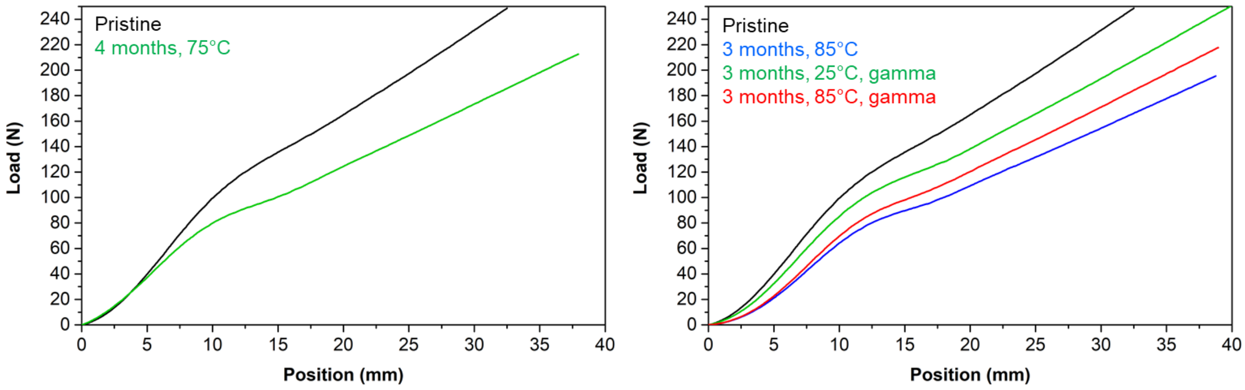

Figure 3-8: Puncture tests of pristine, thermally aged and irradiated APU ester bags

Moreover, APU ester bags that were aged at Sandia National laboratory under temperature and/or radiolysis were also tested. The recorded curves are displayed in Figure 3-8 (right). The pristine APU ester bags show a maximum displacement of 32 mm and a maximum load of 248 N. Aged samples show a maximum displacement of 39 mm, 42 mm and 39 mm and a maximum load of 195 N, 260 N and 218 N corresponding to 3 months at 85°C, 3 months at room temperature under gamma radiation and 3 months at 85°C under gamma radiation, respectively. The performance of these bags after 3 months of accelerated aging under temperature and/or radiolysis, despite slight changes, exhibit an excellent resistance to thermal/radiolysis aging with little to no decrease in maximum load and increased maximum displacement at break.

3.3 Thermal Stability

The thermal stability of the sPVC, aromatic polyether urethane and aromatic polyester urethane bags was tested using TGA. TGA is a method of thermal analysis in which the mass of the sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, as well as chemical phenomena such as thermal decomposition. The reported decomposition temperature is determined by the point at which the material exhibits a weight loss of 5%.

Changes in the thermal stability of accelerated aged and irradiated sPVC and APU samples were measured by TGA in an inert atmosphere. For pure PVC, dehydrochlorination is characterized by a sharp peak of mass loss at 270 to 280°C, whereas no discernible changes below 220°C are expected.[8] In the case of pristine sPVC, mass loss starts at a lower temperature or about 227°C as shown in Figure *3-9* below.

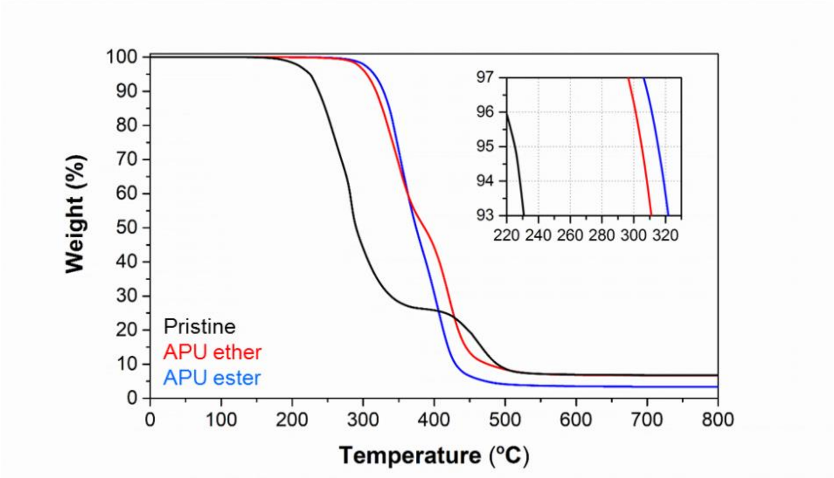

Figure 3-9: Thermogravimetric analysis of pristine sPVC, APU ether and APU ester bags

As shown previously, pristine sPVC starts losing mass at about 227°C. Interestingly, the sPVC sample exposed to the highest alpha dose shows a slight decrease in thermal stability, with 5 wt% mass loss occurring at 218°C. The other accelerated aged samples show no significant changes in thermal stability compared to the control sample (Figure *3-10*).

