

## Degradation of sPVC and Aromatic Polyether Urethane Bags Used in Nuclear Applications

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### ABSTRACT

Plasticized suspension polyvinyl chloride (sPVC) bags are commonly used in combination with metal containers to transport and store nuclear materials. Nuclear material is first packed into an appropriate stainless-steel container that is placed into a plastic bag-out bag, often sPVC, and further positioned into a second metal container. One important drawback of using sPVC, is that it can degrade under severe conditions and release hydrochloric acid that will affect the integrity of the metal containers. In this work, we have exposed promising alternatives to sPVC: aromatic polyether urethane (APU-ether) and aromatic polyester urethane (APU-ester) to accelerated aging by subjecting them to gamma radiation and thermal conditions to simulate the harsh environments normally encountered in the storage of nuclear materials. Mechanical, physical and chemical properties including changes in hydrophobicity were evaluated before and after exposures. The preliminary results demonstrate that both APU-ether and APU-ester are more durable under thermal aging and irradiation than sPVC and provide new insights into the durability of polymer materials for nuclear storage. This study will serve as the foundation for a rational selection of new bag-out bag materials to be considered in the industry.

### INTRODUCTION

The storage and transport of nuclear materials are essential operations in the nuclear industry that require special consideration. Storage containers are engineered to prevent pressure build-up, particulate release, and water from entering the container in the event that the facility sprinkler system is activated.<sup>1</sup> Usually the nuclear material is first packed in a metal container, which is itself contained in a polyvinyl chloride (PVC) bag, which is further packed in a secondary metal vessel. The main role of the plastic bag is to isolate the contaminated inner vessel and prevent any material release in case it becomes breached.

PVC is an attractive thermoplastic due to its desirable properties such as manufacturability, cost, hydrophobicity, low flammability, and resistance to both acidic and alkaline environments. These properties can be enhanced by the incorporation of additives that can make up as much as 40% of the total weight of the material.<sup>2-6</sup> PVC is a hard and brittle solid that can be turned into a soft and compliant material by the addition of plasticizers. Depending on the environmental conditions, additives can diffuse

out of the plastic such that aging and degradation of plasticized PVC (sPVC) will affect the material's chemical and mechanical properties.<sup>7-8</sup>

Inspection of sPVC bags used in long-term nuclear storage containers showed evident changes in appearance and mechanical properties. Furthermore, unidentified liquid droplets were found outside the inner metal container, which also exhibited evidence of corrosion.<sup>9-10</sup> These findings prompted the authors to examine the degradation of sPVC bags and to find replacement candidates. In fact, there are numerous studies demonstrating that, PVC, under exposure to heat or radiation loses hydrochloric acid (HCl) when it undergoes dehydrochlorination (DHC).<sup>4,6</sup> A recent overview by Starnes et al. summarizes the main PVC DHC mechanisms, such as DHC initiation from the preliminary existence of structural defects with low thermal stability.<sup>11</sup> Additionally, the presence of functional groups (hydroperoxides, hydroxyls, and carbonyls) generated during thermal oxidative degradation are thought to also participate in the DHC process.

We selected sPVC-replacement candidates from a selection of polyurethanes, a family of polymer materials, due to their many applications as adhesives, sealants, coatings, and elastomers.<sup>12-13</sup> They are composed of alternating soft segments (polyethers or polyesters) and hard polar urethane segments, formed from the condensation reaction between a diisocyanate and one or more diols.<sup>14-15</sup> These materials offer flexibility, tear strength and possess excellent hydrolysis resistance, making them ideal for storage applications.

In this work, we investigate the thermal and radiation stability of two commercially available alternatives to sPVC bags commonly used for storage of nuclear materials: aromatic polyether urethane (APU-ether) and aromatic polyester urethane (APU-ester). The long-term aging study of these materials consists of exposure to a combination of gamma radiation and/or thermal treatments that allow for a complete understanding of the aging processes. Such long-term studies are rarely reported in the literature and provide insights into long-term material behavior. The changes in chemistry and thermal properties were assessed by a range of characterization techniques including Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), swelling experiments and contact angle measurements. The combination of these diverse methods provided useful insights on the degradation of these materials when used for the storage of nuclear materials.