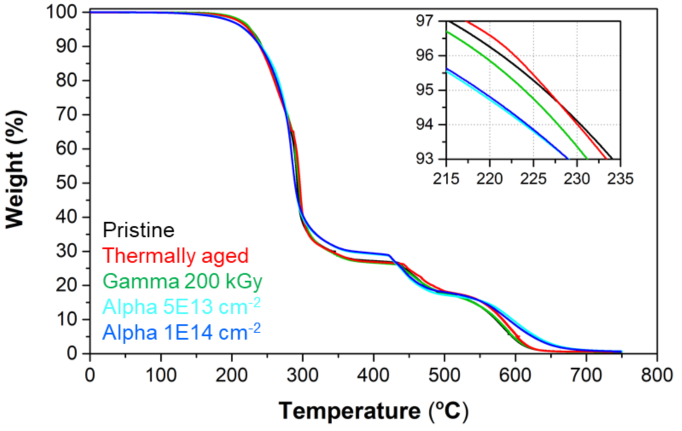

Figure 3-10: Thermogravimetric analysis of pristine, thermally aged and irradiated sPVC bags

Additionally, APU ether bags were also subjected to thermogravimetric analysis under inert atmosphere, showing a drastic improvement in thermal stability with an onset mass loss at 315°C as shown in Figure *3-11*. The material, after being exposed to aging conditions: 3 months at 85°C, 3 months at room temperature under gamma radiation and 3 months at 85°C under gamma radiation has shown little to no change with a stable mass loss onset at 315°C +/- 2°C. It is worth pointing out that this polymeric material has greater thermal stability than sPVC, which exhibits 68% mass loss at this same temperature range.

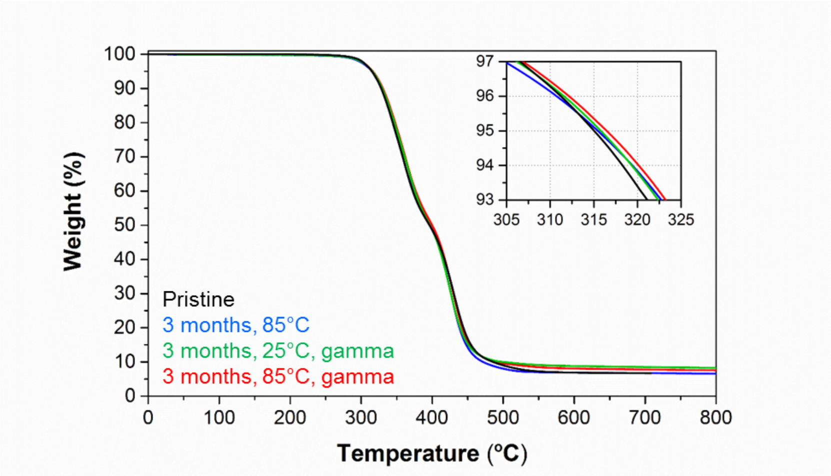

Figure 3-11: Thermogravimetric analysis of pristine, thermally aged and irradiated APU ether bags

Finally, the thermogravimetric analysis of APU ester bags was obtained under inert atmosphere, showing a drastic improvement compared to sPVC but also an improvement compared to APU ether bags with an onset mass loss at 333°C as shown in Figure *3-12*. The material, after being exposed to the same aging conditions: 3 months at 85°C, 3 months at room temperature under gamma radiation and 3 months at 85°C under gamma radiation shows a small decrease in temperature onset at 327°C +/- 2°C.

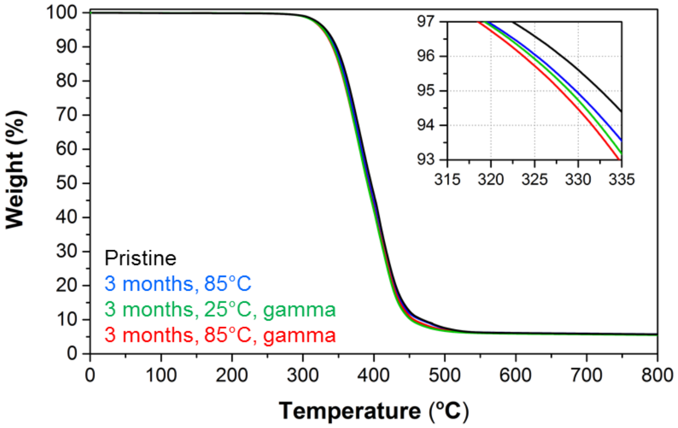

Figure 3-12: Thermogravimetric analysis of pristine, thermally aged and irradiated APU ester bags

Again, this polymeric material has greater thermal stability than sPVC, which exhibits 68% mass loss at this same temperature range.

3.4 Chemical Stability

Gas analysis of the headspace provides useful insights on polymer degradation mechanisms since gases are formed due to atom or side-chain abstraction, and are then indicative of damage to the polymer. Analysis of the gases present in the headspace was performed by mass spectroscopy for aromatic polyether urethane samples aged under either radiative conditions (20 Mrad) or thermal conditions (10 days at 135°C). Concentrations of the most abundant gases detected in the headspace are listed in Table 1. It is interesting to note that the concentration of oxygen decreased when aged thermally. Our results indicate that the amount of oxygen consumed is higher for thermal degradation than for radiative conditions indicating oxidation of the material. Furthermore, under thermal conditions an increased amount of both carbon monoxide and carbon dioxide is generated. This result is expected when polymers undergo oxidative degradation.

Table 1 Head space analysis by mass spectroscopy of aged aromatic polyether urethane material

Species	**Aromatic Polyether Urethane (20 Mrad)**	**Aromatic Polyether Urethane (10 days at 135°C)**
H_2	0.42%	0.38%
O_2	18.52%	11.73%
CO *(*Estimated*)*	1.81%	5.71%
CO_2	0.26%	3.02%
CH_4	8.5 ppm	5.2 ppm
H_2O	47.7 ppm	45.4 ppm
CH_3CHO (acetylaldehyde)	2.6 ppm	27.2 ppm
C_4H_8 (butene)	49.1 ppm	77.6 ppm

The G-values, which represent the number of cross-links generated per 100 eV of energy absorbed (1/100 eV is equivalent to 1.036 E-7 mol/J) were also estimated for aromatic polyether urethane, plasticized PVC and pure PVC irradiated in air at a dose of 20 Mrad. The given G-values obtained from the literature[9] for both the plasticized PVC and pure PVC material clearly shows that gamma radiation induces the generation of HCl. The HCl generated likely contributes to corrosion of the metal containers used in nuclear storage. As expected, the aromatic polyether urethane material does not generate any HCl under radiative conditions. The total G value for the aromatic polyether urethane material is significantly less than that for either the plasticized PVC or pure PVC material (17x less and approximately 49x less respectively). This means that under radiative conditions the PVC based materials degrade significantly more rapidly than the aromatic polyether urethane.

3.4.1 FT-IR

The chemical fingerprint of the sPVC, aromatic polyether urethane (APU-ether) and aromatic polyester urethane (APU-ester) bags was tested using Fourier transform infrared (FT-IR) spectroscopy. This technique is used to identify chemical bonds in a material by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to monitor the changes in a material. The spectra obtained from pristine, thermally aged and irradiated sPVC and APU-ether are shown in Figure *3-13*: FT-IR spectra of thermally aged sPVC (A, B) and APU ether bags (C)below.

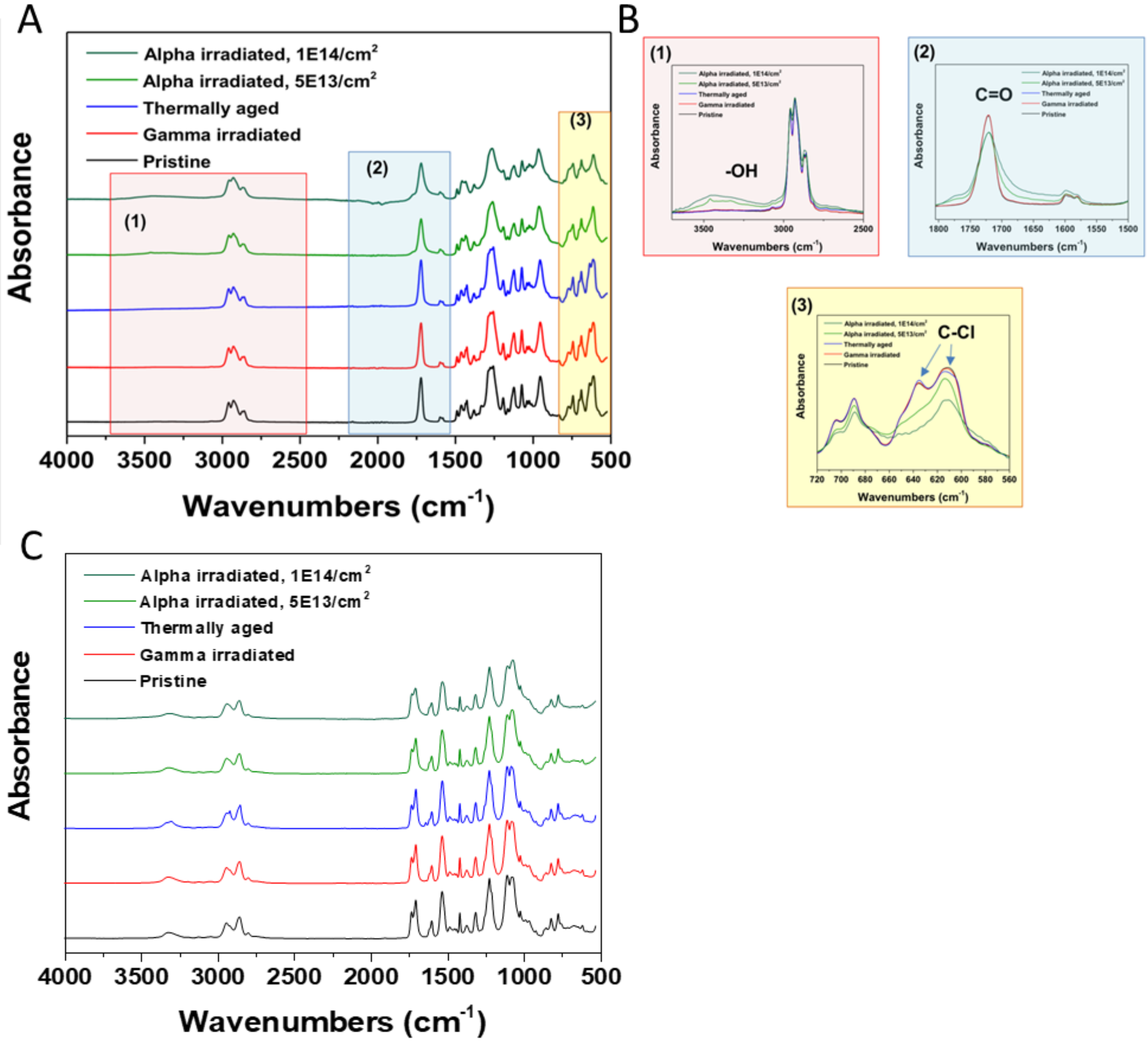

Figure 3-13: FT-IR spectra of thermally aged sPVC (A, B) and APU ether bags (C)

Effects of various aging treatments on the chemical composition of sPVC and APU were investigated by FT-IR spectroscopy. Frequency shifts in the FT-IR spectrum indicates specific molecular interactions between plasticizer and polymer—essential for compatibility. The hydrogen atom attached to the chlorine-bearing carbon atom of PVC is slightly acidic due to the high electronegativity of the chlorine atom. The oxygen atom of the carbonyl group of an ester group is electron-rich, allowing for weak acid–base interactions between PVC and the ester group of a plasticizer. For example, the absorbance of the carbonyl group of dibutyl phthalate shifts to a lower frequency when it is blended with PVC.