## **AGING OF SPVC AND ACCELERATED AGING STUDY**

Previous work has shown that current sPVC bags used in the storage and transport of nuclear material age rapidly, showing a darkening and crumbling of the material, while releasing a chlorine-like smell and leaving liquid residues and the bottom of the containers.<sup>16</sup> Careful analysis has shown that the chlorine-like smell was due to DHC, while residues were, in fact, highly toxic plasticizers (<sup>1</sup>H NMR analysis of the droplets confirmed the presence of diisodecyl phthalate, DOP). Conclusions from the previous work performed on sPVC have revealed that the HCl formation, which can lead to corrosion of metal containers and the loss of plasticizer, is deleterious to mechanical, physical, and chemical properties. The effect of DHC is distinctly evident in the decrease in sPVC hydrophobicity shown in Figure 1, which is a vital characteristic of plastic bags for the storage of nuclear materials. Contact angle measurements were performed using an automated drop dispenser and deposition system as an efficient way to determine the hydrophobicity of a material by determining the angle that a drop water forms at the surface. A 2  $\mu$ l drop of dionized water was dropped on the material surface and the static contact angle was then determined

using the software (Kruss). A minimum of 5 replicates were performed on each surface of the test sample and the values reported are an average of the measurements. sPVC contact angle starts at 93° for the pristine sample, which is hydrophobic and progressively decreases to more hydrophilic contact angles, such as 73° for alpha irradiated samples. These changes in wettability are likely due to the presence of hydrophilic compounds such as HCl generated through DHC or alcohols through the degradation of DOP.<sup>17</sup> APU-ether samples show a contact angle that remains mostly centered around 92°, aside from the thermally aged sample, showing a contact angle of 102°, that is likely due to hydrophobic soft segment domains migrating towards the surface of the material.<sup>18</sup>

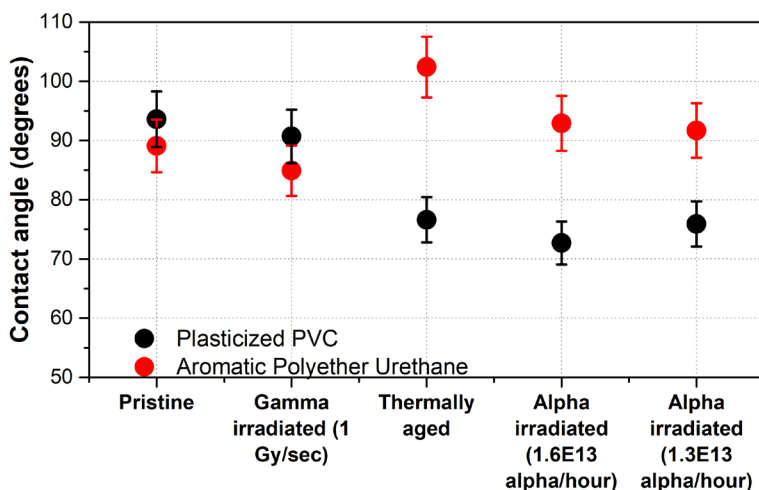


Figure 1: Evolution of the contact angle of sPVC and APU-ether as a function of aging conditions.

These findings prompted the in-depth study of dependable alternatives to sPVC that would likely perform well under harsh conditions encountered in the storage and transport of nuclear materials such as APU-ether and APU-ester. These materials were subjected to accelerating aging conditions such as gamma radiation and/or high temperatures. A fraction of the aged materials were pulled out at regular time intervals: 3, 6 and 12 months to determine the changes occurring in the materials over these aging periods (Figure 2).