As shown in Figure 15B, three significant changes due to in alpha irradiated sPVC bag are observed at 610 and 635 cm^{-1} corresponding to the stretching of the C-Cl bonds in PVC, at 1723 cm^{-1} corresponding to the stretching of ester C=O bonds in the plasticizer, and at around 3400 cm^{-1} corresponding to the stretching of the -OH bonds resulting from the degradation of the plasticizer.[10-13] These results indicate that sPVC bag is not stable under the radiation condition leading to the loss of plasticizer from the bag and to HCl off-gassing issue to accelerate the degradation of the bag. On the other hand, no significant change of APU bag observed by FT-IR as shown in Figure 15C, meaning that no chemical change of APU were occurred under various aging treatments.

Different thermally aged conditions have been used to evaluate the thermal resistance of the sPVC, APU-ether, and APU-ester bags. As shown in Figure 16, no chemical changes were observed for all bags, indicating that there is no change of the chemical structure of all bags. The sharp peaks at 3316, 2916, 2846, 1639, and 1568 cm^{-1} are caused by the ethanol cleaning solvent for the FT-IR equipment. [12] APU-ether (Figure *3-14* B,C) and APU-ester Figure *3-14* D,E) bags under thermal and irradiated conditions were investigated to evaluate the combined effect.

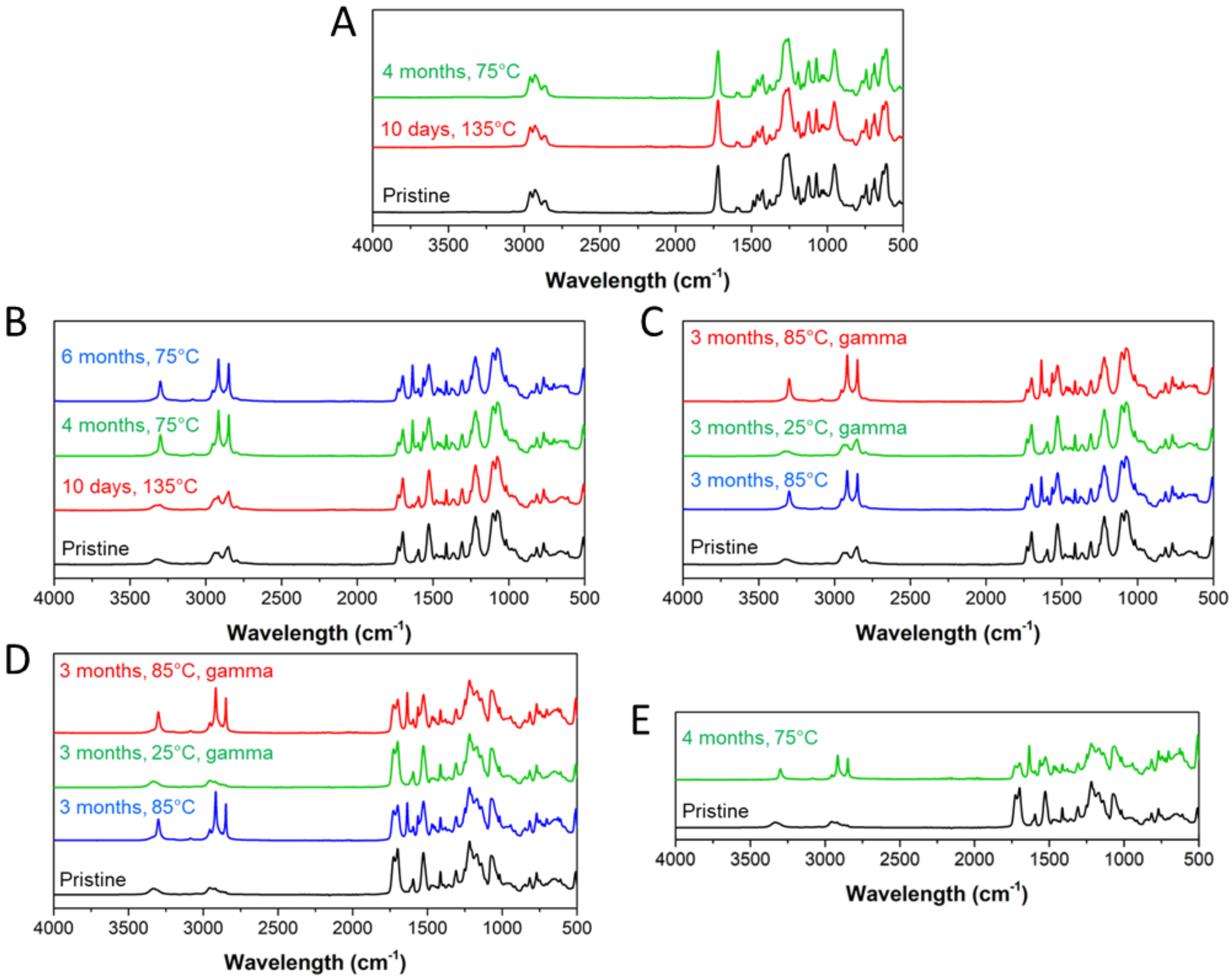

Figure 3-14 FT-IR spectra of pristine, thermally aged and irradiated sPVC (A) , APU ether bags (B, C) and APU ester bags (D, E)

APU ether and APU ester bags maintain chemical properties under various exposed conditions without any significant change of FT-IR peak. This indicates that both bags have excellent tolerance to thermal aging under those conditions.

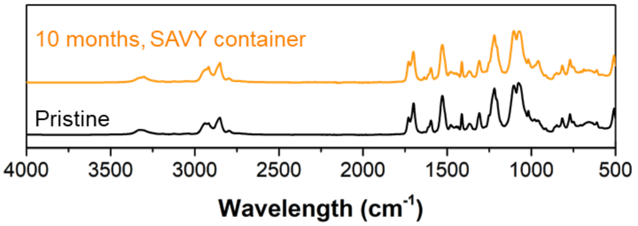

Figure 3-15: FT-IR spectra of APU-ether bags under real operation condition

FT-IR of APU-ether bag has been observed after 10 months operation under real conditions and compared with the pristine sample. As shown in Figure *3-15*, no significant change has occurred, exhibiting a superior resistance to thermal and irradiated aging, even under real operation conditions.

3.5 Solvent Swelling

Solvent swelling measurements are an efficient way to determine how much solvent a material can intake but also more importantly, how much material is lost after drying. The material lost are usually small compounds and molecule such as plasticizers, color etc. In this work, solvent swelling measurements allow to measure how much these small molecules and compounds constitute the material and how much their loss could possibly affect the properties of the bag. Solvent swelling measurements are shown in Figure *3-16* below. The solvent intake of sPVC bags are on average of 4% of their initial mass, and the solvent loss after drying shows a mass loss above 25%. This is due to the large amount of plasticizer present in the material to give its flexibility and workability. In fact, the material deprived of plasticizer appear stiffer to the touch and that effect is confirmed by the tensile and puncture tests in Figure 3-6. The APU ether and APU ester bags show a larger solvent intake ranging from 12% up to 27%. After the samples are dried, the mass loss averages at 1.5% in both cases which reveals the presence of small molecules, the loss of which should have little to no impact on the overall performance.

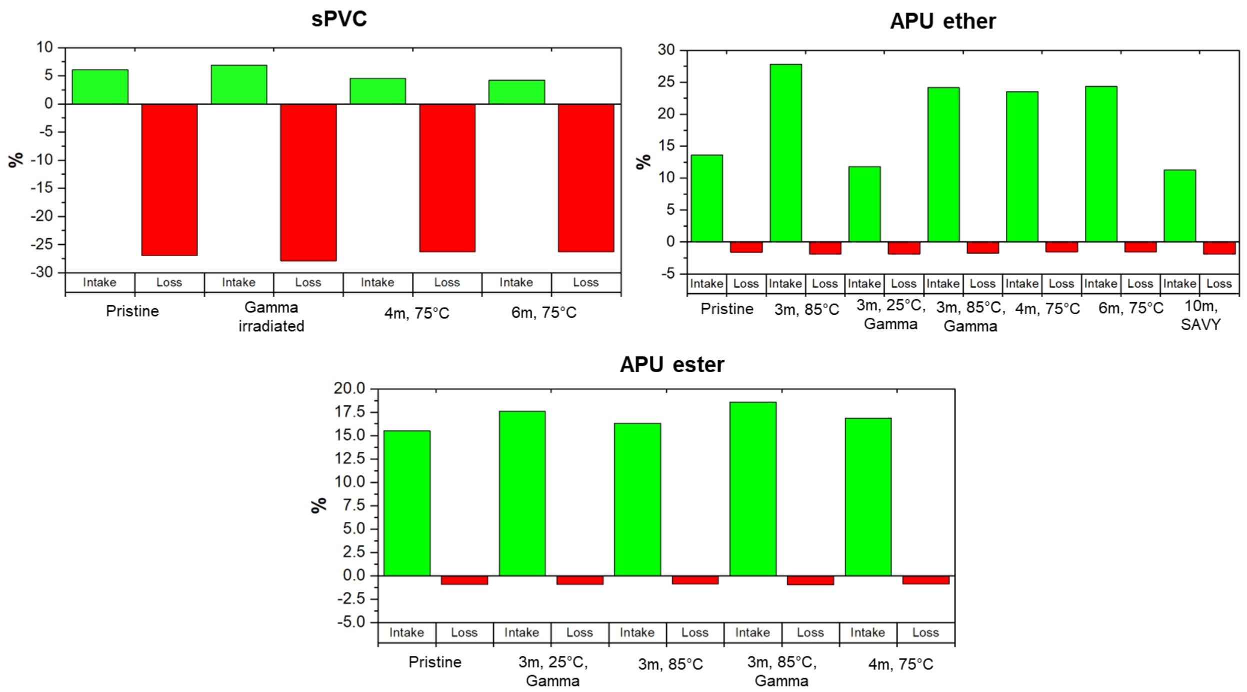

Figure 3-16: Solvent swelling tests for pristine, thermally aged and irradiated sPVC, APU ether and APU ester bags.

This experiments shows that APU bags do not have a significant amount of small molecules in their matrix and that this can only be beneficial on the long term durability. In fact, when the bags contain a significant amount of small compounds (*i.e*. sPVC bags), the mechanical and chemical properties are greatly affected as shown in Figures 4, 8, 12 and 16.