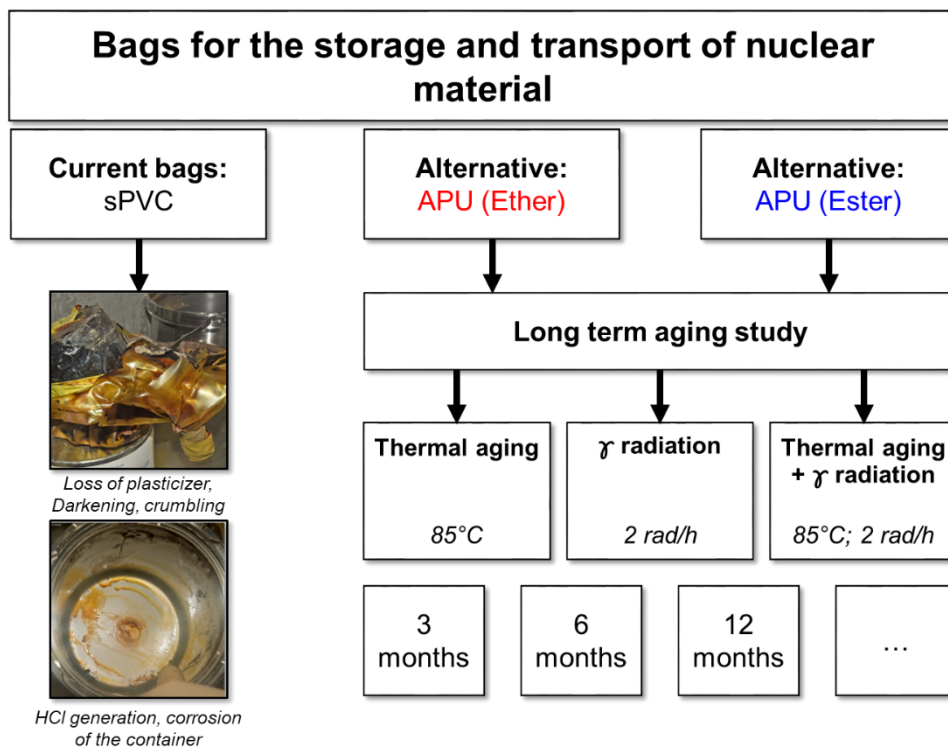


Figure 2: Diagram of the long-term aging study performed on APU-ether and APU-ester materials.

APU-ether and APU-ester samples were placed into aluminum canisters sealed with copper discs (Figure 3). The aging in canisters allows for gas samples to be collected at the end of the study for further analysis by mass spectroscopy. This technique was successfully used in previous aging studies.<sup>19</sup>

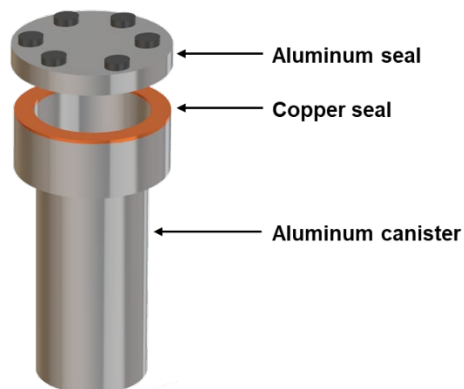


Figure 3: Schematic of the aluminum canisters used for accelerated aging and gas collection of APU-ether and APU-ester samples

## ACCELERATED AGING OF POLYURETHANES

The accelerated aging of APU-ether and APU-ester are crucial to determine their long-term stability and behavior in storage. Chemical, physical and mechanical changes can be monitored to help predict the performance over the material's lifetime. Chemical changes due to thermal aging and radiolysis were investigated by FT-IR spectroscopy. FT-IR spectra were obtained in attenuated total reflection (ATR) mode using an average of 32 scans from 500 to 3500  $\text{cm}^{-1}$ . A background spectrum was collected before each sample. The FT-IR spectra of pristine and samples subjected to accelerated aging of APU-ether and APU-ester are shown in Figure 4a and 4b, respectively and peak assignments are listed in Table 1.<sup>20-22</sup>