3.6 Contact Angle Measurements

Contact angle measurements are a quick and efficient way to determine the hydrophobicity of a material by measuring the angle that a drop of solvent forms at the surface. In this work, contact angle measurements allow to monitor the changes in surface properties and assess whether the material is retaining its hydrophobic properties, an important characteristic of plastic bags for storage, or if the surface properties of the bag are evolving. Contact angle measurements are shown in Figure *3-17* below.

The pristine sPVC bag shows hydrophobic properties with a contact angle of 94°. Thermally aged and irradiated bags seem to not retain their hydrophobic properties with a drastic drop in contact angle, down to 77°, 91°, 73° and 76° for the bags aged 10 days at 135°C, the gamma irradiated bags, the alpha irradiated bags (5E13 and 1E14 cm^{-2}), respectively. The pristine APU ether bag shows a contact angle of 108° and whether the bag was aged thermally or irradiated, the contact angle remains at the very least the same or tends to increase with a contact angle varying between 106°and 113°. The same thing can be witnessed with the APU ester bags with an initial contact angle of 109° and a retention of the hydrophobic properties with a contact angle varying between 108° and 115°.

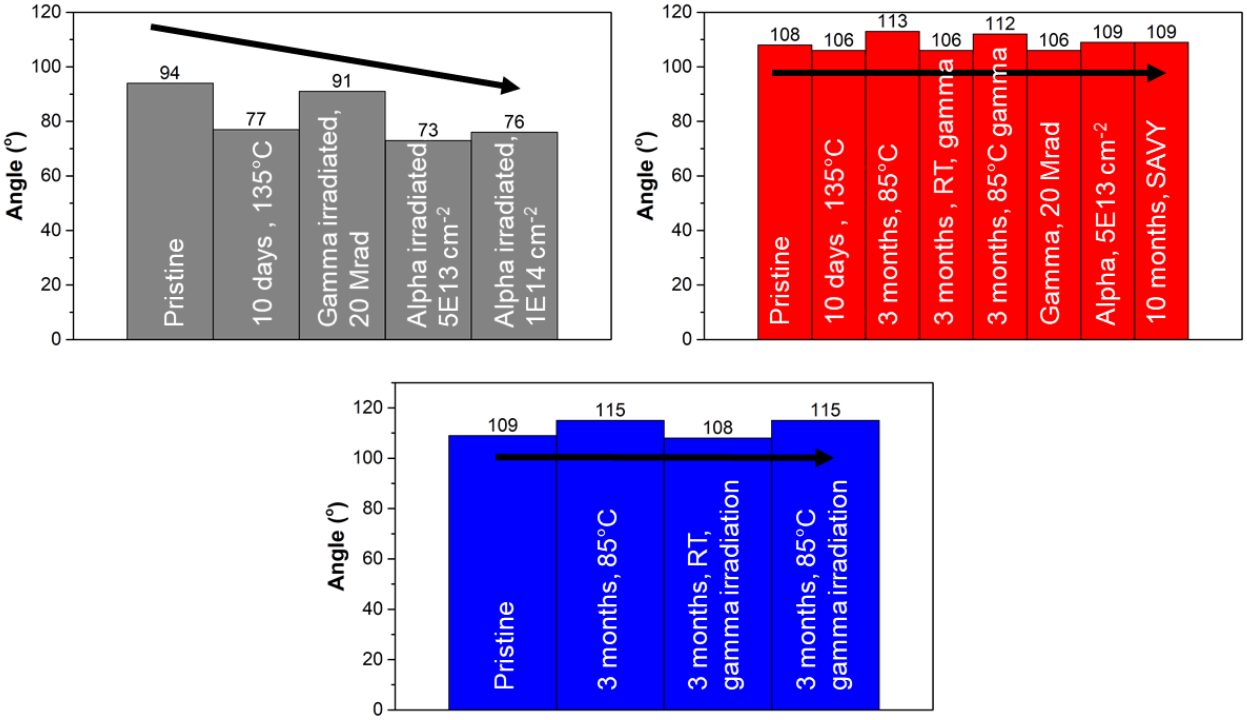

Figure 3-17: Contact angles for pristine, thermally aged and irradiated sPVC, APU ether and APU ester bags.

This experiments shows the excellent hydrophobicity superior resistance to temperature and radiation of aromatic polyurethanes.

3.7 In-Glovebox Sample

The low dose samples were placed in close proximity of the 3013 full-scale experiments within the insulation portion of the experiment [14]. The study exposed the APU ether and sPVC samples to both heat and a radiolytic environment. After approximately 8 months the samples were checked for the degradation criteria listed in the methodology section. The APU ether did show faint signs of discoloration (Figure 3-18), but when it was pulled on to stretch it out, it was as flexible as a pristine sample of the same material and showed no signs of embrittlement. The sPVC sample also showed signs of discoloration (Figure 3-19) and was not stiff or brittle when pulled on.

The high dose samples are still in the drop box they were placed into one and a half months ago. Unfortunately, no photos or qualitative data was collected due to the fact that the Pu-238 account have been locked out and will not be reopened until the beginning of July 2018. An update to this report will be available when data has been collected for the high dose study.

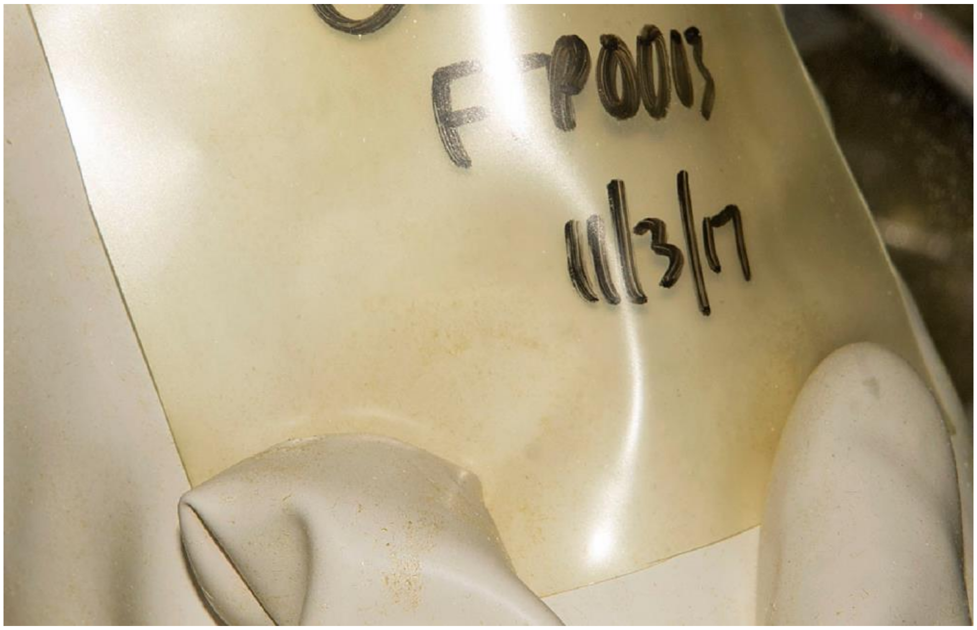

Figure 3-18 Low dose APU ether sample after 8 months of exposure

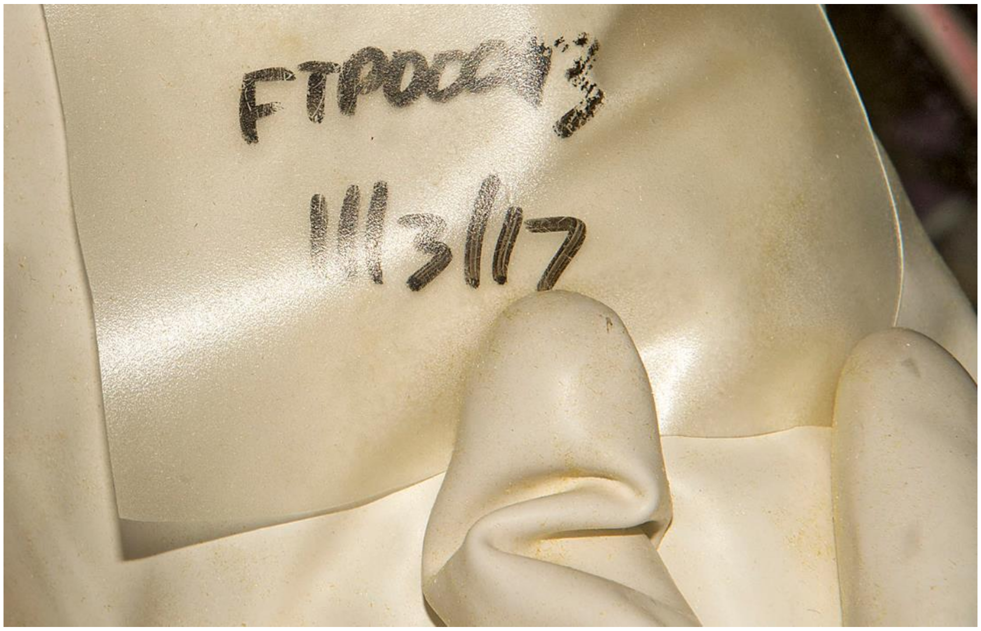

Figure 3-19 Low dose sPVC sample after 8 months of exposure

3.8 Cold Bag-Out Trial

The first bag material to be used was the sPVC, which is what is currently being used in PF-4. The comments from the operators was that they did not notice any differences in the way this bag behaved on the cold glovebox. This result was expected but needed to be verified before gathering the information on the alternative bag materials.

Next, the APU ether was used and a bag change (Figure 3-20) was performed over the sPVC. Once the APU ether bag was on the bag-out bag port a dummy item was placed into the new bag and a stub was created and cut off of the glovebox. The last thing to evaluate with this material was to install a new bag made of the same material onto the bag-out port to evaluate the bag change operation. The operators did notice that the bag material had slight trouble sliding on itself unlike with the sPVC which slides freely on itself. The difference in the sPVC and the APU ether is that the APU ether does not have a textured surface on one side like the sPVC does. The textured feature of the sPVC bag is something that has been added for the sole reason of allowing better handling characteristics. It has been confirmed by the plastic manufacturer that it is possible to add the textured surface to the APU ether to get better handling characteristics. The vendor of the plastics has sent LANL a sample of the textured material and it has less of a tendency to stick on itself. It should be noted that there are no additives used to create this texture and no additives are used after the sheets of plastic have been produced.

Figure 3-20 A bag change being performed on the APU ester

Finally, the APU ester was used and a bag change was performed over the APU ether. Once the APU ester bag was on the bag-out bag port a dummy item was placed into the new bag and a stub was created and cut off of the glovebox. The last thing to evaluate with this material was to install a new bag made of the same material onto the bag-out port to evaluate the bag change operation. The operators did notice that the bag material had quite a bit more friction between itself, in fact the operators had trouble getting the new bag onto the bag-out port during the bag change.