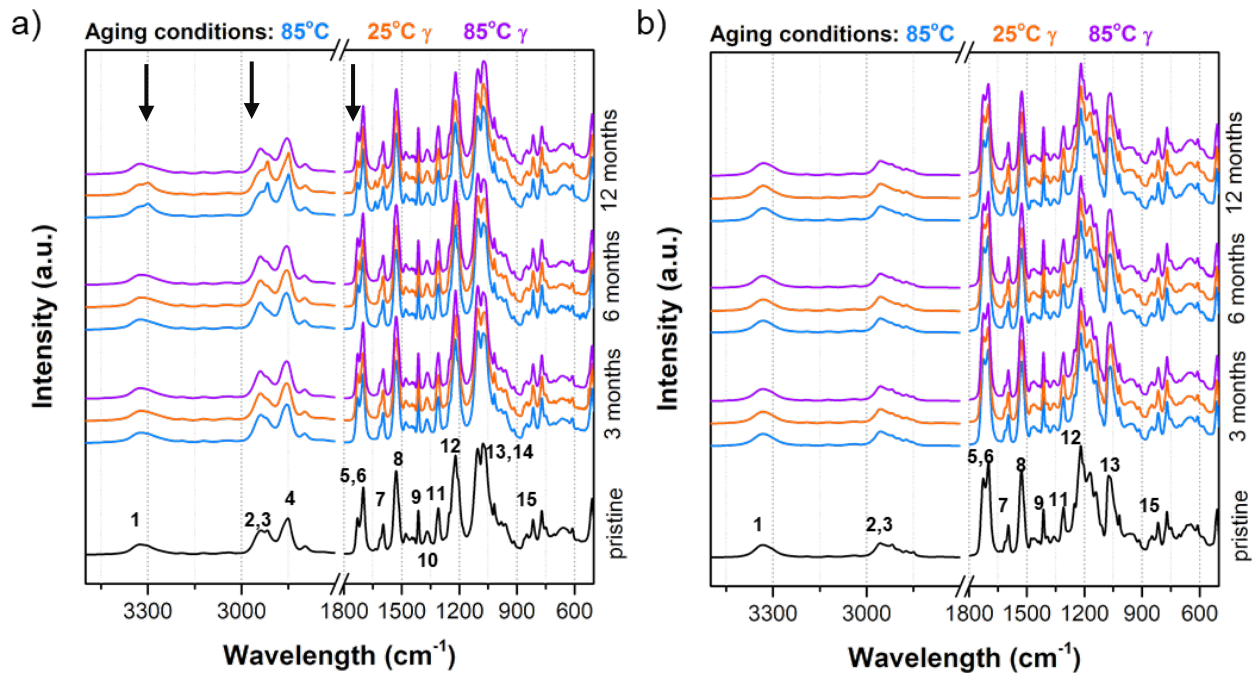


Figure 4: FT-IR spectra of pristine and samples subjected to accelerated aging of a) APU-ether and b) APU-ester

The spectra of thermally aged and irradiated APU-ether and APU-ester samples show no significant changes when compared to their respective control sample. In fact, the only visible changes are visible in the APU-ether samples aged for 12 months. For these samples, small shoulder peaks at 3292  $\text{cm}^{-1}$  in the urethane N-H stretching region, at 2860  $\text{cm}^{-1}$  in the  $\text{CH}_2$  stretching region and at 1646  $\text{cm}^{-1}$  in the C=O stretching region are observed, which indicate a disruption of the hydrogen-bonding ordered structure. An additional change at 1093  $\text{cm}^{-1}$  is observed, possibly indicating soft segment ether degradation. Further, damage to the urethane groups by retrourethanization would lead to an intensity increase of the characteristic band at 2266  $\text{cm}^{-1}$ .<sup>23</sup>

Table 1: Peak identification for the FT-IR spectra of APU-ether and APU-ester samples.

Peak number	Position of peak (cm <sup>-1</sup> )	Chemical group
1	3312	-NH stretching
2	2937	-CH <sub>3</sub> stretching
3	2859	-CH <sub>2</sub> stretching
4	2787	-CH stretching
5	1718	carbonyl C=O stretching
6	1687	amide I (C=O)
7	1593	Aromatic C=C stretching
8	1537	Amide II (NH deformation)
9	1406	C=C
10, 11, 12	1359, 1303, 1250	CH <sub>2</sub> bending and wagging
13, 14	1093, 1068	C-O-C stretching
15	812	C-H wagging

Swelling experiments are useful to characterize polymer networks, offering valuable information such as crosslink density, chain scission, and reorganization between hard and soft domains due to aging. Additionally, these experiments allow for quantification of low molecular weight molecules present in the network such as plasticizers and other additives. Samples of each material were weighed “as received” and then swollen in toluene for 48 hours. After swelling to equilibrium, the excess toluene was removed, and the samples were weighed once again to determine the solvent intake. The samples were subsequently dried in a vacuum oven for 48 hours and then weighed to determine any loss of material. Figure 5a shows the swelling of APU-ether samples as a function of the aging conditions and duration. All samples swell in a range from +52 to +59 wt%. There seems to be little to no difference between samples either as a function of aging condition or duration. Next, figure 5b shows the swelling of APU-ester. Similarly, the swelling of the ester-based materials are encompassed in a narrow range, from +23 to +26 wt %. There seems to be little to no variation between samples. Note that APU-ether and APU-ester samples aged at room temperature seem to swell slightly more than those aged at 85°C. Finally, Figure 5c shows the weight losses corresponding to low molecular weight compounds of APU-ether and APU-ester samples. All samples seem to lose low amounts of material, ranging from 1 to 3 wt%, indicating low incorporation of additives. Both materials show constant swelling at equilibrium, and constant losses when dried, denoting little changes to the polymer network with thermal aging or radiation.

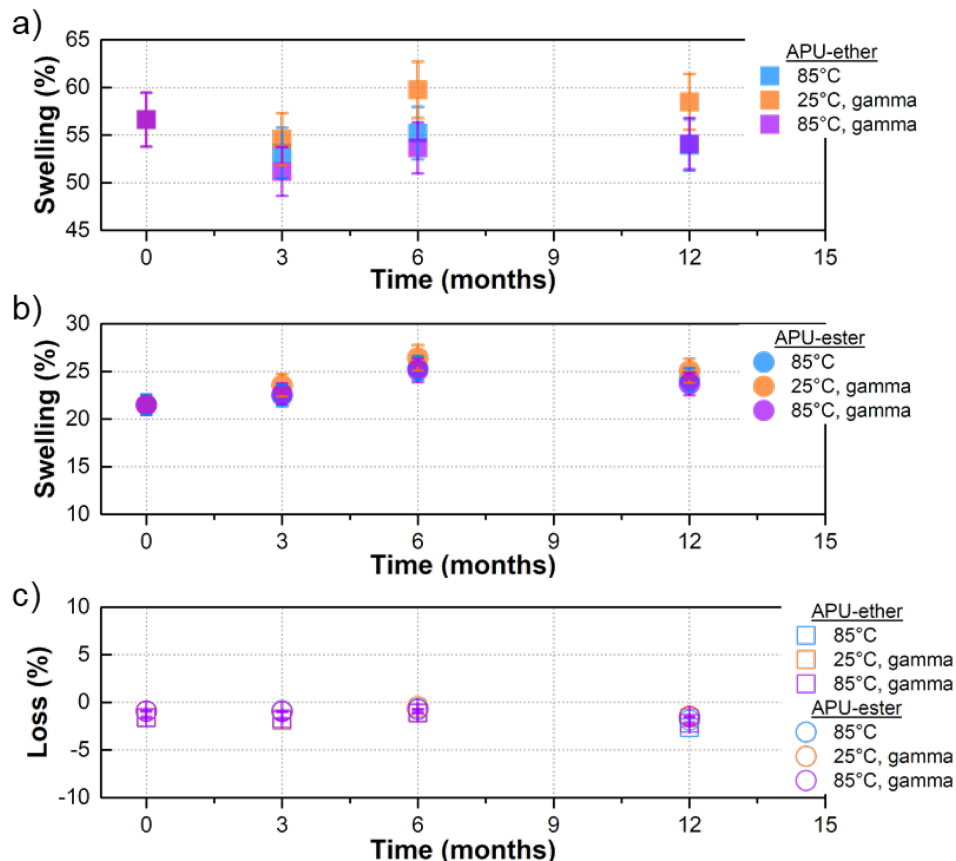


Figure 5: Swelling experiments on a) APU-ether, b) APU-ester and losses from these experiments

Changes in the thermal stability of APU-ether and APU-ester samples were measured by TGA under  $N_2$  atmosphere. The temperature was ramped at  $10\text{ }^\circ\text{C}/\text{min}$  from room temperature to  $850\text{ }^\circ\text{C}$ . The TGA of pristine samples are shown in Figure 6a. Both curves exhibit similar decomposition steps, the first one is attributed to the decomposition of isocyanate groups, whereas the second step is related to the decomposition of diol and ether groups with a peak of mass loss at  $400^\circ\text{C}$ .<sup>24</sup> The inset shows the decomposition temperature ( $T_d$ ) of both materials (temperature at which 95% of the initial mass is left) *i.e.*  $312^\circ\text{C}$  and  $320^\circ\text{C}$  for APU-ether and APU-ester, respectively. Note that at these temperatures, previous reports have shown that most of sPVC is decomposed ( $T_d \sim 225^\circ\text{C}$ ).<sup>16</sup>