At the end of the cold bag-out trial the operators were asked whether the fact that the materials had a higher degree of friction between themselves would have a significant impact on the bag-out operations in PF-4. The operators indicated that the high friction would not be a “show stopper”, but would be desirable if it was possible to reduce the friction. The most notable attribute from the cold bag-out exercise was that the APU ether stub (Figure 3-21, B) was much tighter than the APU ester stub (Figure 3-21, C) after the dummy item was bagged out and cut from the remaining bag on the bag-out port. It should be noted that the density of stub is similar between the sPVC (Figure 3-21, A) and the APU ether (Figure 3-21, B) and would be expected to perform similarly with regards to maintaining a seal. The fact that that APU ether had a tighter stub than APU ester was assumed to be due to the fact that the APU ester bag material was not able to slide on itself as easily compared to the APU ether. Although no tests were performed to evaluate the sealing properties of the two stubs it could be deduced that the APU ether would be more likely to trap any contamination that is in the stub relative to the APU ester.

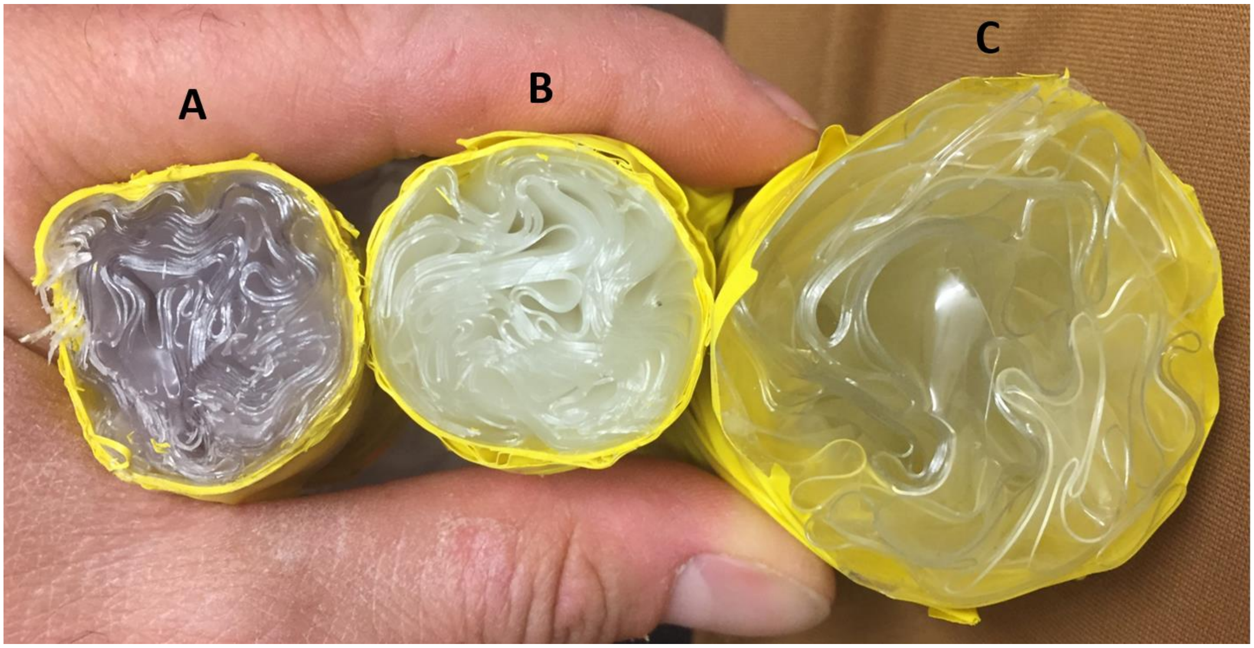

Figure 3-21 A comparison of stubs from each bag-out bag material. (from left: sPVC, APU ether, APU ester)

4 Summary and Conclusion

Plastic bags made of plasticized suspension polyvinyl chloride (sPVC) are commonly used in conjunction with metal containers to help store and transport nuclear materials. This plastic has a number of desirable properties like being highly resistant to acidic and alkaline conditions and being easy to handle under difficult working conditions. However, it is well-known that degradation of sPVC results in HCl formation which can lead to corrosion of metal containers as well as loss of plasticizer which results in degradation of mechanical properties. In this work, our team assessed two aromatic polyurethane replacement candidates for sPVC. More specifically, plastic bags made from aromatic polyether urethane and aromatic polyester urethane were artificially aged to evaluate their stability when exposed to harsh environmental conditions.

These new materials along with sPVC were exposed to alpha, gamma and thermal conditions to simulate the unique environments commonly encountered in the storage of nuclear materials. Mechanical, physical and chemical properties including changes in hydrophobicity were evaluated before and after exposures. Our initial results demonstrate that these two types of polyurethanes perform better than sPVC. No significant changes were observed on mechanical properties (tensile stress and puncture resistance), thermal stability, chemical composition, and off-gassing when aged under a combination of radiation and thermal treatments. These important results provide the basis for the selection of APU ether bag-out bag material to be considered in future nuclear material storage.

In order to begin implementing a new bag material into PF-4 a revision to TA55-SPEC-01000 would need to occur so that the warehouse could order and stock the material. It is recommended that the approach be considered a pilot program to slowly phase in the new bag material with item that are currently understood to be compatible with these plastics. Further testing is recommended to evaluate the degradation effects of alpha radiation and the combined long term effects of radiation and thermal degradation on the new material.

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