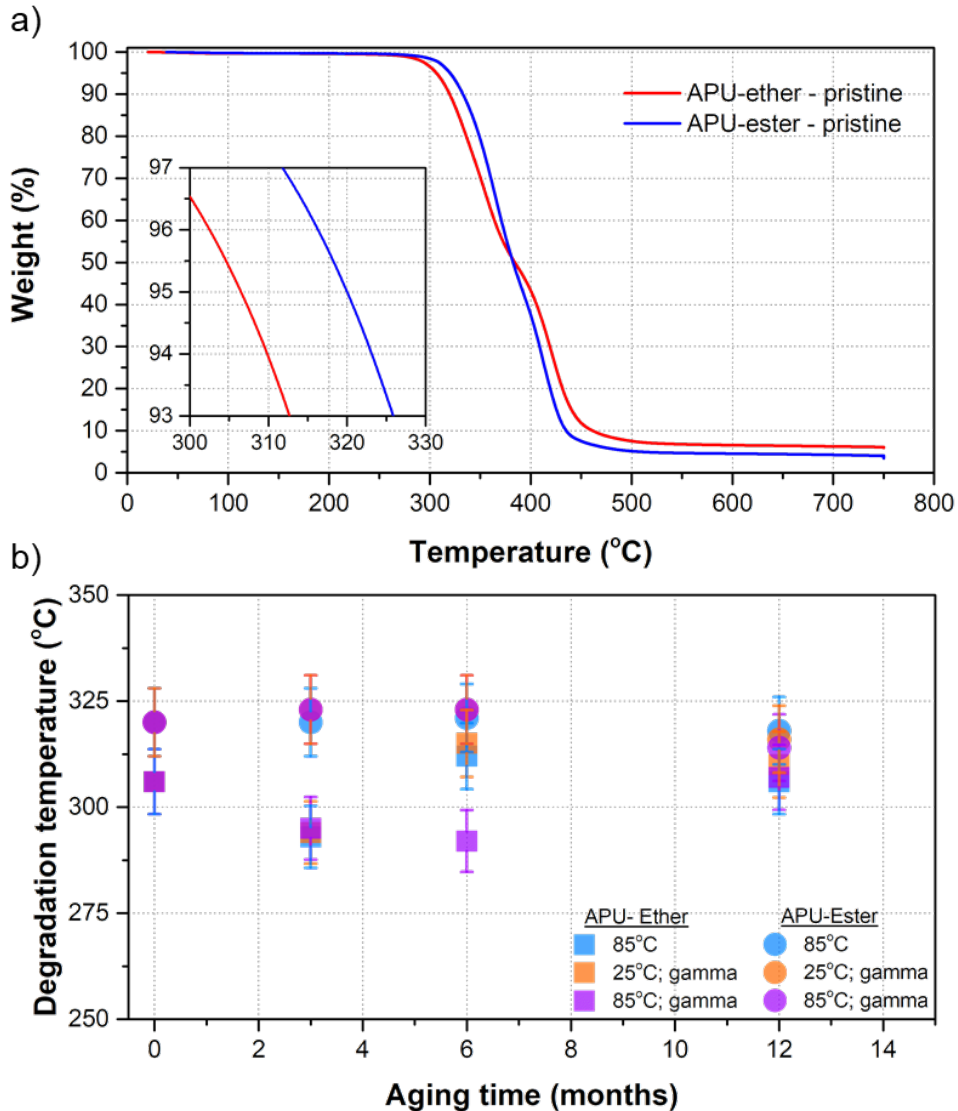


Figure 6: a) TGA of APU-ether and APU-ester and b) summary of the degradation temperatures (mass loss > 5 wt %) as a function of time of materials subjected to accelerated aging

Figure 6b summarizes the degradation temperatures ( $T_d$ ) recorded of samples that were subjected to accelerated aging as a function of the aging duration. The  $T_d$ s of APU-ether are centered around 310°C, showing that there is little to no change in thermal stability. Similarly,  $T_d$ s of APU-ester remain constantly centered around 320°C regardless of the aging time and conditions.

## CONCLUSIONS

Previous studies have shown that sPVC materials age rapidly under high temperatures and/or radiation, releasing high concentrations of plasticizer as well as HCl, which in turn affect the chemical and mechanical properties of the bags and corrode the metal containers, jeopardizing the long-term storage of nuclear materials. The alternatives to sPVC, namely APU-ether and APU-ester were chosen because of their known stability under harsh conditions, prompting a long-term aging study to understand the changes these materials undergo. The preliminary results after a 12-months aging period under thermal aging



and/or gamma radiation have demonstrated the stability of these two aromatic polyurethane materials in terms of chemical signature through FT-IR, crosslinking density through swelling experiments, losses of low molecular compounds and decomposition temperatures through TGA. Further analysis of the chemical, thermal and mechanical properties using a wide range of techniques such as nuclear magnetic resonance, mass spectroscopy, puncture and tension tests and differential scanning calorimetry will complement the ongoing investigation on the durability of these materials and will guide the next generation of polymeric bags for the storage and transport of nuclear materials.

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